Lectures can be downloaded from www.iitk.ac.in/che/nv.htm

ChE TRIAD e-LECTURE SERIES

Heterogeneous Chemical Reaction Engineering

\[ \frac{dCA}{dx} = \frac{d^2CA}{dx^2} + \frac{\partial}{\partial x} \left( \frac{\partial CA}{\partial x} \right) \]

Finite Difference Based Numerical Methods

\[ B = -D \frac{\partial V}{\partial x}; C = \frac{k}{V}, \Delta h = L/N \]

\[ R_{obs} = ak_m \left[ C_{A,b} - \left( \frac{R_{obs}}{k\eta_{intra}} \right)^\frac{1}{R} \right] \]

\[ \eta_{intra} = \eta_{intra}(n, \phi); \phi = L \left( kC_{A,b}^{n-1} \right)^\frac{1}{D_{pore}} \]

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Transport Phenomena in Chemical Engineering
Lecture #01

Reference books

1. Transport Phenomena by BSL
2. Analysis of Transport Phenomena by Deen
Selective examples are also taken from
3. Boundary Layer Theory by Schlichting and Gersten
4. Physicochemical Hydrodynamics by Levich
5. Transport Phenomena Fundamentals by Joel Plawsky
6. Convective Heat and Mass Transfer by Kays, Crawford, Weigand

Transport Phenomena (continuum, laminar flow, incompressible fluid or flow at low Mach number, Newtonian fluid)

Course in three parts: (1) Set up the equations describing the physical change in nature (vector analysis, divergence theorem, etc.)

(2) Prototype problems/examples in momentum, heat and mass transport (analytical techniques: Sturm Liouville, PDE solver etc.). These are relatively simpler problems or examples, dealing with the laminar flow of an incompressible, Newtonian fluid.

(3) Approximate solution to complex problems (physics and math). These deal with flow at high Reynolds numbers (boundary layer theory), and that at high Peclet numbers (concentration and thermal boundary layers). The analytical solutions often use stream function. In this part of the course, there are one or two introductory lectures on turbulent flow.

⇒ Scalars, vectors and tensors

Scalar – Numeric value such as mass, temperature

Vector – Magnitude and direction: \( \vec{v} , \vec{q}, \vec{g} \)

eg. \( \vec{v} = iv_x + jv_y + kv_z \); \( \vec{q} = iq_x + jq_y + kq_z \); \( \vec{g} = kg_z \)

- Flux of a scalar is a vector (all the time?).

- Tensor: \( \vec{t} \) eg. shear stress \( \equiv \) flux of a vector (momentum); all the time?
Let us understand stress tensor in the context of solid mechanics (fluid dynamics will be taken up later):

\( \tau \) in \( x \) direction will have vectors in \( x, y, z \) directions.

\[
\tau_{ij} = \begin{bmatrix}
\tau_{xx} & \tau_{xy} & \tau_{xz} \\
\tau_{yx} & \tau_{yy} & \tau_{yz} \\
\tau_{zx} & \tau_{zy} & \tau_{zz}
\end{bmatrix}; \quad \tau_{ij} = \text{general component}
\]

All it means is that \( \tau \) has a magnitude, direction it acts along, and the area upon which it acts.

Conventionally, \( \tau_{xx} \equiv \sigma_{xx}, \quad \tau_{yy} \equiv \sigma_{yy}, \quad \tau_{zz} \equiv \sigma_{zz} \)

**Scalar Product:**
\[
\vec{A} \cdot \vec{B} = |A||B|\cos\theta
\]
\[
= A_x B_x + A_y B_y + A_z B_z
\]

Operator \( \rightarrow \) Divergence

\( \operatorname{eg.} \nabla \cdot \vec{V} : \nabla \equiv \text{vector} = i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z} \)

\( \nabla \cdot \vec{V} = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \); \( \vec{V} = iV_x + jV_y + kV_z \)

**Vector Product:**
\[
\vec{A} \times \vec{B} = \vec{C} = |A||B|\sin\theta \hat{k}
\]

where, \( \hat{k} \) is the unit vector normal to both \( A \& B \) (plane);

\[
\vec{A} \times \vec{B} = \begin{vmatrix}
i & j & k \\
A_x & A_y & A_z \\
B_x & B_y & B_z
\end{vmatrix}
\]
Curl Operator \( \nabla \times \vec{V} = \begin{vmatrix} i & j & k \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ V_x & V_y & V_z \end{vmatrix} \) (\( \vec{V} \) can be 1D or 2D or 3D)

eg. vorticity \( \vec{\omega} = \text{curl} \, \vec{V} \) (curl of velocity) = \( \nabla \times \vec{V} \)

Vorticity is zero, implying that the element on fluid does not rotate about its own axis \( \Rightarrow \) irrotational flow.

\( \nabla \times \vec{V} \neq 0 \) 'rotation'

\( \nabla \times \vec{V} = 0 \) 'no rotation'

A “zero-mass” object, for example, a piece of paper marked with cross sign does not rotate in an irrotational flow.

\[ \nabla \psi \equiv \text{grad} \, \psi \equiv \text{vector} \equiv i \frac{\partial \psi}{\partial x} + j \frac{\partial \psi}{\partial y} + k \frac{\partial \psi}{\partial z} \]

(\( \text{scalar} \))

Recall: Curl of a grad (scalar) or \( \nabla \times \nabla \psi = 0 \) (in a conservative field, say gravitational field)

\[ \nabla^2 \equiv \nabla \cdot \nabla \equiv \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \equiv \text{scalar} \]

\textbf{Substantial or material derivative}

\[ \frac{df}{dt} = \left( \frac{\partial}{\partial t} + \vec{V} \cdot \nabla \right) f \quad (f \equiv \text{property}) \]

\[ = \left( \frac{\partial}{\partial t} + V_x \frac{\partial}{\partial x} + V_y \frac{\partial}{\partial y} + V_z \frac{\partial}{\partial z} \right) f \]

Fixed \( (x, y, z) \) other coordinates are fixed.

eg. Moving in the flow field with the fluid’s velocity \( (V_x, V_y, V_z) \): time – rate of change in the property as seen/noted/observed by the observer \( \equiv \frac{df}{dt} \)

Total derivative

\[ \frac{df}{dt} = \left( \frac{\partial}{\partial t} + dx \frac{\partial}{\partial x} + dy \frac{\partial}{\partial y} + dz \frac{\partial}{\partial z} \right) f \]

\[ \text{chosen velocities by the observer} \]

Moving in the flow field with chosen velocities \( (V_x, V_y, V_z) \)

(If observer is moving along a fluid, \( \frac{dx}{dt} = V_x, \frac{dy}{dt} = V_y, \frac{dz}{dt} = V_z \); \( \frac{df}{dt} = \frac{df}{dt} \))
eg. $C_{fish}$ in a stream/lake: $C(t, x, y, z)$

1. $x, y, z$ is fixed $\frac{dc}{dt} \big|_{x,y,z}$ (standing on a bridge over the lake)
2. $\frac{dc}{dt}$ (take a boat and let it move with fluid or switch off the engine)
3. $\frac{dc}{dt}$ (take a boat and choose your own velocity)

All three log-books will look alike

$$t \quad \dashline{3} \quad y \quad \dashline{3} \quad \underline{c} \quad \dashline{3} \quad you \ cannot \ tell \ which \ derivatives$$

Revisit: Tensors/ Dyadics

Scalar: Zero order 1 Component

Vector: 1st order 3 Components

Tensors: 2nd order 9 Components.

$$\mathcal{T} = \begin{bmatrix} T_{xx} & T_{xy} & T_{xz} \\ T_{yx} & T_{yy} & T_{yz} \\ T_{zx} & T_{zy} & T_{zz} \end{bmatrix} ; \text{ The scalars } T_{ij} \text{ are the components of the tensor } \mathcal{T}$$

Multiply (?) two vectors:

$$\vec{A} \vec{B} \text{ (also a tensor)} = \begin{bmatrix} A_xB_x & A_xB_y & A_xB_z \\ A_yB_x & A_yB_y & A_yB_z \\ A_zB_x & A_zB_y & A_zB_z \end{bmatrix} \Rightarrow \text{ diadics product: there are 9 scalar components}$$

No operator '. ' or ' $\times$ ' in-between

Thus, in a fluid-flow field of velocity vector $\vec{u}$, $\rho\vec{u}\vec{u}$ represents a tensor (convective momentum flux) having usual 9 scalar components, with the general $\rho u_iu_j$ component representing the $\rho u_i$ or $j$-momentum transferred across the i-plane or in the direction perpendicular to j-k plane by the convective flow ($u_i$):

$$\begin{bmatrix} u_xu_x & u_xu_y & u_xu_z \\ u_yu_x & u_yu_y & u_yu_z \\ u_zu_x & u_zu_y & u_zu_z \end{bmatrix}$$

Similar to the previous example of $\tau_{ij}$, the momentum (vector) of the fluid flow creates momentum flux (tensors), parallel and normal to the flow in the fluid element, and therefore, there are 9 scalar components. Such scenario will be discussed later for turbulent flow.

eg. $\vec{V} \cdot \nabla \vec{V}$ appears in NS equation.

See this term: $\nabla \vec{V} \equiv$ It is also a tensor with 9 components. $\nabla_i V_j \equiv$ scalar components of the tensor
\[
\begin{bmatrix}
\frac{\partial}{\partial x_i} V_i & \frac{\partial}{\partial x_i} V_j & \frac{\partial}{\partial x_i} V_k \\
\frac{\partial}{\partial x_j} V_i & \frac{\partial}{\partial x_j} V_j & \frac{\partial}{\partial x_j} V_k \\
\frac{\partial}{\partial x_k} V_i & \frac{\partial}{\partial x_k} V_j & \frac{\partial}{\partial x_k} V_k
\end{bmatrix}
\]

- \(i - \text{momentum}\)
- \(j - \text{momentum}\)
- \(k - \text{momentum}\) (column-wise)

I leave this to you to give a suitable interpretation of the different scalar components.

**Kronecker deltas** (convenient to use for mathematically handling tensors operation)

Conventional notations: \(\vec{A} \cdot \vec{B} = |A||B|\cos \theta = \sum_{i=x,y,z} A_i B_i = A_x B_x + A_y B_y + A_z B_z\)

\[\sum_i \delta_i A_i \cdot \sum_j \delta_j B_j = \sum_i \sum_j \delta_{ij} A_i B_j = \sum_i A_i B_i \quad \left(\delta_{ij} = 1 \quad \text{if} \quad i = j \right) \quad \text{Kronecker deltas}
\]

\[= A_x B_x + A_y B_y + A_z B_z \quad \text{same as before.}
\]

\[\delta_i, \delta_j \text{ are the unit vectors;}
\]

\[\delta_{ij} \text{ is the Kronecker delta.}
\]

**Rules:**

\[\delta_{ij} = \begin{cases} +1 & \text{if} \quad i = j \\ 0 & \text{if} \quad i \neq j \end{cases}
\]

\[\epsilon_{ijk} = \begin{cases} +1 & \text{if} \quad ijk = 123, 231, \text{ or } 312 \\ -1, & \text{if} \quad ijk = 321, 132, \text{ or } 213 \\ 0 & \text{otherwise} \end{cases}
\]

\[\delta_i, \delta_j = \delta_{ij} \text{ (scalar)}
\]

\[\delta_i \times \delta_j = \sum_{k=1}^{3} \epsilon_{ijk} \delta_k \text{ (vector); } \quad \delta_i \delta_j : \delta_k \delta_l = \delta_{il} \delta_{jk} \text{ (scalar)}
\]

Verify \(\otimes\) and also, \(\vec{V} \times \vec{\omega} = \begin{bmatrix} \delta_i & \delta_j & \delta_l \\ V_1 & V_2 & V_3 \\ \omega_1 & \omega_2 & \omega_3 \end{bmatrix} = \times \times
\]

\[= \sum_i \delta_i V_i \times \sum_j \delta_j \omega_j = \sum_i \sum_j \sum_k \epsilon_{ijk} \delta_k V_i \omega_j = \sum_i \sum_j \sum_k \epsilon_{ijk} \delta_i V_j \omega_k \quad \text{same as } \times \times
\]

\[T = \begin{bmatrix} T_{xx} & T_{xy} & T_{xz} \\ T_{yx} & T_{yy} & T_{yz} \\ T_{zx} & T_{zy} & T_{zz} \end{bmatrix} \quad (9 \text{ components, } 3 \text{ directions})
\]
can be written as \( T_{ij} = \sum_i \sum_j \delta_i \delta_j T_{ij} \) (9 components, 3 directions)

\( \Rightarrow \) Multiplication of two vectors \((\vec{A} \vec{B})\) or dyadic product (Note there is no \( X \) or \( \vec{B}' \) is a tensor or dyad).

\[
\vec{A} \vec{B} = \sum_i \sum_j \delta_i \delta_j A_i B_j = \begin{pmatrix} A_x B_x & A_x B_y & A_x B_z \\ A_y B_x & A_y B_y & A_y B_z \\ A_z B_x & A_z B_y & A_z B_z \end{pmatrix}
\]

Consider a dot product of a vector \& a tensor to show:

\[
\vec{A} \cdot (\vec{A} \vec{B}) = (A_x T_{xx} + A_y T_{yx} + A_z T_{zx})i + (A_x T_{xy} + A_y T_{yy} + A_z T_{zy})j + (A_x T_{xz} + A_y T_{yz} + A_z T_{zz})k
\]

Similarly, show that \( \nabla \cdot (\vec{A} \vec{B}) = (\vec{A} \cdot \nabla) \vec{B} + \vec{B} (\nabla \cdot \vec{A}) \)

\( \Rightarrow \) Many of such tensor operations such as \( \nabla \cdot \vec{V}, \nabla \times \vec{V} \), \( \vec{v} \cdot \vec{V} \), \( \vec{v} \cdot \vec{V} \) \& \( \nabla \vec{V} \) are performed using Kronecker deltas. See the appendix of BSL and check the following equalities, as an exercise:

1. \( \sigma : \vec{t} = \sum \sum \sigma_{ij} \tau_{ij} \)
2. \( \nabla \cdot (\vec{A} \vec{B}) = (\vec{A} \cdot \nabla) \vec{B} + \vec{B} (\nabla \cdot \vec{A}) \)
3. \( \tau : \nabla \vec{V} \equiv + \varepsilon = \mu \phi \)
4. \( \tau : \nabla \vec{V} = \nabla (\tau \vec{V}) - \vec{V} (\nabla \tau) \) if \( \tau_{ij} = \tau_{ji} \) (symmetric tensor)

Component wise

\[
\frac{\partial}{\partial x_i} A_i B_j = (A_i \frac{\partial}{\partial x_i}) B_j + B_j (\frac{\partial}{\partial x_i} A_i)
\]

Also show that \( \nabla \vec{V} \neq \vec{V} \nabla \) and \( \nabla \vec{V} \neq \vec{V} \nabla \)

**Example:** \( \sigma = \begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{pmatrix} \) \( \tau = \begin{pmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \tau_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & \tau_{33} \end{pmatrix} \)

\[
\sigma : \vec{t} = \sum \sum \delta_i \delta_j \sigma_{ij} ; \quad \tau = \sum_k \sum_l \delta_k \delta_l \tau_{kl}
\]

\[
\sigma : \vec{t} = \sum \sum \sum \delta_{kl} \sigma_{ij} \sum_k \sum_l \delta_k \delta_l \tau_{kl} = \sum \sum \sum \sum \delta_{ii} \delta_{jj} \sigma_{ij} \tau_{kl}
\]

\[
= \sum \sum \sum \sum \delta_{ij} \sigma_{ij} \tau_{kl} \rightarrow \begin{cases} \text{when } l = i & \delta_{ii} = \delta_{ii} = 1 \\ \text{and } \tau_{kl} = \tau_{ki} \end{cases}
\]

\[
= \sum \sum \sum \sum \sigma_{ij} \tau_{ji} \rightarrow \begin{cases} \text{when } k = j & \delta_{jk} = \delta_{jj} = 1 \\ \text{and } \tau_{ki} = \tau_{ji} \end{cases}
\]

\[
= \sum \sum \sum \sigma_{ij} \tau_{ji} \rightarrow \begin{cases} \text{scalar} \end{cases}
\]
Lecture #02

General Property Balance (continuum)

Some basics first:

**Line Integral**

\[ \int_{1}^{2} \vec{A} \cdot d\vec{l} = \int_{1}^{2} A \cos \theta \, dl = \text{work done if } \vec{A} = \text{Force} \]

**Surface Integral**

Magnitude of a property-flux, \( \vec{A} \) through \( ds \) = \( (\vec{A} \cdot \hat{n}) \, ds \)

Total property, surface integral = \( \iint_{S} (\vec{A} \cdot \hat{n}) \, ds \)

\[ = \iint_{S} A \cos \theta \, ds \]

(\( \hat{n} \) is \( \perp \) to \( ds \) and is considered to be the direction of \( d\vec{s} \))

**Integral Theorems**

If \( \forall \) is the closed region in a space, whose outer surface is \( S \),

Then \( \iint_{S} (\vec{A} \cdot \hat{n}) \, dS = \iiint_{\forall} (\nabla \cdot \vec{A}) \, d\forall \)

(space change over \( d\forall \))

(Divergence Theorem/Green’s Theorem)

Likewise for a scalar \( \psi \)

\[ \iint_{S} (\psi \cdot \hat{n}) \, dS = \iiint_{\forall} (\nabla \psi) \, d\forall \] (vector)

For a tensor \( \tau \)

\[ \iint_{S} (\vec{\tau} \cdot \hat{n}) \, dS = \iiint_{\forall} (\nabla \cdot \vec{\tau}) \, d\forall \] (vector)
Stoke’s Theorem:
\[ \oint_S (\nabla \times \vec{A}) \cdot \hat{n} \, dS = \oint_C \vec{A} \cdot d\vec{l} \] (curl of a conservative vector is zero)

Frame of Reference (Coordinate Framework)

⇒ Eularian coordinate framework

Identify a volume, \( V \) in space at \( (x, y, z) \). Fluid flows through the volume. Identity time-changes across the volume.

different fluid elements. In this case, independent variables would be \((t, x, y, z)\)

⇒ Lagrangian coordinate framework

Identify a piece of mass (fluid element) and describe what happens to the body (as if the fluid element is tagged and you are following it). Independent variable would be time only because \((x, y, z) \equiv f(t) \) or \((x, y, z)\) are time-dependent.

eg. cannon balls projectile

General Property Balance Equation (see H.W. -1.5)

Take arbitrary volume \( V \) fixed in space, bounded by surface \( S \).

Fluid flow
\[ \vec{V}(x, y, z, t) \]
Consider some property, $\psi$ \( \frac{\text{property}}{\text{cm}^3} \)  

\[ \text{Flux}, \overrightarrow{\Phi} = \frac{\text{property}}{\text{cm}^2 \cdot \text{s}} \]

**Time rate of change of property within volume:** \( \frac{\partial}{\partial t} \left( \iiint_{\mathcal{V}} \psi \, d\mathcal{V} \right) \)

**Net flow (transfer) of property across surface:**  
\[ \iint_{S} (\overrightarrow{\Phi} \cdot \hat{n}) \, dS \]

**Generation term** (rate at which property is generated in the volume \( \mathcal{V} \)):

\[ = \iiint_{\mathcal{V}} \psi_{g} \, d\mathcal{V} \quad \psi_{g} = \text{generation rate of } \psi, \quad \left( \frac{\text{property}}{\text{s} \cdot \text{cm}^3} \right) \]

**Balance:** \( \frac{\partial}{\partial t} \left( \iiint_{\mathcal{V}} \psi \, d\mathcal{V} \right) = - \iint_{S} (\overrightarrow{\Phi} \cdot \hat{n}) \, dS + \iiint_{\mathcal{V}} \psi_{g} \, d\mathcal{V} \)

\( \overrightarrow{\Phi} \) Consists of at least two parts:

a) **Convection**, $\psi$ is carried by velocity $\vec{V}$ (convective flow)

\[ \text{Flux} \equiv \psi \vec{V} \quad \left( \frac{\text{property}}{\text{s} \cdot \text{cm}^2} \right) \]

b) Some $\psi$ is transferred by non-convection (diffusion, radiation) \( \Rightarrow \) Call this flux $\overrightarrow{\Psi}$

\[ \overrightarrow{\Phi} = \psi \vec{V} + \overrightarrow{\Psi} \quad \left( \frac{\text{property}}{\text{s} \cdot \text{cm}^2} \right) \]

\[ \text{convective part} \quad \downarrow \quad \text{non-convective part} \]

Substitute,

\[ \frac{\partial}{\partial t} \iiint_{\mathcal{V}} \psi \, d\mathcal{V} = - \iint_{S} (\psi \vec{V} + \overrightarrow{\Psi}) \cdot \hat{n} \, dS + \iiint_{\mathcal{V}} \psi_{g} \, d\mathcal{V} \]

\[ \Rightarrow \frac{\partial}{\partial t} \left( \iiint_{\mathcal{V}} \psi \, d\mathcal{V} \right) + \iint_{S} (\psi \vec{V}) \cdot \hat{n} \, dS = - \iint_{S} \overrightarrow{\Psi} \cdot \hat{n} \, dS + \iiint_{\mathcal{V}} \psi_{g} \, d\mathcal{V} \]

\[ \frac{\partial}{\partial t} \left( \iiint_{\mathcal{V}} \psi \, d\mathcal{V} \right) = \left( \iiint_{\mathcal{V}} \frac{\partial \psi}{\partial t} \, d\mathcal{V} \right) \]

**Applying Divergence theorem,**

\[ \iint_{S} (\psi \vec{V}) \cdot \hat{n} \, dS = \iiint_{\mathcal{V}} (\nabla \cdot \vec{V}) \psi \, d\mathcal{V} \]

\[ \iint_{S} \overrightarrow{\Psi} \cdot \hat{n} \, dS = \iiint_{\mathcal{V}} \nabla \cdot \overrightarrow{\Psi} \, d\mathcal{V} \]

\[ \iiint_{\mathcal{V}} \left[ \frac{\partial \psi}{\partial t} + \nabla \cdot \vec{V} \right] \, d\mathcal{V} = \iiint_{\mathcal{V}} \left[ -\nabla \cdot \overrightarrow{\Psi} + \psi_{g} \right] \, d\mathcal{V} \]

Considering that \( \mathcal{V} \) is arbitrary,
11

(1) \( \psi = \rho \left( \frac{g}{cm^3} \right) \)

(1) \( \psi = \rho \vec{V} \left( \frac{g-cm/s}{cm^3} \right) \)

(2) \( \psi = PE + KE + U \) (cal/cm³)

(3) \( \psi = C_i \) (moles/cm³) (species)

(1) **Conservation of mass**: Continuity (single (pure) fluid; no mixture)

\[
\psi = \rho, \quad \psi_g = 0, \quad \vec{V} = 0 \quad \text{(non – convective mode) of fluid transport}
\]

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \vec{V} = 0
\]

or \( \frac{\partial \rho}{\partial t} + \sum_{i} \rho \frac{v_i}{\partial x_i} = 0 \) (Einstein equation/nomenclature)

(Einstein’s nomenclature: whenever a subscript is repeated, it implies summation)

(mass of a pure fluid in a CV varies with time because of convective transport only)

\[ \nabla \cdot \rho \vec{V} = \rho (\nabla \cdot \vec{V}) + (\vec{V} \cdot \nabla) \rho \]

or, \( \frac{\partial}{\partial x_i} \rho v_i = \rho \frac{\partial v_i}{\partial x_i} + v_i \frac{\partial \rho}{\partial x_i} \)

\[ \frac{\partial \rho}{\partial t} + (\vec{V} \cdot \nabla) \rho + \rho \nabla \cdot \vec{V} = 0 \quad \Rightarrow \quad \frac{d\rho}{dt} + \rho \nabla \cdot \vec{V} = 0 \]

\( \frac{d\rho}{dt} \) (moving with the fluid)

If \( \rho = \text{const} \) (incompressible fluid)

\( \frac{d\rho}{dt} = 0; \quad \rho \neq \rho(x,y,z) \)

\[ \nabla \cdot \vec{V} = 0 \quad \text{or div} \vec{V} = 0 \]

or \( \frac{\partial v_i}{\partial x_i} = 0 \) (mass is conserved; also note we have used Einstein’s nomenclature)

In cylindrical or spherical coordinate system, a different type of velocity gradient terms appear in the equation. You may not memorize these terms but for sure should refer the appendix of BSL to become familiar with all terms in different coordinate systems. Also, the emphasis should be on the physical meaning of the terms. For example, in a 2D flow-field, \( \frac{\partial (rv_i)}{\partial r} \) represents the rate of change in mass flowrate in \( r \)-direction (if you multiply it with \( 2\pi \rho \)), which must be the same as that in \( x \)-direction for total mass flowrate to be conserved.
Lecture #03

Linear momentum balance

\[ \psi = \rho \vec{V} \] momentum/unit volume (a vector)

Therefore, general property balance is a vector equation (unlike the previous continuity equation), and therefore, flux term of the vector-property must be one order higher than the property, which is a tensor or dyad.

\[ \Rightarrow \frac{\partial \psi}{\partial t} + \nabla \cdot \psi \vec{V} = -\nabla \cdot \vec{P} + \vec{F} \] (general property balance)

\[ \frac{\partial (\rho \vec{V})}{\partial t} + \nabla \cdot \rho \vec{V} \vec{V} = -\nabla \cdot \vec{P} + \vec{F} \] (time rate of change of momentum)

\[ \frac{\partial \rho v_i}{\partial t} + \frac{\partial \rho v_k v_i}{\partial x_k} = -\frac{\partial P_{ki}}{\partial x_k} + F_i \] Einstein notation (repeat indices indicate summation)

Note: Newton’s 2nd law of motion defines \( \vec{F} = \) net body force on fluid, i.e. gravity (restriction)

Further simplification: \( \nabla \cdot \rho \vec{V} \vec{V} = \vec{V} (\nabla \cdot \rho \vec{V}) + (\rho \vec{V} \cdot \nabla) \vec{V} \) (recall previous lecture on Kronecker deltas)

Also, \( \frac{\partial (\rho \vec{V})}{\partial t} = \rho \frac{\partial \vec{V}}{\partial t} + \vec{V} \frac{\partial \rho}{\partial t} \) : \( \nabla \cdot \rho \vec{V} \)

\[ \text{LHS} = \rho \frac{\partial \vec{V}}{\partial t} + (\rho \vec{V} \cdot \nabla) \vec{V} + \vec{V} \left( \frac{\partial \rho}{\partial t} + \nabla \cdot \rho \vec{V} \right) \]

\[ = \rho \left( \frac{\partial \vec{V}}{\partial t} + \left( \vec{V} \cdot \nabla \right) \vec{V} \right) \text{ zero from continuity} \]
\[ \rho \left( \frac{\partial \vec{V}}{\partial t} + \left( \vec{V} \cdot \nabla \right) \vec{V} \right) = -\nabla \cdot \vec{P} + \vec{g} \]

Equation becomes \( \rho \left( \frac{\partial \vec{V}}{\partial t} + \left( \vec{V} \cdot \nabla \right) \vec{V} \right) = -\nabla \cdot \vec{P} + \vec{g} \)

(Assumption: \( \rho \) is not constant)

**Einstein equation:**

\[ \rho \left( \frac{\partial v_i}{\partial t} + v_k \frac{\partial v_i}{\partial x_k} \right) = -\frac{\partial P_{ki}}{\partial x_k} + g_i \] : i - momentum balance using Einstein’s nomenclature

\[ i = x: \rho \left( \frac{\partial v_x}{\partial t} + v_y \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} + v_z \frac{\partial v_x}{\partial z} \right) = -\frac{\partial P_{xx}}{\partial x} - \frac{\partial P_{yx}}{\partial y} - \frac{\partial P_{zx}}{\partial z} + g_x \]
\[ y = \rho \left( \frac{\partial V_y}{\partial t} + V_x \frac{\partial V_y}{\partial x} + V_y \frac{\partial V_y}{\partial y} + V_z \frac{\partial V_y}{\partial z} \right) = -\frac{\partial P_{xy}}{\partial x} - \frac{\partial P_{yy}}{\partial y} - \frac{\partial P_{zy}}{\partial z} + \psi_{xy} \]

Restrict to body force = gravity

\[ \vec{g} = \frac{\text{momentum}}{\text{volume-}s} = \frac{\text{force}}{\text{unit volume}} = \rho \vec{\mathbf{g}} \]

So far, \( \frac{\partial \rho}{\partial t} + \nabla \cdot \rho \vec{V} = 0 \) (continuity)

\[ \rho \left( \frac{\partial \vec{V}}{\partial t} + \vec{V} \cdot \nabla \vec{V} \right) = -\nabla P + \rho \vec{g} \Rightarrow \text{(linear momentum balance or equation of motion)} \]

(\( \rho \neq c \) and NF or NNF and laminar or turbulent)

We still cannot solve \( \vec{V} \) and \( \rho(x, y, z) \) unless we get \( P \) in terms of \( \vec{V} \) (velocity and density fields)

Therefore, we need insight into \( P \) (surface forces/non-convective flux/pressure tensor)

Assume \( P \) contains two parts:

a) One part which is non-zero for fluid at rest.

b) The other part which depends on fluid motion.

\[ P = p \delta + \tau \]

Thermodynamic pressure (due to state of the fluid)

\[ \text{viscous stress} = \begin{pmatrix} p + \tau_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{yx} & p + \tau_{yy} & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & p + \tau_{zz} \end{pmatrix} \]

Recall: \( \tau_{ij} \equiv \text{Flux of } j \text{ - momentum transferred in } i \text{ direction or across } j-k \text{ surface or plane?} \)

(or, force acting in \( j \text{ direction on } 'i' \text{ plane or } \perp \text{ to } j-k \text{ surface or plane?} \)

eg.

\[ \begin{array}{c}
\text{direction of flux} \\
\text{direction of momentum}
\end{array} \]

fluid above the \( j-k \) surface is sheared and moves

Further discussion on \( \tau_{ij} \):
Apply conservation of angular momentum to a fluid element of volume \( d\mathcal{V} = dx dy dz \) & let \( dx, dy, dz \to 0 \).

Show \( P_{xy} = P_{yx} \) or \( P_{ij} = P_{ji} \) or \( \tau_{ij} = \tau_{ji} \) or \( \underline{\tau} = \underline{\tau}^T \) (see old version of BSL)

⇒ Shear stress is symmetric (a fluid element cannot rotate or spin because it is a fluid)

⇒ Deen: For the overwhelming majority of fluids, including gases, homogeneous liquids of low molecular weight, polymeric liquids, and most suspensions it is safe to assume that the stress tensor is symmetric. Exceptions are in ferro fluids. The limitation on the conclusion that \( \underline{\tau} \) is symmetric due not to any violation of the general principle of conservation of angular momentum, but rather to the fact that some external torques may still exist in fluids.

⇒ To this end, one still cannot solve the equation of motion (consequence of linear momentum), unless we know how \( \underline{\tau} \) depends on \( \mathbf{V} \), which requires a ‘constitutive’ equation relating the non-convective term (flux), \( \underline{\tau} \) to \( \mathbf{V} \) in some ways.

It is found that in simple real fluids, \( \underline{\tau} \) depends only on the local first derivative of velocity i.e. on the relative motion of neighboring particles. Convective momentum cannot be transferred if fluid layers are at rest wrt each other.

\[
\mathbf{V'} - \mathbf{V} = \left( \frac{\partial}{\partial \mathbf{r}} \mathbf{V} \right) \cdot \mathbf{\delta r} + \text{approx.}
\]

\[
= (\nabla \mathbf{V}) \cdot \mathbf{\delta r}
\]

\( \mathbf{\delta r} \rightarrow \mathbf{\delta r} \mathbf{\delta r} \equiv \mathbf{D} \) (velocity gradient dyad)

\[
\mathbf{D} \equiv D_{ij} = \frac{\partial V_i}{\partial x_j} \begin{cases} 9 \text{ components of velocity gradients} \end{cases}
\]

\[
\mathbf{V} = \{V_x, V_y, V_z\}
\]

\[
\mathbf{\delta r} = \{x, y, z\}
\]

We cannot have a linear dependence between \( \underline{\tau} \& \mathbf{D} \) (\( \underline{\tau} \neq k \mathbf{D} \)) because \( \underline{\tau} \) is symmetric and \( \mathbf{D} \) is non-symmetric. \( \mathbf{D} \) can be written as the sum of a symmetric tensor and a non-symmetric tensor.

\[
\mathbf{D} = \frac{1}{2} (\mathbf{D} + \mathbf{D}^T) + \frac{1}{2} (\mathbf{D} - \mathbf{D}^T)
\]

\( \underline{\tau} \) symmetric \( \frac{1}{2} \) \( \mathbf{D} + \mathbf{D}^T \) \( \underline{\tau} \) non-symmetric \( \frac{1}{2} \) \( \mathbf{D} - \mathbf{D}^T \)

or, \( D_{ij}(\neq D_{ji}) = \frac{1}{2} (D_{ij} + D_{ji}) + \frac{1}{2} (D_{ij} - D_{ji}) \)
\[
\begin{align*}
\left( \frac{\partial v_j}{\partial x_i} + \frac{\partial v_i}{\partial x_j} \right) & \quad \text{always symmetric} \\
\left( \frac{\partial v_j}{\partial x_i} - \frac{\partial v_i}{\partial x_j} \right) & \quad \text{always non-symmetric}
\end{align*}
\]

\[D_{ij} = E_{ij} + \Omega_{ij}\]

Rate of strain tensor (symmetric)

Vorticity tensor (non-symmetric)

\[
\text{Note: vorticity, } \vec{\omega} = \nabla \times \vec{V}
\]

The first tensor relates to the **local rate of deformation** and the second relates to **rotation**.

Thus, \( \tau \) can depend only on the symmetric portion of \( D \) i.e. on \( E_{ij} \).

\( 2D \Omega_{ij} \) implies **pure rotation** about own axis of a fluid element \( \equiv \) rigid body rotation / non-deformation. \( \Omega_{ij} = 0 \Rightarrow \text{No rotation in a fluid} \)  See chapter 5.2 of Deen’s book, including examples 5.2.1 and 5.2.2, for details.

On \( E_{ij} \) (no uniform translation or rigid-body rotation)

Suppose \( E_{ij} = \begin{bmatrix} \alpha & 0 \\ 0 & \alpha \end{bmatrix} \) of diagonal terms are zero.

This describes the following type of deformation:

(for incompressible fluid, areas are same: linear deformation)

Suppose \( \Omega_{ij} = \begin{bmatrix} 0 & \beta \\ -\beta & 0 \end{bmatrix} \) : only off diagonal elements/terms are non-zero & they have to be same \( \left( \frac{\partial v_x}{\partial y} = \frac{\partial v_y}{\partial x} \right) \)

(angular deformation or rotation only \( \Rightarrow \) lengths are the same; for incompressible fluid, areas must be the same)
Check out some of the introductory courses on fluid dynamics. In general, the fluid element translates, dilates, rotates, and distorts, the latter two considered as angular deformation. Some textbooks (Schlichting) terms the kinds of fluid motions as extension, shear deformation, deformation, and rigid body rotation.

To this end, for a class of fluids called **Newtonian fluid**

a) Incompressible fluid

\[ \tau = -\mu \mathbf{E} = -\mu \left[ \nabla \mathbf{V} + \nabla \mathbf{V}^T \right] \] (Newton’s law of viscosity): constitutive type of equation

Here, \( \mu \) is a scalar quantity (viscosity) and does not depend on \( \mathbf{E} \)

b) Compressible fluid

\[ \tau = -\mu \mathbf{E} + \frac{2}{3} \mu \nabla \cdot \mathbf{V} \]

\[ \tau_{xx} = -\mu \left( 2 \frac{\partial V_x}{\partial x} \right) + \frac{2}{3} \mu \nabla \cdot \mathbf{V} \]

\[ \tau_{yy} = -\mu \left( 2 \frac{\partial V_y}{\partial y} \right) + \frac{2}{3} \mu \nabla \cdot \mathbf{V} \]

\[ \tau_{xy} = \tau_{yx} = -\mu \left( \frac{\partial V_x}{\partial y} + \frac{\partial V_y}{\partial x} \right) \]

Equation of motion (for a compressible Newtonian fluid)

\[ \rho \left( \frac{\partial \mathbf{V}}{\partial t} + (\nabla \cdot \mathbf{V}) \mathbf{V} \right) = -\nabla p - \nabla \tau + \rho \mathbf{g} \]

\[ = -\nabla p + \nabla \mu \left( \nabla \mathbf{V} + \nabla \mathbf{V}^T \right) - \nabla \frac{2}{3} \mu \left( \nabla \cdot \mathbf{V} \right) \delta + \rho \mathbf{g} \]

\[ (\nabla \cdot p \delta = \nabla p) \]

Unknowns are \( \mathbf{V} (\mathbf{r}, t) \), \( \rho (\mathbf{r}, t) \), \( p(\mathbf{r}, t) \) and \( \mu (\mathbf{r}, t) \)

- We need three more equations to solve

\[ \mu = \mu(\rho) - (1) \]

\[ \rho = \rho(p) - (2) \]

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{V} = 0 - (3) \]

In Einstein notation,
\[
\rho \frac{\partial v_i}{\partial t} + \rho \left( v_j \frac{\partial}{\partial x_j} \right) v_i = -\frac{\partial}{\partial x_i} p + \frac{\partial}{\partial x_j} \mu \left\{ \frac{\partial}{\partial x_j} v_i + \frac{\partial}{\partial x_i} v_j \right\} - \frac{2}{3} \frac{\partial}{\partial x_j} \mu \frac{\partial v_i}{\partial x_i} + \rho g_i
\]

If \( \rho = \text{const} \) \( \Rightarrow \nabla \cdot \vec{V} = 0 \) or \( \frac{\partial v_i}{\partial x_i} = 0 \) (incompressible fluid)

\[ \mu = \text{constant} \]

\[
\rho \frac{\partial v_i}{\partial t} + \rho \left( v_j \frac{\partial}{\partial x_j} \right) v_i = -\frac{\partial}{\partial x_i} p + \mu \frac{\partial}{\partial x_j} \frac{\partial}{\partial x_j} v_i + \mu \frac{\partial}{\partial x_j} \frac{\partial}{\partial x_i} v_j + \rho g_i
\]

**Schwarz's Rule:**

\[
\frac{\partial^2 y}{\partial x_i \partial x_j} = \frac{\partial^2 y}{\partial x_j \partial x_i}
\]

Therefore, \( \frac{\partial}{\partial x_j} \frac{\partial}{\partial x_i} v_j = \frac{\partial}{\partial x_i} \left( \frac{\partial}{\partial x_j} v_j \right) = 0 \)

\( \nabla \cdot \vec{V} = 0 \) or \( \frac{\partial v_j}{\partial x_j} = 0 \)

(constant fluid density \( \rho = c \); incompressible fluid)

Therefore,

\[
\rho \frac{\partial v_i}{\partial t} + \rho \left( v_j \frac{\partial}{\partial x_j} v_i \right) = -\frac{\partial p}{\partial x_i} + \mu \frac{\partial^2 v_i}{\partial x_j \partial x_j} + \rho g_i
\]

\[
\rho \left( \frac{\partial^2 \vec{V}}{\partial t^2} + \vec{V} \cdot \nabla \vec{V} \right) = -\nabla p + \mu \nabla^2 \vec{V} + \rho \vec{g} \quad \Rightarrow \text{Navier – Stokes equation}
\]

- Conservation of linear momentum for const \( \rho, \text{const } \mu, \text{NF} \)

- Component-wise, the NS equation is as follows:

\[
\rho \left( \frac{\partial v_x}{\partial t} + V_x \frac{\partial v_x}{\partial x} + V_y \frac{\partial v_x}{\partial y} + V_z \frac{\partial v_x}{\partial z} \right) = -\frac{\partial p}{\partial x} + \mu \left( \frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} + \frac{\partial^2 v_x}{\partial z^2} \right) + \rho g_x
\]

You should become familiar with similar expressions in cylindrical and spherical coordinate systems. These expressions are listed in the appendix of all books on transport phenomena.
Homework 1 - 6
(These should be submitted as the course progresses. The instructor will inform.)

HW – 1

Q1. (a) Show that if \( \tau \) is symmetric, i.e. \( \tau_{ij} = \tau_{ji} \)

\[ \tau : \nabla \vec{V} = \nabla \cdot (\tau \cdot \vec{V}) - \vec{V} \cdot (\nabla \cdot \tau) \]

(b) If \( \tau = \begin{pmatrix} 3 & 2 & -1 \\ 2 & 2 & 1 \\ -1 & 1 & 4 \end{pmatrix} \) ; \( \vec{v} = \begin{pmatrix} 5 \\ 3 \\ -2 \end{pmatrix} \), evaluate \( \vec{V} \cdot [\tau \cdot \vec{V}] , \tau : \tau, \vec{V} \cdot \vec{V} \)

Show that

(c) \( \nabla \cdot s \vec{V} = (\nabla s \cdot \vec{V}) + s(\nabla \cdot \vec{V}) \)

(d) \( \nabla \cdot \nabla \vec{V} = \nabla (\nabla \cdot \vec{V}) - [\nabla \times [\nabla \times \vec{V}] \]

(e) \( \nabla \cdot \nabla \vec{V} = \frac{1}{2} \nabla (\vec{V} \cdot \vec{V}) - [\vec{V} \times [\nabla \times \vec{V}] \]

2: Consider the cylindrically symmetric flow field given by \( \vec{V}(r, t) = \theta(t) \cdot \hat{r} \) where \( \theta(t) \) is a time-dependent source at the origin, \( r = 0 \) (a singular point). The velocity of a material point, starting at (or near) \( r = 0 \) decays experimentally with time from a value of \( v_o \). What function of \( t \) must \( \theta(t) \) be in order for this to be true?

3. A sensitive electronic instrument on board a balloon must not experience a rate of change in temperature larger than \( \neq 0.01 \text{ K/s} \) for proper functioning. The atmosphere temperature changes with the height above the ground, and also, with time after sunrise, as given by

\[ T = (288.2 - 6.5 \times 10^{-3} z)(2 - e^{-0.01 t}) K, \text{ where } z \text{ is the height in 'm' above the ground and } 't' \text{ is the time in hour after sunrise.} \]

Find the maximum permissible rate of ascent of balloon when it is about to leave the ground immediately after sunrise?

4. The relation between shear stress, \( \tau \) and the rate of deformation tensor, \( \Xi \) for a NNF is given by

\[ \tau_{ij} = -\eta \Xi_{ij}, \text{ where } \eta \text{ is given by } \sqrt{\frac{1}{2} (\Xi : \Xi)} \]
Calculate, \( \eta' \) of the fluid in a velocity field given by \( \vec{V} = 3xy\hat{i} + 4x^2z\hat{j} - yz\hat{k} \), at the location (1,-1,1) in the flow.

(5) Derive the general property balance for a control volume whose boundaries are moving with fluid velocity \( V \). Use Leibnitz’s theorem:

\[
\frac{\partial}{\partial t} \iiint_V \psi \, dV = \iiint_V \frac{\partial \psi}{\partial t} \, dV + \iint_S \psi (v_s, n) \, dS
\]

where, \( V = V(t) \) and \( S = S(t) \). \( v_s \) is the surface velocity vector.

HW – 2

(1) Determine the force required to move a thin plate of 30×60 cm² size through a liquid of viscosity, \( \mu = 0.05 \frac{kg}{m \cdot s} \) at a velocity of 0.40 m/s. The liquid is filled between two long parallel plates as shown in figure below:

(2) Consider an isothermal, incompressible fluid flowing radially between two concentric porous spherical shells. Assume steady laminar flow with \( V_r = V_r(r) \).

(a) Show by use of the equation of continuity that \( r^2 V_r = \text{Const} \).

(b) Show that the radial pressure distribution may be expressed in terms of \( p \) as

\[
(p - p_R) = \frac{1}{2} \rho V_R^2 \left(1 - \left(\frac{R}{r}\right)^4\right)
\]

(3) In a long cylindrical tube, fluid is initially stationary. At \( t = 0^+ \), the fluid is allowed to flow vertically down under the influence of gravity. Assume axis symmetry, and solve for \( V_z(t, r) \), where \( z \) is the direction of gravity and \( r \) is the radial co-ordinate.

If \( \nu = 3.45 \times 10^{-4} \frac{m^2}{s}, R = 0.7 \text{ cm} \), determine how long it will take for centre – line velocity to reach 90% of the maximum velocity.
(4) Consider a rectangular volume element within the fluid as shown in the following figure:

![Diagram](image)

Show that $\tau_{yx} = \tau_{xy}$. Both $\tau_{yx}$ and $\tau_{xy}$ are shear stresses acting on point $(x, y, z)$, i.e., show the stresses $\tau_{ij}$ and $\tau_{ji}$ are symmetric.

(5) Obtain a solution for the unsteady tangential flow in a coaxial annulus when the fluid is at rest for $t < 0$, and the outer cylinder rotates with angular velocity $\omega$ to cause laminar viscous flow for $t > 0$. Solve for both SS and transient flows.

(6) Obtain a similar solution for the unsteady axial flow in a coaxial annulus, when $t > 0$, a constant $\Delta P (P_o - P_L)$ is applied across the cylinder.

(7) For an incompressible, NF and 2D planner flow, Show that vorticity $\omega$ satisfies diffusion equation:

$$\frac{D\omega}{Dt} = \nu \nabla^2 \omega,$$

similar to the other diffusion equations, namely,

$$\frac{D\mathbf{V}}{Dt} = \nu \nabla^2 \mathbf{V}; \frac{DT}{Dt} = \alpha \nabla^2 T; \frac{DC}{Dt} = D \nabla^2 C$$

**HW – 3**

Q1: It is desired to estimate the rate of heat loss from the meteorological installation shown in figure below from an experiment on a small geometrically similar model of $1/5$ the linear dimensions. The desired surface temperature of the installation and the expected air temperature and wind velocity and direction are known. Under these expected condition, both free and forced convection are probably important, and it, therefore, appears reasonable that the reduced velocity distribution will depend upon both $Re$ and $Gr$. It is desired to use air in the model experiment and
to maintain similarity between the model and full-scale apparatus by varying air pressure and velocity. The temperature dependence of fluid properties may be ignored.

(a) What pressure and relative air velocity should be used in the model experiment to maintain dynamic similarity?

(b) What will be the relative heat – flux form the model?

Q2: Develop governing equations and solve for temperature profiles for unsteady state heat conduction in solids (a) sphere and (b) cylinder. Initial temperature of solid is $T_0$. The outside surface temperature of solids are maintained constant at $T_1$.

Q3. Oil is flowing in the Trans Alaska pipeline in laminar flow. The pipe is fully insulated (adiabatic walls) in order not to melt the permafrost. Viscous heating is important, since $Br$ is large. The temperature at $z = 0$ is $T_0$ everywhere. Derive an expression for SS temperature profile as a function of axial and radial distances. Sketch the temperature profile for large and short values of $z$.

HW - 4
BSL Chapter 18
Q1. 18 A.7
Q2. 18 B.2
Q3. 18 C.1. (a, c, d, e). Do not do part (b)!
Q4. 18 C.3.

HW – 5
Q 1. Re-solve BSL 2.5 (flow of two adjacent immiscible fluids)
   2. Lecture 17 (condensation of a saturated steam over a flat vertical plate)
      a. Solve velocity profile, $v_z(x)$
      b. Derive the expression for $\delta_f(x)$
c. Calculate local Nusselt number, \( Nu(x) \)

d. Show that \( \bar{h} = \frac{4}{3} (h_f \text{ at } x = L) \)

3. Creeping flow (BSL example 4.2-1)
   a. Solve for \( V_r, V_\theta \)
   b. Solve for pressure distribution on sphere
   c. Determine Stoke’s law
   (Go as far as possible. It is a tedious problem)

4. (a) Starting with the complex potential
   \( \omega(z) = -V_\infty R \left( \frac{z}{R} + \frac{R}{z} \right) \) for the potential flow around a circular cylinder of radius \( R \), when the approach velocity is \( V_\infty \), show that the form drag is zero on the cylinder – BSL example 4.3-1.

   **Resolve** the problem in polar coordinate \( \psi(r, \theta) \) - Deen example 8.3 – 1

5. What is the flow field for the problem of opposite impingement of two incompressible, infinitely wide, axi-symmetrical cylindrical jets. What is the stream function, and the potential function? Sketch them. Consider the case where the stagnation plane is flat.

HW – 6

**Q1.** Relative magnitude of molecular and eddy viscosity:- determine \( \mu(t)/\mu(l) \) at \( s = R/2 \) for water flowing at SS in a long smooth round tube under the following conditions:

\[ R = \text{tube radius} = 100 \text{ mm}, \tau_0 = 1650 \text{ kg/s/m}^2, \rho = 1.25 \text{ kg/m}^3, \nu = 15 \times 10^{-6} \text{ m}^2/\text{sec} \]

**Q 2.** Estimate the energy dissipation rate in cumulus cloud both per unit mass and for the entire cloud. Base your estimates on velocity and length scales typical of cumulus clouds. Also estimate the Kolmogorov microscale, \( l_n \). Use \( \rho = 1.25 \text{ kg/m}^3 \) and \( \nu = 15 \times 10^{-6} \text{ m}^2/\text{sec} \)

**Q 3.** The large eddies in turbulent flow have length scale \( l \), a velocity scale \( V(l) = u \), and a time scale \( t(l) = \frac{l}{u} \). The smallest eddies have length scale \( n \), a velocity scale, \( v \) and a time scale \( t \).

Estimate the characteristic velocity \( V(r) \) and the characteristic time \( t(r) \) of eddies of size \( r \), where \( r \) is any length in the range \( n < r < l \). Do this by assuming that \( V(r) \) and \( t(r) \) are determined by \( e \) and \( r \) only. Show that your results agree with the known velocity and time scales of \( r = l \) and \( r = n \). The energy spectrum of turbulence is a plot of \( E(K) = K^{-1}V^2(k) \), where \( K = \frac{1}{r} \) is the “wave number” associated with eddies of size \( r \). Find an expression for \( E(K) \).
Notes: (1) Property balance is independent of choosing reference frames.

(2) General property balance can also be derived starting with the material rate of change and using the Reynolds transport equation;

\[
\frac{D\psi}{Dt} = \frac{\partial}{\partial t} \iiint_{cv} \psi dV + \iint_S \psi (V_s \cdot n) dS, \text{ where the last term can be written as } \iint_S (\nabla \cdot \psi V_s) dV
\]

So far,

(1) \textbf{NS equation} (\(\rho = \text{const}, \ \mu = \text{const}, \ NF\))

\[
\rho \left( \frac{\partial \vec{V}}{\partial t} + (\vec{V} \cdot \nabla) \vec{V} \right) = -\nabla p + \mu \nabla^2 \vec{V} + \rho \vec{g} \quad \text{(vector eq)}
\]

(2) \(\nabla \cdot \vec{V} = 0\) : equation of continuity

Now, there are 3 momentum (scalar components) and 1 continuity equations. So, \(\vec{V}(V_x, V_y, V_z)\) and \(p\) can be solved.

Notes: (1) When it is possible to solve \(\vec{V}\) using continuity alone without momentum balance, we have a kinematic solution. In such case, we have a 1st order ODE and we need only one bc for each non-zero component.

(2) \textbf{In general,} NS and continuity must be solved simultaneously to determine \(\vec{V} & p\).

\[
\Rightarrow \quad \text{a) PDE}
\]

\[
\text{b) Non-linearity on dependent variable: } (\vec{V} \cdot \nabla) \vec{V}
\]

\[
\left( V_x \frac{\partial V_x}{\partial x}, \text{ etc} \right)
\]

Leads to non-stable, chaotic behavior: difficult to solve

\[\rightarrow \text{Turbulence} \]

( unsteady state ) \(\frac{\partial \vec{V}}{\partial t} \Rightarrow \text{parabolic wrt time} \]

In space \((x, y, z)\) NS makes it an elliptic equation (difficult to solve)

(3) \(\mu \nabla^2 \vec{V} = \mu \nabla \left( \nabla \cdot \vec{V} \right) - \mu \nabla \times \left( \nabla \times \vec{V} \right) = -\mu \nabla \times \left( \nabla \times \vec{V} \right) \) (show it as an exercise)

Viscous term \((\rho = c)\):

\[
\mu \nabla^2 \vec{V} = 0 \quad \text{if either } \mu = 0 \quad \text{(inviscid fluid)}
\]

\[
or \ \nabla \times \vec{V} = 0 \quad \text{or both.}
\]

irrotational

Go one step back, \(\nabla \cdot \vec{V} = 0\) : \textit{no molecular flux (non – convective)} (shear forces are zero)
\[
\rho \frac{D\vec{V}}{Dt} = -\nabla p + \rho \vec{g}
\]
\Rightarrow \rho \left( \frac{\partial \vec{V}}{\partial t} + (\vec{V} \cdot \nabla) \vec{V} \right) = -\nabla p + \rho \vec{g} \quad \text{(non linear on } \vec{V})

- Euler’s equation (no viscous effect or term, i.e. fluid is inviscid or irrotational? or both??)

Under SS, integrate along a streamline to derive Bernoulli’s equation (see BSL; to be revisited later in the course).

**Some more on viscosity:**

\[ \tau \text{ depends on } \dot{E} = \frac{1}{2} \left( \frac{\partial}{\partial t} + \left( \frac{\partial}{\partial x} \right)^T \right) \]

Rate of strain-tensor

For NF and \( \rho = c \):

\[ \tau = -\mu \dot{E}, \text{ where scalar } \mu \neq f(E) \Rightarrow \text{linear. It may be a function of } (T,P) \]

**NNF:**

\[ \tau \text{ depends non-linearly on } \dot{E} \]

\[ \tau = \eta \left( \dot{E}, \dot{E} \right) \]

\[ \text{a scalar function of the tensor } \dot{E} \]

Thus, \( \eta \) must depend on scalar invariants of \( \dot{E} \)

Such as \( I_1 = \dot{E} : \dot{E} \) - scalar

\[ I_2 = \dot{E} : \dot{E} \] - do-

\[ I_3 = \text{Det } \dot{E} \] - do-

It turns out that \( I_1 = 0 \) for incompressible fluids

Since, \( E_1 : \dot{E} = 2 \nabla \cdot \vec{V} = 0 \)

\[ \eta = \eta \left( I_2, I_3 \right) \]

Usually, influence of \( I_3 \) is negligible,

\[ \eta = \eta \left( E, E \right) \]

eg. \( \eta = m \left( \sqrt{I_2} \right)^{n-1} \) (pseudoplastic, thixotropic)
- Osborn de waals model (BSL)

**Note:** No elastic property considered so far, only viscosity

Like in viscoelastic fluid.

**Dimensional Analysis**

The governing conservation equations should be non-dimensionalized before solving:

(a) Dimensionless numbers (groups) resulting out of non-dimensionalization can be used to make approximation. However, in doing so, the characteristic variables (length, time, etc) must be correct (physically consistent).
(b) Such parameters can be used as scaling parameters which allows one equation to be used for both scales of phenomenon.

**Reverting to NS equation:**

![Diagram of geometrical similarity][1]

But two different fluids \((\mu, \rho)\) and velocities \((\vec{V})\)

Non-dimensionalize as far as possible by choosing the characteristic values of parameters such that each variable is scaled to be of the order of 1.

Define \(x^* = \frac{x}{l}\): characteristic length \(l\) is the length over which change takes place in \(x\) direction, such that \(0 < x^* < 1\).
\[
\begin{align*}
    y^* &= \frac{y}{l}, \quad z^* = \frac{z}{l} \\
    t^* &= \frac{t}{t_{\text{char}}}, \quad t_{\text{char}} = \frac{l}{V} \\
    V_x^* &= \frac{V_x}{V}, \quad V_y^* = \frac{V_y}{V}, \quad V_z^* = \frac{V_z}{V} \\
    p^* &= \frac{p}{\rho V^2} \left( \frac{p}{p_0} ? \right), \quad g^* = \frac{g}{g_c} \to F/\text{mass} \\
    \frac{\partial}{\partial t^*} = \frac{\partial}{\partial t}/t_{\text{char}} = \frac{l}{V} \frac{\partial}{\partial t} \\
    \{ \nabla^* = l \nabla, \quad \nabla^* = l^2 \nabla^2 \} \\
\end{align*}
\]

**NS:** \( \rho \frac{D\vec{V}}{Dt} = -\nabla p + \mu \nabla^2 \vec{V} + \rho \vec{g} \)

\[
\begin{align*}
    \frac{\rho V^2 D\vec{V}^*}{l} &= -\frac{\rho V^2}{l} \nabla^* p^* + \frac{\mu V}{l^2} \nabla^2 \vec{V}^* + \rho g^* g_c \\
    \frac{D\vec{V}^*}{Dt^*} &= -\nabla^* p^* + \left[ \frac{\mu}{\rho V l} \right] \nabla^2 \vec{V}^* + \left[ \frac{g_c}{V^2} \right] g^* \\
\end{align*}
\]

\( \text{scaled to order 1} \to O(1) \)

(1) \( \left[ \frac{\rho V l}{\mu} \right] = \text{Re (dimensionless; Reynolds \#)} \)

(2) \( \left[ \frac{V^2}{g_c L} \right] = \text{Fr} \quad (\text{Froude \#}) \)

(A) If two different systems have
(a) same dimensionless BCs
(b) same dimensionless equations

They have same dimensionless solution: \( V^*(x^*) \)

(a) is true when they have geometric similarity:

\[ \bigtriangleup \bigtriangleup \quad \text{or} \quad \bigcirc \bigcirc \]

(b) is true when they have dynamic similarity (same \( \text{Re} \) & \( \text{Fr} \))

In such case, two systems are consistent with each other as far as scaling up or down is concerned.

(B) \( \text{Re} \) indicates the relative importance of different terms/effects in the equation:

\[
\begin{align*}
    \text{inertial effects} & \quad \frac{D\vec{V}^*}{Dt^*} \quad \text{order} \quad \left[ \frac{\mu}{\rho V l} \right] \nabla^2 \vec{V}^* \quad \text{order} \\
    \text{viscous effects} & \quad \text{order} \quad \left( \frac{\rho V l}{\mu} \right) \text{order} \\
\end{align*}
\]
Fr indicates the relative importance of different terms/effects in the equation:

\[
\frac{\text{inertial effects}}{\text{gravitational effects}} \approx \frac{\frac{\partial \mathbf{V}^*}{\partial t^*}}{\left[ \frac{g c}{v^2} \right] g^*} \approx \left( \frac{g c}{v^2} \right)
\]

So, the non-dimensionalized NS equation becomes

\[
\frac{D \mathbf{V}^*}{Dt^*} = -\nabla^* p^* + \frac{1}{Re} \nabla^* \mathbf{V}^* + \frac{1}{Fr} g^*
\]

**Case 1:** If \( Re \ll 1 \) & \( Fr \gg 1 \) (gravitational effect is negligible)

Then the NS equation becomes

\[
\nabla^* \mathbf{V}^* = 0 \Rightarrow \nabla^2 V = 0 \quad (Fr \equiv \frac{V^2}{g c L})
\]

In the above equation, all terms are of the order 1, except coefficient. They determine whether the effects of terms are negligible or not. If \( Re = 0.1 \ per \ say \), the order becomes 10 and all other terms are \( \sim 1 \Rightarrow creeping \ flow \) (viscous effect dominates)

**Case 2:** Likewise, if \( Re \gg 1 \)

\[
\frac{D \mathbf{V}^*}{Dt^*} = -\nabla^* p^* + \frac{1}{Fr} g^* \left( \frac{1}{Re} \nabla^* \mathbf{V}^* \right) \text{ drops out, and the modified equation is Euler’s equation}
\]

**Note:** In the latter case 2BCs are gone. Also, recall that, to be able to decide correctly whether \( Re \gg 1 \ or \ll 1 \), leading to dropping or retaining the viscous term in the equation, characteristic lengths must be physically consistent (correct), else there will be enormous error in physical results/data --- to be discussed later in the context of boundary layer theory.
Lecture #05

Mechanical/Kinetic Energy Balance

Balance of mechanical energy: \( \frac{1}{2} \rho V^2; \text{cal}/m^3 \text{ or } J/m^3 \)

General balance equation: property/cm³-s

If we put \( \psi = \frac{1}{2} \rho V^2 \); the equation cannot distinguish between \( \vec{\psi} \) (non-conductive mode of KE transport) and \( \vec{\psi}_g \) (generation or source of KE) ⇒ needs a different approach

Alternative: Take a dot \( \vec{V} \) into the linear momentum balance or NS equation:

\[
\vec{V}. \left[ \rho \frac{DV}{Dt} = -\nabla p - \nabla . \tau + \rho \vec{g} \right]
\]

\[
\rho V \frac{DV}{Dt} = -\nabla p - \nabla . \tau + \vec{V} \cdot \rho \vec{g}
\] - eq. (1)

L.H.S. ⇒ \( \rho V \frac{DV}{Dt} = \rho \frac{d}{dt} \left( \frac{1}{2} \rho V^2 \right) = \rho \left( \frac{\partial}{\partial t} + \nabla . \vec{V} \right) \frac{V^2}{2} \)

\[
= \frac{\partial}{\partial t} \left( \frac{1}{2} \rho V^2 \right) + \nabla . \left( \frac{1}{2} \rho V^2 \right) \vec{V} \quad : \text{add} \left( \frac{\partial \rho}{\partial t} + \nabla . \rho \vec{V} = 0 \right) \times \frac{V^2}{2} \quad (\rho \neq c)
\]

R.H.S. ⇒ \(-\nabla . p \vec{V} - p(-\nabla . \vec{V}) - \nabla . \left[ \tau . \vec{V} \right] + \left[ \tau : \nabla \vec{V} \right] + \rho V g \)

\(1^{st} \text{ term} \quad 2^{nd} \text{ term} \)

(H.W. : Show that \( \tau : \nabla \vec{V} = \nabla . \left[ \tau . \vec{V} \right] - \vec{V} \cdot \nabla . \tau \))

ME balance:

\[
\frac{\partial}{\partial t} \left( \frac{1}{2} \rho V^2 \right) + \nabla . \left( \frac{1}{2} \rho V^2 \vec{V} \right) = -\nabla . p \vec{V} - p(-\nabla . \vec{V}) - \nabla . \left[ \tau . \vec{V} \right] - \left[ \tau : \nabla \vec{V} \right] + \rho V g \quad : \text{eq. (2)}
\]

\( \text{unsteady state term} \quad \text{convective transport} \quad \text{work done by pressure} \quad \text{reversible conversion to internal energy} \quad \text{work done by viscous forces} \quad \text{work done by gravity} \quad \text{irreversible conversion to internal energy (viscous heating)} \)

\( -\nabla . \left( \phi \vec{V} \right) = \phi \vec{V} \)

is always +ve (see H.W.)

Now, let us seek the equation of change for internal energy, or total energy (?):

\[
\text{General property balance} \Rightarrow \frac{\partial \psi}{\partial t} + \nabla . \psi \vec{V} = -\nabla . \vec{\psi} + \vec{\psi}_g \quad : \text{cal}/s - m^3
\]
Let us start with $\psi = \text{Total energy} = (IE + KE + PE)/\text{volume} = \rho \left( U + \frac{1}{2} v^2 + \phi \right) (\text{J/m}^3)$

$\psi_g = 0; \overline{\dot{V}} = \text{energy flux (non – convective)}$; it contains two terms:

(a) $\dot{q}$: conduction, radiation $\left( \text{cal/s} - \text{m}^2 \right)$
(b) surface work $\overline{P} \cdot \overline{V} \left( \text{cal/s} - \text{m}^2 \right)$

(Analogous to $p \left( \frac{dV}{dt} \right) = \iint p \left( \frac{dl}{dt} \right) dS = \iint pVdS$)

$p \cdot \overline{V} = (p \delta + \tau) \cdot \overline{V} = p\overline{V} + \tau \overline{V}$

$\nabla \cdot P \cdot \overline{V} = \nabla \cdot p\overline{V} + \nabla \cdot \tau \cdot \overline{V}$

And equation is

$$\frac{\partial}{\partial t} \rho \left( U + \frac{1}{2} v^2 + \phi \right) + \nabla \cdot p\overline{V} \left( U + \frac{1}{2} v^2 + \phi \right) = -\nabla \cdot \dot{q} - \nabla \cdot p\overline{V} + \nabla \cdot \tau \cdot \overline{V}$$

or $\rho \frac{D(U + \frac{1}{2} V^2 + \phi)}{Dt} = -\nabla \cdot \dot{q} - \nabla \cdot p\overline{V} + \nabla \cdot \tau \cdot \overline{V}$ [subtract $\left( \frac{\partial \rho}{\partial t} + \nabla \cdot \rho \overline{V} \right) = 0$ from LHS term]

Let $\phi$ ($PE$) be due to gravity:

$\tilde{g} = -\nabla \phi \rightarrow \text{grad of a scalar}$

$$\rho \frac{D \phi}{Dt} = \rho \frac{\partial \phi}{\partial t} + \rho \overline{V} \cdot \nabla \phi = -\nabla \cdot \rho \overline{V} \cdot \tilde{g}$$

$$\rho \frac{D}{Dt} \left( U + \frac{1}{2} V^2 \right) = -\nabla \cdot \dot{q} - \nabla \cdot p\overline{V} + \nabla \cdot \tau \cdot \overline{V} + p\overline{V} \cdot \tilde{g}$$

- (3)

observer is moving with fluid

Subtract ME eq. (2) from eq. (3)

$$\rho \frac{\partial U}{\partial t} + \rho \left( \overline{V} \cdot \nabla \right) U = -\nabla \cdot \dot{q} - p\overline{V} - \tau \cdot \nabla \overline{V}$$

unsteady IE change

IE convected

molecular heat transfer

reversible work done to IE

irreversible conversion to IE

observer is moving with fluid
Inspect equations (2) and (3) (or IE and ME balances)

(1) $-\tau: \nabla \vec{V}$ is always +ve (IE always increases because of viscous heating; there is nothing called viscous cooling! ME always decreases on the other hand.

- Such energy-change is irreversible.
- When we speak of an isothermal system in a flowing system, it is clear that it is an assumption. There is no true isothermality per say. Flowing fluid will always be heated.

(2) $p \left( -\nabla \cdot \vec{V} \right)$ appears in both eqs as +ve and -ve, but it can be +ve or –ve. Fluid expands: IE ↓ ME ↑ (work done by fluid) or fluid is compressed, IE ↑ ME ↓ (work done on fluid)

Considering $T$ is measurable, IE balance is used as the working equation:

$$\rho \frac{dU}{dt} = -\nabla \cdot \vec{q} - p \nabla \cdot \vec{V} - \tau: \nabla \vec{V}$$

(viscous heating, irreversible)

(change in IE)

(conduction on (non – convective flux)

(reversible work (expansion or compression))

(Note that this equation allows chemical reactions, change in composition, $\rho \neq c$)

For now, restrict to no-chemical reaction or non-reactive flow:

Let $U = U(T, \forall)$

$$dU = \left( \frac{\partial U}{\partial \forall} \right)_T d\forall + \left( \frac{\partial U}{\partial T} \right)_\forall dT$$

$$= \left[ -p + T \left( \frac{\partial p}{\partial T} \right)_\forall \right] d\forall + C_\forall dT$$

$$\rho \frac{dU}{dt} = \rho \left[ -p + T \left( \frac{\partial p}{\partial T} \right)_\forall \right] \frac{d\forall}{dt} + \rho C_\forall \frac{dT}{dt}$$

Now, $\frac{d\forall}{dt} = \frac{d(1/\rho)}{dt} = -\frac{1}{\rho^2} \frac{d\rho}{dt} = -\frac{1}{\rho^2} \left[ -\rho \nabla \cdot \vec{V} \right]$  

Substituting,

$$\rho C_\forall \frac{dT}{dt} = -\nabla \cdot \vec{q} - \rho \left[ -p + T \frac{\partial p}{\partial T} \right] \left[ \frac{1}{\rho} \nabla \cdot \vec{V} \right] - p \nabla \cdot \vec{V} - \tau: \nabla \vec{V}$$

$$\rho C_\forall \frac{dT}{dt} = -\nabla \cdot \vec{q} - T \left( \frac{\partial p}{\partial T} \right)_\forall \nabla \cdot \vec{V} - \tau: \nabla \vec{V}$$

(no reaction)

One can also show,
\[ \rho C_p \frac{dT}{dt} = -\nabla \cdot \vec{q} - T \left( \frac{\partial V}{\partial T} \right)_p \frac{dp}{dt} - T \nabla \cdot \vec{V} \]

Now, we need to relate \( \vec{q} \) to \( T \) via the constitutive equation, similar to \( \tau \) relating to \( \vec{V} \):

e.g. \( \tau = \mu [\nabla \vec{V} + \nabla \vec{V}^T] \quad (\text{For } NF) \)

and \( -\tau : \nabla \vec{V} = +\mu [\nabla \vec{V} + \nabla \vec{V}^T] : \nabla \vec{V} = +\nu (\phi^2) \)

Fourier’s Law, \( \vec{q} = -k \nabla T \hat{n} \)

property of material

\[ \rho C_v \frac{dT}{dt} = \nabla \cdot k \nabla T \hat{n} - T \left( \frac{\partial p}{\partial T} \right)_V \nabla \vec{V} + \phi^2 \quad (4a) \]

\( (\nabla \vec{V} = 0 \text{ for incompressible fluid}) \)

Therefore, if \( \rho = c, \ k = \text{const}, \ \phi^2 = \text{negligible} \),

\[ \rho C_v \frac{dT}{dt} = \rho C_v \left( \frac{\partial T}{\partial t} + \nabla \cdot \vec{V} \right) = k \nabla^2 T \quad (4b) \]

If we allow for a chemical reaction, the equation is easily modified as

\[ \rho C_v \frac{dT}{dt} = \rho C_v \left( \frac{\partial T}{\partial t} + \nabla \cdot \vec{V} \right) = k \nabla^2 T + (r)(-\Delta H) \quad (\text{cal/s-cm}^3) \quad (4c) \]

, where \( r \) is the rate of reaction in moles/s-cm\(^3\) and \( \Delta H \) is the heat of reaction in cal/moles, which could be +ve or –ve depending on the endothermic or exothermic reaction, respectively. However, we require an additional species conservation equation (to be discussed later). Features of the equation are

(1) PDE
(2) linear in \( T \) unlike momentum equation (non-linear on \( \vec{V} \))
(3) elliptic in space
(4) scalar equation

Recall NS:

\[ \rho \left( \frac{\partial \vec{V}}{\partial t} + (\vec{V} \cdot \nabla) \vec{V} \right) = -\nabla p + \mu \nabla^2 \vec{V} + \rho \vec{g} \]

Now, the variables are \( \vec{V}, p, T \) \( (\text{non – isothermal, but without reaction, why?}) \)

the equations are also 3: Continuity, NS, Energy

And,

physical property: \( \mu = \mu(T), \ k = k(T) \)
Gas law: \( p = \rho RT \) or \( p = p(\rho, T) \)
or \( \rho = \rho_o \) (constant density / incompressible fluid, or liquid)\)
Lecture #06

Coupling between energy & momentum equations: Free convection or buoyance - driven flow

(Incompressible fluid: \( \nabla \cdot \vec{V} = 0 \))

\[
\rho \frac{d\vec{V}}{dt} = -\nabla \tau - \nabla p + \rho \vec{g} \quad (1) \quad (p \text{ is the actual pressure and not dynamic pressure})
\]

Two extreme situations of coupling (or no-coupling)

(1) In forced convection, \( \nabla p \)' is due to an externally applied source term for momentum generation. In free convection, no external source or pressure is imposed and \( \nabla p \) is the same with or without flow. In such case, solve for velocity fields from NS equation and superimpose the solutions or velocity fields on energy balance equation—thus there is no coupling.

(2) In free convection, difference in \( \rho(x,y,z) \) arises because of \( \nabla T \) (or concentration in a mixture), but without \( \vec{g} \) natural convection can not take place.

\[ \nabla p = \bar{\rho} \vec{g} \equiv \text{static pressure difference} \]

Flow is not induced because of \( \nabla p \) per say, but because of \( \bar{\rho} \vec{g} \) relative to \( \rho \vec{g} \), where \( \rho \) is the local fluid density. In other words, each fluid layer rises (or falls) because of its density that is different from the neighboring fluid layer (\( \bar{\rho} \))

Therefore,

\[
\rho \frac{d\vec{V}}{dt} = -\bar{\rho} \vec{g} - \nabla \tau + \rho \vec{g}
\]

\[ = -\nabla \tau - \vec{g}(\bar{\rho} - \rho) \]

Boussinesq approximation (1):

\[
\frac{\Delta \rho}{\bar{\rho}} \ll 1
\]

maximum change in \( \rho \)

Now, \( \rho = \bar{\rho} + \left( \frac{\partial \rho}{\partial T} \right)_p (T - \bar{T}) \) - Taylor’s series (leading term only) and assuming \( \rho \neq \rho(p) \)

\[ = \bar{\rho} - \bar{\rho} \beta (T - \bar{T}) \]

coeff. of volume expansion. \( \beta = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_T \)

The modified momentum conservation equation or NS equation

(1) \( \rho \frac{d\vec{V}}{dt} = -\nabla \tau - \bar{\rho} \vec{g}(T - \bar{T}) \)  

(2) \( \nabla \cdot \vec{V} = 0 \) \( (\rho = \text{constant wrt } p \text{ but not with respect to } T) \)
**Boussinesq approximation (2):** \( \rho \) can be replaced everywhere by the constant value \( \bar{\rho} \), except in the buoyancy term. Therefore, for a constant \( \rho \) and \( \mu \) fluid:

\[
\frac{d\vec{V}}{dt} = \nu \nabla^2 \vec{V} - \bar{g} \beta (T - \bar{T}) \quad \text{(free convection)}
\]

**Note:** \( \bar{T} \) is unknown and so is \( \bar{\rho}(T) \) and is different from situation (problem) to situation (problem). Energy balance equation is required to solve for \( T \) and \( \bar{T} \):

\[
\rho C_p \frac{dT}{dt} = k \nabla^2 T + \phi \nabla \vec{V} \quad \text{(Newtonian fluid)}
\]

\[
\frac{dT}{dt} = \alpha \nabla^2 T \quad \text{(neglecting viscous dissipation term)}
\]

\( \Rightarrow \) Without Boussinesq approximation 2, momentum conservation equation for free convection:

\[
\rho \frac{d\vec{V}}{dt} = \mu \nabla^2 \vec{V} - \bar{\rho} \bar{g} \beta (T - \bar{T}) \quad \text{(\( \rho \neq \bar{\rho} \))}
\]

**Note:** \( \rho \) is not cancelled out, and as per Deen, all solutions have considered approximation 2

A general conservation equation can also be written for **mixed convection** (forced + free convection):

\[
\frac{d\vec{V}}{dt} = -\frac{dp}{p} - \bar{g} \beta (T - \bar{T}) + \nu \nabla^2 \vec{V}
\]

where, \( p \equiv \text{defined as dynamic pressure} \Rightarrow \nabla p = \nabla p - \bar{\rho}g \) (note difference between \( p \) and \( \rho \)). This also implies that dynamic pressure difference is zero in a static fluid.

To this end, for a constant \( \rho \) & \( \mu \) (\( NF \)) fluid:

**Continuity:** \( \nabla \cdot \vec{V} = 0 \)

**Momentum:** \( \rho \frac{d\vec{V}}{dt} = -\nabla p + \mu \nabla^2 \vec{V} + \rho \bar{g} \) (forced convection)

\[
= \mu \nabla^2 \vec{V} - \bar{\rho} \beta \bar{g}(T - \bar{T}) \quad \text{(free convection)}
\]

**Energy:** \( \rho C_p \frac{dT}{dt} = k \nabla^2 T + \phi \nabla \vec{V} \)

Variables are: \( \vec{V}, p, T \) for forced convection

and \( \vec{V} \) and \( T \) for free convection and \( \bar{\rho}(\bar{T}) \)

**Dimensional Analysis:**

**(A) Forced Convection:** Need Characteristic variables for \( l, V, t, p, T \)

\[
v^* = \frac{V}{V} ; \quad x^*, y^*, z^* = \frac{x, y, z}{l} ; \quad t^* = \frac{t}{V} ; \quad T^* = \frac{T - T_o}{T_1 - T_o} : \text{O}(1)
\]
Continuity: \( \nabla \cdot \vec{V}^* = 0 \)

NS: \( \frac{DV^*}{Dt^*} = \frac{1}{Re} \nabla^2 V^* - \nabla^* p^* + \frac{1}{Fr} g^* \)

Energy: \( \frac{DT^*}{Dt} = \frac{1}{RePr} \nabla^2 T^* + \frac{Br}{RePr} \phi V^2 \) (show it as an exercise)

\[ Re = \frac{l_c \bar{\nu} \rho}{\mu} , \quad Fr = \frac{\bar{V}^2}{g l_c} = \frac{\rho \bar{V}^2}{\rho g l_c} , \quad Pr = \frac{V}{\alpha} = \frac{\mu / \rho}{k / \rho C_p} = \text{momentum diff. coeff.} / \text{thermal diff. coeff.} \]

Gases: \( Pr \approx 0.7 \), liquid (water, Hg) \( Pr \approx 1000 \)

Get physical meanings of the dimensionless groups (relative importance or effect of different terms in the transport governing equation or conservation equations):

\[ Br \equiv \text{Brinkman #} = \frac{Br}{RePr} \phi V^2 / \frac{1}{RePr} \nabla^2 V^* = \frac{\mu V^2}{k(T_1 - T_o)} \]

\[ \text{thermal energy produced by viscous dissipation} / \text{conduction transport of thermal energy} \]

\[ RePr = \text{Peclet #} = \frac{DT^*}{Dt^*} / \frac{1}{RePr} \nabla^2 T^* = \left( \frac{\text{convective effect}}{\text{conduction effect}} \right) \text{ of heat transport} \]

\[ Pr = \frac{1}{Re} \left( \nabla^2 V^* \right) / \frac{1}{RePr} \nabla^2 T^* = \frac{\text{molecular momentum transport}}{\text{heat\-conduction transport}} \] (another def? same as before)

**Non-dimensionalization:**
(a) Ascertains relative importance of each feature/effect in equation.
(b) Determines scale between prototype and full dynamical similarity
(c) Determines analogy between momentum and heat transfer. Needs identical non-dimensional equations.

**(B) Free convection:** Needs characteristic length, \( l \) (vertical layer), and velocity, \( v_c = ? \)

1. \( Re = \frac{\rho V l}{\mu} \approx 1 \) (viscosity prevents convective current from increasing; a steady – state \( V_s \) is attained:

   \[ V_s \approx \frac{\mu}{\rho l} \]

2. \( t = \frac{l}{V_s} = \frac{\rho l^2}{\mu} \) is the time to reach SS velocity \( V_s \)

Get \( \frac{DV^*}{Dt^*} = \nabla^2 V^* - T^* Gr g^* \) (dimensionless form of momentum balance in free convection)

where, \( Gr \equiv \text{Grashoff #} = \frac{g \rho^2 \beta (T_1 - T_o) l^3}{\mu^2} \) vertical length; \( T^* = \frac{T - T_o}{T_1 - T_o} \)

(relative importance of buoyancy with respect to viscose effects in natural convection.)
Lecture #07

Equation of Change for Species

Property, $\psi \equiv C_i (\text{moles/cm}^3), \rho_i \left(\frac{g}{\text{cm}^3}\right), \ i = 1,2,3 \ \text{species}$

$\Phi = \text{flux of } \psi = n_i \left(\frac{g}{\text{cm}^2\cdot s}\right) \text{ or } N_i \left(\text{moles/cm}^2\cdot s\right); \ \text{includes convective and non-convective modes}$

General property balance:

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot n_i = r_i \ \text{or} \ \frac{\partial C_i}{\partial t} + \nabla \cdot N_i = R_i \ (n_i, N_i \ \text{are vectors}) \ \text{eq. (1)}$$

$$\sum_i (\frac{\partial \rho_i}{\partial t} + \nabla \cdot n_i) = 0 \ \text{sum over all species (i) in reaction rates}$$

(mass is conserved and not moles)

$\Rightarrow$ As noted earlier, $n_i$ and $N_i$ contain both convective and diffusion fluxes.

$g/s - \text{cm}^2: \ n_i = \rho_i v_i = \rho_i \vec{V} + j_i = \omega_i \sum n_i + j_i = \omega_i n_T + j_i$

velocity of

$i$' component

convective flux

diffusion flux

mass fraction

$\rho_i/\rho$

That brings definition for $\vec{V} = \text{local mass average velocity} = \frac{\sum \rho_i v_i}{\sum \rho_i (= \rho)}$ (bulk flow velocity)

Sum over all species,

$$\sum_i \left(\frac{\partial \rho_i}{\partial t} + \nabla \cdot n_i\right) = \sum r_i \Rightarrow \frac{\partial \rho}{\partial t} + \nabla \cdot n_T = 0; \ \text{summation over all species in eq. (1)}$$

This equation is similar to the mass conservation equation for a pure fluid

$\text{moles/s - cm}^2: \ N_i = C_i v_i = C_i \vec{V}^* + j_i \Rightarrow \vec{V}^* = \text{molar average velocity} = \frac{\Sigma C_i v_i}{\Sigma C_i}$

$molar diffusion flux$

$defined as \ \sum j_i = 0 \ \text{and} \ \sum i j_i = 0$
\[ \sum_i \left( \frac{\partial C_i}{\partial t} + \nabla N_i \right) = \sum R_i \Rightarrow \frac{\partial C}{\partial t} + \nabla N = \sum R_i \neq 0 \] summation over all species in eq. (1)

(mass is conserved and not moles)

**Binary diffusion (A & B only):**

\[
\begin{align*}
J_A &= -C D_{AB} \nabla y_A \rightarrow \text{Fick's 1st law} \quad \left( \text{moles of } A \right)_{s-cm^2} \\
&\quad \text{or Fick's law} \\
J_A &= -\rho D_{AB} \nabla \omega_A = -(C^2 / \rho) M_A M_B D_{AB} \nabla y_A \quad \left( \text{g of } A \right)_{s-cm^2} \\
&\quad \text{relative to the fluid's velocity} \\
&\quad \text{observe moving at} \quad (C, \rho \equiv \text{total})
\end{align*}
\]

Also, note that \( j_i = \rho_i (v_i - \bar{V}) \); \( J_1 = C_1 (v_1 - \bar{V}^*) \) (diffusion flux is relative to bulk avg velocity; inertial frame)

\[ \Rightarrow \text{Show that BSL Table 17.8 - 2: given terms for } j_A, j_A^*, \text{ etc are equivalent for binary mixture.} \]

**General species balance:**

\[
\begin{align*}
g/s - cm^3: & \quad \frac{\partial \rho_A}{\partial t} + \nabla \rho_A \bar{V} = \nabla \cdot \rho D_{AB} \nabla \omega_A + r_A \\
&\quad \text{mass avg. velocity} \quad j_A \\
moles/s - cm^3: & \quad \frac{\partial C_A}{\partial t} + \nabla C_A \bar{V}^* = \nabla \cdot C D_{AB} \nabla y_A + R_A \\
&\quad \text{molar avg. velocity}
\end{align*}
\]

**Special cases:**

(A) Const \( \rho, D_{AB} \) (liquid may be at rest)

\[
\frac{\partial \rho_A}{\partial t} + \rho_A \bar{V} \cdot \bar{V} + \bar{V} \cdot \nabla \rho_A = \nabla \cdot D_{AB} \nabla \rho_A + r_A \\
( \nabla \bar{V} = 0 )
\]

\[
\frac{\partial \rho_A}{\partial t} + \bar{V} \cdot \nabla \rho_A = D_{AB} V^2 \rho_A + r_A \rightarrow g/s - cm^3
\]

Divided by \( m_\omega \) (molecular wt of \( A \))

\[
\frac{\partial C_A}{\partial t} + C_A \bar{V} \cdot \bar{V}^* + \bar{V}^* \cdot \nabla C_A = C D_{AB} V^2 y_A + R_A \rightarrow \text{moles/s - cm^3} \\
\text{(reaction rate)} : \text{This is often used as working equation for species balance}
\]

(B) Const \( C & D_{AB} \) (dilute gas at const \( T \ & p \))

\[
\frac{\partial C_A}{\partial t} + C_A \bar{V} \cdot \bar{V}^* + \bar{V}^* \cdot \nabla C_A = C D_{AB} V^2 y_A + R_A \rightarrow \text{moles/s - cm^3}
\]

But \( \nabla \bar{V}^* \neq 0 = \frac{1}{C} (R_A + R_B) \)
If \( R_A = -R_B \) (special case, equal molar) \( \Rightarrow \nabla \cdot \vec{V}^* = 0 \)

Therefore, \( \frac{\partial C_A}{\partial t} + \vec{V}^* \cdot \nabla C_A = C D_{AB} \nabla^2 y_A + R_A - \frac{c_A}{c}(R_A + R_B) \)

(C) \( \vec{V} \to 0 \) or \( \vec{V}^* \to 0 \) and no reaction, constant properties.

\[ \frac{\partial c_A}{\partial t} = D_{AB} \nabla^2 C_A \]

Let us explore coupling between momentum and species balance equation:

Continuity: \( \nabla \cdot \vec{V} = 0 \) (constant \( \rho \))

Momentum (NS): \( \rho \frac{D\vec{V}}{Dt} = \mu \nabla^2 \vec{V} - \nabla p + \rho \vec{g} \) (Forced convection)

\[ \rho \frac{D\vec{V}}{Dt} = \mu \nabla^2 \vec{V} - \nabla p - \rho \beta \vec{g}(T - T_o) \] (Mixed convection) (note difference between \( p \) and \( p \))

\[ \rho \frac{D\vec{V}}{Dt} = \mu \nabla^2 \vec{V} - \rho \beta \vec{g}(T - T) \] (Free convection)

Recall:

\[ \rho = \rho_o + \left( \frac{\partial \rho}{\partial T} \right)_{T_o,C_i_0} (T - T_o) + \left( \frac{\partial \rho}{\partial C_i} \right)_{T_o,C_i_0} (C_i - C_{i_0}) \] (Taylor series expansion of multivariables)

If \( T = \) constant, we have multi-component mixture under isothermal condition

\[ \rho \frac{D\vec{V}}{Dt} = \mu \nabla^2 \vec{V} - \rho \beta \vec{g}(x_A - x_{A_0}) \] (Free convection)

\[ Gr = \frac{g \beta^2 \beta_A (x_A - x_{A_0})^3}{\mu_f^2}, \text{ another Grashoff number based on concentration difference} \]

Note: constant \( \rho, \mu, k, D_{AB} \) fluid is termed constant physical properties fluid.

Continuity \( \nabla \cdot \vec{V} = 0 \) \( \Rightarrow 1 \)

NS \( \frac{D\vec{V}^*}{Dt} = -\nabla^* \rho^* + \frac{1}{Re} \nabla^* \nabla^* \vec{V}^* + \frac{1}{Fr} \vec{g}^* \) \( \Rightarrow 2 \)

Energy \( \frac{D\vec{T}^*}{Dt} = \frac{1}{Re Pr} \nabla^* \vec{V}^* + \frac{Br}{Re Pr} \vec{\phi}_r^* \) \( \Rightarrow 3 \)
Species \( \frac{DC_A^*}{Dt} = \frac{1}{ReSc} \nabla^2 C_A^* \) (no reaction) \hspace{1cm} (4a) (by analogy, check)

where, \( C_A^* = \frac{C_A - C_{Ao}}{C_{A1} - C_{Ao}} \), similar to \( T^* \) defined earlier and \( Sc = \frac{\mu}{\rho D} \)

- Analogy between (3) and (4) if reaction included as the source term \((R_A^*)\) in eq. (4a)

If \( Pr \approx Sc \) and in the absence of viscous heating and chemical reaction- there is a good similarity between heat & mass transport.

\[
\frac{DT^*}{Dt} = \frac{1}{Pe_h} \nabla^2 T^* \quad \text{and} \quad \frac{DC_A^*}{Dt} = \frac{1}{Pe_m} \nabla^2 C_A^*
\]

\((Pe_h \text{ and } Pe_m \text{ are Peclet#})\)

\[ Sc = \frac{\mu}{\rho D}, \quad Pr = \frac{\mu}{\rho \alpha} \approx 0.7 \quad \text{(gases)} \]

\[ \frac{V}{D}, \quad \frac{V}{\alpha} \approx 1000 \quad \text{(liquid)} \]

\[ Sc = \frac{1}{Re} \left( \frac{\nabla^2 T^*}{\nabla^2 C_A^*} \right) = \frac{\text{molecular momentum transport}}{\text{mass transfer (species) by molecular diffusion}} \]

**General (common) form of species conservation equation:**

\[ \frac{DC_A^*}{Dt} = \frac{1}{Pe_m} \nabla^2 C_A^* + R_A^* \quad \hspace{1cm} (4b) \]

(A definition for \( Pe_m \) can also be written in the similar fashion as was written for \( Pe_h \) in the previous lecture on the non-dimensionalized form of energy balance)

This lecture brings an end to the development of four conservation equations used in TP, namely: continuity, momentum, energy, and species, to solve for four variables \( p, V, T, \) and \( C \), with additional gas law, if required, \( p = p(\rho, T) \). The conservation equations we developed also contain three constitutive types of equations for diffusion or conduction flux:

\[
\tau = -\mu \nabla V = -v \nabla (\rho V) \quad \text{(momentum/s-cm}\^2): \text{Newton’s 1}\text{st law of viscosity}
\]

\[
q = -k \nabla T = -\alpha \nabla (TpCp) \quad \text{(cal/s-cm}\^2): \text{Fourier’s 1}\text{st Law of conduction}
\]

\[
J_A = -D_{AB} \nabla C_A \quad \text{(moles/s-cm}\^2): \text{ Fick’s first law of diffusion}
\]

(\textbf{Note} that the last term in each equation shows the grad of property-concentrations: momentum, thermal energy, and moles each expressed per unit volume. Thus, the flux of the property is proportional to the grad of property-concentration, where the proportionality constant is diffusion coefficient or diffusivity having the unit of cm\(^2\)/s in each case)
Prototype example 1: Rayleigh problem or Stoke’s first problem
(Flow near a plate suddenly set in motion; Jerked plate problem)

\( t = 0 \): a long horizontal plate and fluid on top of it, both at rest

\( v_x(t, y) = ? \quad t > 0 \)

(\textit{unsteady velocity profiles})

\[ \nabla \cdot \bar{V} = 0; \quad \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 \Rightarrow \frac{\partial v_x}{\partial x} = 0 \quad (\text{symmetric from } -\infty \text{ to } \infty \text{ along } x) \]

\[ \frac{\partial v_y}{\partial y} = 0 \Rightarrow v_y \neq f(y) = \text{const} \Rightarrow v_y = 0 \; \text{at } y = 0 \; (\text{no slip condition}) \Rightarrow v_y = 0 \; \text{everywhere.} \]

With \( v_z \) also zero, we are, therefore, discussing a unidirectional unsteady-state flow, viz \( v_x(t, y) = ? \)

\[ \text{NS: } \rho \left( \frac{\partial \bar{V}}{\partial t} + \bar{V} \cdot \nabla \bar{V} \right) = -\nabla p + \mu \nabla^2 \bar{V} + \rho g \] (\( \rho = c, \mu = c, NF \))

\[ x \text{ momentum: } \quad \rho \left[ \frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} + v_z \frac{\partial v_x}{\partial z} \right] = -\frac{\partial p}{\partial x} + \mu \left[ \frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} + \frac{\partial^2 v_x}{\partial z^2} \right] + \rho g \]

\( 2D \) (\( z \)-symmetric)

(no external pressure imposed; symmetric along \( x \)-direction)

\[ \rho \frac{\partial v_x}{\partial t} = \mu \frac{\partial^2 v_x}{\partial y^2} \Rightarrow \frac{\partial v_x}{\partial t} = \frac{\partial^2 v_x}{\partial y^2} \quad \text{on time} \]

\( \text{Some inspection:} \) Parabolic PDE, \( t = 0^+ \); \( v_x = 0 \) for all \( y \geq 0 \); \textit{IC}
\[ t = 0 \quad y = 0 \quad v_x = V_p \quad \{ \text{BCs} \}\]

\[ \to \infty \quad v_x = 0 \quad \{ \text{very far from the plate, fluid remains undisturbed/stationary} \} \]

**Some words on no-slip condition:** It is an experimental observation that under continuum conditions, the relative velocity between the solid and fluid in contact with the solid is zero. If solid is stationary, fluid (last layer) is also stationary. If solid moves, the layer in contact assumes the velocity of the solid.

**What method?** Note semi-infinite domain \((y = 0 : \infty)\);

and, IC = one of the two BCs ⇒ **Combination of variables**

\[ t \text{ and } y; \text{ combine them to one, } \eta. \]

(Separation of variables method will not work)

First, non-dimensionalize \(v_x \Rightarrow \phi = \frac{v_x}{V_p}\)

\[ \frac{\partial \phi}{\partial t} = \nu \frac{\partial^2 \phi}{\partial y^2} \]

Let \(\eta = ayt^a \quad (\alpha, a \text{ are } \#; \text{why not } y^a t?)\)

\[ \frac{\partial \phi}{\partial t} = \frac{\partial \phi}{\partial \eta} \cdot \frac{\partial \eta}{\partial t} = \alpha \frac{\partial \phi}{\partial \eta} at^a \]

\[ \frac{\partial \phi}{\partial y} = \frac{\partial \phi}{\partial \eta} \frac{\partial \eta}{\partial y} = \frac{\partial \phi}{\partial \eta} \alpha t^a \]

\[ \frac{\partial^2 \phi}{\partial y^2} = \frac{\partial}{\partial \eta} \left( \frac{\partial \phi}{\partial \eta} \right) \alpha t^a = \frac{\partial}{\partial \eta} \left( \frac{\partial \phi}{\partial \eta} \right) \alpha t^a \frac{\partial \eta}{\partial y} = \alpha^2 t^{2a} \frac{\partial^2 \phi}{\partial \eta^2} \]

Substitute,

\[ \alpha \frac{\partial \phi}{\partial \eta} ayt^{-1} = \nu \alpha^2 t^{2a} \frac{\partial^2 \phi}{\partial \eta^2} \]

\[ y = \eta / \alpha t^a \]

Therefore, \(\alpha \frac{\partial \phi}{\partial \eta} \frac{\eta}{\alpha t^a} t^{-1} = \nu \alpha^2 t^{2a} \frac{\partial^2 \phi}{\partial \eta^2} \)

In order to have \(t\) vanish from the equation to solve, collect all \(t\)-terms:

\[ \frac{t^{-1}}{t^{2a}} = t^0 = 1 \Rightarrow a = -\frac{1}{2} \]
\[ \eta = \alpha \frac{y}{\sqrt{t}} \]

Equation now becomes;

\[ \frac{d\phi}{d\eta} \left( -\frac{1}{2} \right) \eta = \nu \alpha^2 \frac{d^2\phi}{d\eta^2} \]

\[ \frac{d^2\phi}{d\eta^2} + \frac{\eta}{2\alpha^2\nu} \frac{d\phi}{d\eta} = 0 \quad \text{(a linear ODE)} \]

Set \( \frac{1}{2\alpha^2\nu} = 2 \) (why? An arbitrary constant so that the method works!)

\[ \frac{d^2\phi}{d\eta^2} + 2\eta \frac{d\phi}{d\eta} = 0 \Rightarrow \eta = 0 \ (y = 0), \ \phi = 1 \quad \text{consistencies before & after transformaiton} \]

(IC collapses with one of two BCs: this is how Combination of variables work and PDE is converted to ODE)

Let \( \psi = \frac{d\phi}{d\eta}, \frac{d\psi}{d\eta} + 2\eta \psi = 0 \Rightarrow \psi = C_1 e^{-\eta^2} \)

Therefore, \( \phi = C_1 \int_0^\eta e^{-\eta^2} d\eta + C_2 \)

\[ 1 = C_1 (0) + C_2 \Rightarrow C_2 = 1 \quad (BC \ 1) \]

\[ \phi = C_1 \int_0^\eta e^{-\eta^2} d\eta + 1 \]

\[ 0 = C_1 \int_0^\infty e^{-\eta^2} d\eta + 1 \quad BC(2) \Rightarrow C_1 = -\frac{1}{\int_0^\infty e^{-\eta^2} d\eta} \]

\[ \phi = 1 - \frac{\int_0^\eta e^{-\eta^2} d\eta}{\int_0^\infty e^{-\eta^2} d\eta} = 1 - \frac{2}{\sqrt{\pi}} \int_0^\eta e^{-\eta^2} d\eta = 1 - \text{erf}(\eta) \]

\[ \nu_x = V_p \left( 1 - \text{erf} \left( \frac{\alpha y}{\sqrt{t}} \right) \right) = V_p \left( 1 - \text{erf} \left( \frac{y}{\sqrt{4vt}} \right) \right) \]

At what location, \( \frac{\nu_x}{V_p} = 0.01 \) at a time \( t \)?

\[ 0.01 = 1 - \text{erf} \left( \frac{\delta}{\sqrt{4vt}} \right) \Rightarrow \frac{\delta}{\sqrt{4vt}} = 2 \quad \text{from Error function} \]
\[ \delta = 4 \sqrt{vt} \text{ for } v_x = 1\% \text{ of } V_p \left( \text{or } t \propto \delta^2 / \nu \right) \]

Edge of disturbance in y-direction from plate due to plate movement: fluid above is nearly stationary

\[ \Rightarrow \text{ The penetration depth has a square root of time-dependence.} \]

\[ \Rightarrow \text{ Think of taking snapshots at different times } t > 0 \]

\[ \Rightarrow \text{ There is similarity in the velocity profiles} \]

\[ \text{BCs} \left\{ \begin{array}{l}
\text{last layer of fluid is always at } V_p \text{ and} \\
\text{the layer at } '\infty' \text{ distance is stationary for all times.}
\end{array} \right. \]

Question can be posed differently: at a fixed '\( \delta \)' describe \( v_x(t) \) ⇒

\[ \text{Notes: (1) Method is called "Combination of variables" or "Similarity transform": requires (a) a semi-infinite domain in space and (b) IC & 1 BC should be the same (match)} \]

(2) Physical intuition suggests profiles \( v_x(t, y) \) are similar.

(3) \( x \) - momentum \textit{diffuses} in 'y' direction (although no \( V_p \) was imposed in \( x \) - direction)

\( \left( \tau_{yx} = \mu \frac{\partial v_x}{\partial y} \right) \) How about \( \tau_{xy} \), considering that shear stress is symmetric? Which momentum now \textit{diffuses} in which direction? There is an ambiguity in such question. The definition of \( \tau_{yx} \) should remain the same as discussed in the previous lectures: \( x \) is the direction of force (momentum) and \( y \) is the direction of the normal to the plane the force acts.

(4) Analogous examples in heat & mass transport (freezing of a water-lake or ice formation in a refrigerator – tray or mass transfer in a falling film)

\[ \frac{\partial T^*}{\partial t^*} = \alpha \frac{\partial^2 T^*}{\partial y^*} \quad \text{or} \quad \frac{\partial C^*}{\partial t^*} = D \frac{\partial^2 C^*}{\partial y^*} \] (Fourier's or Fick's 2\text{nd} law?)

\[ \Rightarrow \text{ See the analogous diffusion equations in momentum, heat and mass transport. But ensure that the non-dimensionalized initial and boundary conditions are also identically the same to be able to use the same non-dimensionalized solutions as derived above.} \]
Prototype example 2: Unsteady-state laminar flow or start-up flow in a tube

\[ t = 0^*: \text{fluid is stationary} \]

\[ t = 0: \text{impose } \frac{\nabla p}{l}, \text{flow starts } \Rightarrow v_z(t, r) = ? \text{ at } t = 0^* \]

Restriction \( \rho = \text{const}, \text{ NF, } \mu = c, \text{ axis} – \text{symmetric} \).

**Solution:** Continuity: \((\nabla \cdot \vec{V} = 0)\): \( \frac{1}{r} \frac{\partial (rv_z)}{\partial r} + \frac{\partial v_z}{\partial z} = 0; \) \( v_\theta = 0: \Theta - or \text{ axis} – \text{symmetric} \)

(cylindrical co-ordinate)

Also, \( v_r = 0: r - \text{symmetric} \). (Note that if a conical tube \( v_r \neq 0; \text{flow is not } r\text{-symmetric.} \))

Therefore, \( \frac{\partial v_z}{\partial z} = 0 \) (from Continuity). Alternatively, assuming a fully developed flow in \( z \)-direction (not on time-domain) or neglecting the entrance-exit effects in the tube, \( \frac{\partial v_z}{\partial z} = 0 \). This implies that \( (rv_r) \) is a constant (from Continuity). Since, \( v_r \) is 0 at the tube wall or \@ \( r = R \), it is 0 everywhere. In any case, flow is unidirectional.

**NS:** (z momentum)

\[ \rho \frac{\partial v_z}{\partial t} + \rho \left( v_z \frac{\partial v_z}{\partial z} + v_r \frac{\partial v_z}{\partial r} \right) = -\frac{\partial p}{\partial z} + \mu \left[ \frac{\partial^2 v_z}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial v_z}{\partial r} \right) \right] + \rho g_z \]

\[ \rho \frac{\partial v_z}{\partial t} = -\frac{\partial p}{\partial z} + \mu \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial v_z}{\partial r} \right) \]

: Work on hydrodynamic pressure: \( \nabla p = \nabla \rho \rightarrow \rho g \) so that the solution is the same in a horizontal or vertical tube due to \( \nabla p \), or without referring to the direction of gravity.

\[ \frac{\partial p}{\partial z} = \frac{d p}{dz} = \frac{p_i - p_o}{l} = -\frac{p_o - p_i}{l} \] (linear assumption for pressure gradient?)

(Considering that \( v_z \) is a function of \( r \) only and the hydrodynamic pressure \( p \) is the function of \( z \) only, the assumption is not required. Also, one can write \( r \)- and \( \Theta \) – momentum equations with \( v_z = v_r = 0 \), and consider \( p \) separate from actual pressure \( p \) to show that \( p = p(z) \) only)

**Non-dimensionalize:**
\[ \phi = \frac{v_z}{v_{\text{max}}^2} = \frac{v_z}{(\Delta p R^2 / 4 \mu l)^2} \]

One can solve SS flow:

\[ \text{Put } \frac{\partial v_z}{\partial t} = 0 \text{ and integrate the above equation twice in } r - \text{direction: } v_{\text{max}} = \frac{\Delta p R^2}{4 \mu l} \]

- Hagen – Poiseuille’s eqn.

How about \( t_c \) (characteristic time)?

\[ \xi = \frac{r}{R}, \quad \tau = \frac{t}{t_c} \quad (t_c \neq \frac{l}{v_{\text{max}}} \text{ because } l \text{ is arbitrary?}) \]

\( t_c \) remains unknown; but remember that if all but one characteristic variables are known, the remaining can be calculated/estimated:

Substitute, \[ \frac{\rho \Delta p R^2}{t_c 4 \mu} \frac{\partial \phi}{\partial \tau} = \frac{\Delta p}{l} + \frac{\mu \Delta p}{R^2 4 \mu l} R^2 \frac{1}{4} \frac{\partial}{\partial \xi} \frac{\partial}{\partial \xi} \frac{\partial \phi}{\partial \xi} \]

\[ t_c = \frac{\rho R^2}{\mu} = \frac{\mu^2}{m^2/S} : \text{time to reach SS. Flow profile is bounded in } r \text{ direction; } v = 0 \text{ at } r = R \text{ (no slip- condition). } \Delta p \text{ is applied axially (in } z \text{ direction), profiles develop in ‘} r \text{‘ direction ‘by momentum conduction/diffusion? } t_c \text{ is the time for the fluid at the center line to reach } v_{\text{max}} = \frac{R^2}{v}. \]

Alternatively, if you are convinced that \( t_c \) or characteristic time = \( \frac{R^2}{v} \) because pressure is imposed in \( z \)-direction and radial velocity is zero, you can start with \( \tau = \frac{t}{t_c} \) with \( t_c = \frac{\rho R^2}{\mu} \) and \( \phi = \frac{v_z}{v_c} \), you will get the same result for \( v_c \) as \( \frac{\Delta p R^2}{4 \mu l} \). To this end, the non-dimensionalized equation is

\[ \frac{\partial \phi}{\partial \tau} = 4 + \frac{1}{\xi} \frac{\partial}{\partial \xi} \left( \xi \frac{\partial \phi}{\partial \xi} \right) \]

**IC:** \( \tau = 0, \phi = 0 \text{ for all } \xi \)

**BCs (for all } \tau > 0): \xi = 1, \phi = 0 \text{ (no – slip condition)} \]

\[ \xi = 0, \phi = \text{finite } (v_{\text{max}}) \Rightarrow \frac{\partial \phi}{\partial \xi} = 0 \text{ (symmetric)} \]

**Notes:** (1)Similarity Transform or Combination of variables- No good because we have a bounded domain.

(2) Separation of variables? No because the equation is non-homogeneous. You will not be able to separate: \( \phi(\tau, \xi) \neq \phi(\xi) T(\tau) \)

Therefore, remove non-homogeneity first:

\[ \phi(\tau, \xi) = \phi_{SS}(\xi) - \phi_c(\tau, \xi) \]

SS term departure function from SS function? Or a residual function?? Or, just a mathematical term??

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In any case, it is clear that \( \phi(\tau, \xi) \) has been defined such that \( \phi_t \) gradually vanishes with increasing \( \tau \) so that the SS solution is \( \phi_{SS} \) and we have a fully developed SS velocity profile.

Plugging, \(-\frac{\partial \phi_t}{\partial \tau} = 4 + \frac{1}{\xi \partial \xi} \cdot \frac{\partial \phi_{SS}}{\partial \xi} - \frac{1}{\xi \partial \xi} \cdot \frac{\partial \phi_t}{\partial \xi}\)

\( \phi_{SS} \) is the solution of \( 0 = 4 + \frac{1}{\xi \partial \xi} \cdot \frac{\partial \phi_{SS}}{\partial \xi} \Rightarrow \phi_{SS} = 1 - \xi^2 \) (Poiseuille velocity profile)

\( \phi_t \) is the solution of \( \frac{\partial \phi_t}{\partial \tau} = \frac{1}{\xi \partial \xi} \cdot \frac{\partial \phi_t}{\partial \xi} \)

**IC:** \( \tau = 0 \) \( \phi_t = \phi_{SS} \) (check IC on \( \phi \))

**BCs:**
\[
\begin{align*}
\xi = 0 & \quad \phi_t = \text{finite}; \quad \frac{\partial \phi_t}{\partial \xi} = 0 \\
\xi = 1 & \quad \phi_t = 0
\end{align*}
\]

(Check \( \phi(\tau, \xi) = \phi_{SS}(\xi) - \phi_t(\tau, \xi) \). Also check IC and BCs on \( \phi \).)

\[
\phi = 1 - \xi^2 - \phi_t(\tau, \xi)
\]

Now TRY \( \phi_t(\tau, \xi) = T(\tau) \xi(\xi) \) (Separation of variables: the method works if the domain is bounded, and the governing equations as well as initial/boundary conditions are homogenous).

\[
\xi \frac{dT}{d\tau} = T \frac{1}{\xi \partial \xi} \cdot \frac{\partial \xi}{\partial \xi}
\]

\[
\frac{1}{\xi} \frac{dT}{d\tau} = \frac{1}{\xi} \left( \frac{1}{\xi \partial \xi} \cdot \frac{\partial \xi}{\partial \xi} \right) = -\alpha^2; \quad \Rightarrow \quad T = C_0 e^{-\alpha^2 \tau} \text{ and } \frac{1}{\xi} \left( \frac{1}{\xi \partial \xi} \cdot \frac{\partial \xi}{\partial \xi} \right) = -\alpha^2
\]

\[
\xi^2 \frac{d^2 \xi}{d\tau^2} + \xi \frac{d \xi}{d\tau} + \xi^2 \alpha^2 \xi = 0
\]

- Homogeneous linear ODE

The equation is a special form of \( x^2y'' + xy' + (x^2 - n^2)y = 0 \) with \( n = 0 \)

- For Bessel’s equation of order \( n = 0 \). General solution is

\[
\begin{align*}
y &= C_1 I_n(x) + C_2 K_n(x) \\
\downarrow & \updownarrow \\
\text{BF of 1st kind} & \text{BF of 2nd kind}
\end{align*}
\]

\( n = 0: \)

\[
\begin{align*}
I_0 & \quad \begin{array}{c} 2.4 \quad 5.5 \quad 8.654 \\
2.4 \quad 5.5 \quad 8.654 \\
\end{array} \\
\end{align*}
\]
Here (on comparison), \( x = \alpha \xi \), \( y = \xi \)

\[ \xi = C_1 J_0(\alpha \xi) + C_2 K_0(\alpha \xi) \]

Therefore, \( \phi_t(\tau, \xi) = C_0 e^{-\alpha^2 \tau} [C_1 J_0(\alpha \xi) + C_2 K_0(\alpha \xi)] \]

\[ = C_0 e^{-\alpha^2 \tau} [J_0(\alpha \xi) + C_2 K_0(\alpha \xi)] \quad (C_0, C_2, \text{ and } \alpha \text{ are to be determined}) \]

**BC 1.** \( \xi = 0 \quad \phi_t = \text{finite for all } \tau \Rightarrow C_2 = 0 \) (Note \( K_0 \) is infinite at \( \xi = 0 \))

\[ \phi_t = Ae^{-\alpha^2 \tau} J_0(\alpha \xi) \]

**BC 2.** \( \xi = 1 \quad \phi_t = 0 \Rightarrow J_0(\alpha) = 0 \)

\( \alpha \) has many roots \( \Rightarrow \alpha_n \)

Sum over all solutions:

\[ \phi_t = \sum_{n=1}^{\infty} A_n e^{-\alpha_n^2 \tau} J_0(\alpha_n \xi) \]

**IC** \( \tau = 0 \), \( \phi_t = \phi_{SS} \)

Therefore, \( 1 - \xi^2 = \sum_{n=1}^{\infty} A_n \)

Use orthogonal property to calculate \( A_n \)

\[ \int_0^1 J_n(\alpha_i x) J_n(\alpha_j x) x \, dx = 0 \quad (i \neq j) \]

\[ = \frac{1}{2} [J_n(\alpha)]^2 \quad (i = j) \]

\[ \int_0^1 (1 - \xi^2) J_0(\alpha_m \xi) \xi \, d\xi = \sum_{n=1}^{\infty} A_n \]

\[ = \frac{A_m}{2} [J_1(\alpha_m)]^2 \Rightarrow \frac{8}{\alpha_m^3} J_1(\alpha_m) = \frac{A_m}{2} [J_1(\alpha_m)]^2 \Rightarrow A_m = \frac{8}{\alpha_m^3 J_1(\alpha_m)} \]

Solution is,

\[ \phi_t = \sum_{n=1}^{\infty} \frac{8}{\alpha_n^3 J_1(\alpha_n)} e^{-\alpha_n^2 \tau} J_0(\alpha_n \xi) \]

\[ \phi = (1 - \xi^2) - \sum_{n=1}^{\infty} \frac{8}{\alpha_n^3 J_1(\alpha_n)} e^{-\alpha_n^2 \tau} J_0(\alpha_n \xi) \quad \alpha_n = 2.4, 5.5, \ldots \]

*H.W. if \( K \neq 0 \) or flow in annulus:

![Diagram](image) \quad K = \frac{r_1}{r_2} \neq 0
Solved velocity profiles $\phi(\tau, \xi)$:

\[ \phi_{ss} = 1 - \frac{g^2}{\ell} \]

(See the old version of BSL book. There are table and figure to determine or estimate the time $\tau$ for the centerline velocity to reach certain % SS velocity. The maximum velocity is within 10% of SS value when $\tau = 0.45$, or $\phi = 0.9$ at $\tau = 0.45$ and $\xi = 0$.)

**Reference for Bessel functions**: Advanced Engineering Mathematics by Erwin Kreyszig

- Bessel’s equation of order $n$:
  \[ x^2 y'' + xy' + (x^2 - n^2)y = 0 \quad (n \geq 0) \]
  Solution is,
  \[ J_n(x) = x^n \sum_{m=0}^{\infty} \frac{(-1)^m x^{2m}}{2^{2m+n} m! m+n!} \]
  
  - Bessel Function of the 1st Kind
  \[ J_{-n}(x) = x^{-n} \sum_{m=0}^{\infty} \frac{(-1)^m x^{2m}}{2^{2m-n} m! m-n!} \]
  But if $n$ is an integer then
  \[ J_n(x) = (-1)^n J_{-n}(x) \]
  Therefore, if $n$ is not an integer
  \[ Y(x) = C_1 J_n(x) + C_2 J_{-n}(x) \]
  which will be a general solution of the Bessel equation.

If $n$ is an integer then;
\[ Y(x) = C_1 J_n(x) + C_2 K_n(x) \]
forms the general solution, where $K_n(x)$ is the Bessel function of the 2nd kind and given by
\[ Y(x) = \frac{2}{\pi} J_n(x) \left( \ln \frac{x}{2} + Y \right) + \frac{x^n}{\pi} \sum_{m=0}^{\infty} \frac{(-1)^m (h_m + h_{m+n}) x^{2m}}{2^{2m+n} m! m+n!} - \frac{x^{-n}}{\pi} \sum_{m=0}^{n-1} \frac{n-m-1! x^{2m}}{2^{2m-n} m!} \]
\[ x > 0, h_0 = 0, \quad h_s = 1 + \frac{1}{2} + \frac{1}{3} + \cdots + \frac{1}{s} \quad (s \neq 0) \]

- Orthogonal Property of Bessel Function
\[
\int_0^1 J_n(\alpha x)J_n(\alpha_j x) \, x \, dx = 0 \quad (i \neq j)
\]
\[
= \frac{1}{2}[J'_n(\alpha)]^2 \quad (i = j)
\]

- Some useful relationships
  1) \[ [x^n J_n(x)]' = x^n J_{n-1}(x) \]
     \[ [x^{-n} J_{-n}(x)]' = -x^{-n} J_{n+1}(x) \]
  2) \[ J_{n-1}(x) + J_{n+1}(x) = \frac{2n}{x} J_n(x) \]
     \[ J_{n-1}(x) - J_{n+1}(x) = 2 J_n'(x) \]
  3) \[ J'_n(x) = -J_1(x) \]
     \[ J'_1(x) = J_0(x) - x^{-1} J_1(x) \]
  4) \[ \int x^n J_{n-1}(x) \, dx = x^n J_n(x) + C \]
     \[ \int x^{-n} J_{n+1}(x) \, dx = -x^{-n} J_n(x) + C \]
     \[ \int J_{n+1}(x) \, dx = \int J_{n-1}(x) \, dx - 2J_n(x) \]

**For Homework problems:**

5) If \[ S_o(\alpha_n \xi) = K_o(\alpha_n K) J_o(\alpha_n \xi) - J_o(\alpha_n K) K_o(\alpha_n \xi) \]

Then \[ \int_K^1 S_o(\alpha_n \xi) S_o(\alpha_m \xi) \, \xi \, d\xi = \frac{1}{\alpha_m} [S^2_o(\alpha_m) - K S^2_o(\alpha_m K)] \]

\[ \int_K^1 S_o(\alpha_m \xi) \, d\xi = \frac{1}{\alpha_m} [S^2_1(\alpha_m) - K S^2_1(\alpha_m K)] \]

6) If \[ Z_1(\alpha_n \xi) = J_1(\alpha_n \xi) K_1(\alpha_n K) - J_1(\alpha_n K) K_1(\alpha_n \xi) \]

Then \[ \int_K^1 [Z_1(\alpha_n \xi)]^2 \, \xi \, d\xi = \frac{1}{\alpha_n} [Z^2_1(\alpha_n) - K^2 Z^2_1(\alpha_n K)] \]

\[ \int_K^1 Z_1(\alpha_n \xi) \, d\xi = -\frac{1}{\alpha_n} [Z_1(\alpha_n) - Z_1(\alpha_n K)] \]
Lecture #10

Prototype example 3: Flow in a permeable tube or bundles of hollow fibers (Lubrication Approximation)

The lubrication approximations were originally applied to address the flow of a thin film of fluid between two solids in relative motion, for example, flow of lubricating oils in slider bearing or sliding cylinder (See Deen 6.6). However, the approximations are also applicable to the flow in a tapered channel (or cylinders/tubes) with narrow gaps:

, and also, to the present example of flow in a permeable tube or hollow fiber of a membrane (Deen):

**Assumptions:** No entrance effect, SS, walls are permeable and \( v_w \) is known as the permeate flux \( J_\omega = \frac{Q_\omega}{2\pi RL} \)

**Note:** In the present case, there are two non-zero velocities, unlike in the previous two prototype examples where there was one non-zero velocity component (unidirectional flow) to solve for.

Recall the previous start-up flow example: (1) Inertial term, \( \mathbf{v} \cdot \nabla \mathbf{v} = 0 \) (no inertial effect) or

\[
v_x \frac{\partial v_x}{\partial x} + v_r \frac{\partial v_x}{\partial r} = 0
\]

because we had a fully developed flow with \( \frac{\partial v_x}{\partial x} = 0 \), implying

\[
\Rightarrow r v_r = \text{constant (from Continuity)} \Rightarrow \text{Therefore, } v_r = 0 \text{ (because of no-slip condition at walls)}
\]

(2) Also, \( \frac{\partial p}{\partial x} = \frac{dp}{dx} \) = constant

Therefore, the governing NS equation was modified as

\[
\rho \left[ \frac{\partial v_x}{\partial t} + \mathbf{V} \cdot \nabla \mathbf{v} \right] = -\frac{\partial p}{\partial x} + \mu \left[ \frac{\partial^2 v_x}{\partial x^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial v_x}{\partial r} \right) \right]
\]

In the present case, again start with Continuity:

\[
\frac{\partial v_x}{\partial x} + \frac{1}{r} \frac{\partial (rv_x)}{\partial r} = 0
\]
Considering $\frac{\partial v_x}{\partial x} \neq 0$ as the permeate stream flows out of the tube, $\frac{\partial (r v_r)}{\partial r} \neq 0$. Therefore, $v_r \neq 0$ (total flowrates in $(x+r)$ directions are conserved). All it means is that the flow is not unidirectional and we have to solve for both $v_x$ and $v_r$.

NS equations:  
\begin{align*}
\text{x-momentum: } & \rho \left( v_x \frac{\partial v_x}{\partial x} + v_r \frac{\partial v_x}{\partial r} \right) = -\frac{\partial p}{\partial x} + \mu \left( \frac{\partial^2 v_x}{\partial x^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial v_x}{\partial r} \right) \right) \\
\text{r-momentum: } & \rho \left( v_x \frac{\partial v_r}{\partial x} + v_r \frac{\partial v_r}{\partial r} \right) = -\frac{\partial p}{\partial r} + \mu \left( \frac{\partial^2 v_r}{\partial x^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial v_r}{\partial r} \right) \right)
\end{align*}

And, $v_x = v_x(x,r) = ?$ and $v_r = v_r(x,r) = ?$ (it is convenient to work on hydrodynamic pressure, $p$)

**Approximations** (or physical intuitions?)

1. Inertial effects are negligible $\vec{V} \cdot \nabla \vec{V} \approx 0$ (flow is usually small)
2. viscous — axial term is smaller than the corresponding radial term: $\frac{\partial^2 v_x}{\partial x^2} \ll \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial v_x}{\partial r} \right)$
3. $p = p(x)$ or $\frac{\partial p}{\partial r} \ll \frac{\partial p}{\partial x}$

x-momentum: $\mu \frac{\partial}{\partial r} \left( r \frac{\partial v_x}{\partial r} \right) = \frac{\partial p}{\partial x}$: Lubrication approximations

It should be mentioned that a physical intuition for the present flow-situation should also indicate the same approximations. The majority or primary flow in a fiber or membrane tube is indeed in x-direction. The permeate flowrates (flow in r-direction) are usually small, implying that the inertial term is negligible. The situation is similar to creeping flow or flow around a sphere at low Reynolds number, when the inertial term is neglected in comparison to viscous term. With permeate flow being secondary or smaller than the axial or primary flow, $v_r \ll v_x$, and the flow may be considered to be *approximately* unidirectional or 1D. Similarly, pressure-drop occurs mostly in x-direction to overcome the viscous effects, and that in r-direction is small, or $\frac{\partial p}{\partial r} \ll \frac{\partial p}{\partial x}$. Therefore, $p = p(x)$ only. **Scaling** analysis can also be used to examine consistency in the above assumptions.

**Revisit Continuity and NS equations:**

\[
\frac{v_r}{v_x} \sim \frac{R}{L_x} \Rightarrow R \ll L_x \text{ of the hollow fiber} \\
\text{Therefore, } v_r \ll v_x \quad \{ \text{From continuity} \}
\]

\text{main flow-direction} \quad (\text{Note } v_r \text{ is small, but not zero; flow is nearly unidirectional})

Now, compare 'x' and 'r' momentum terms (dominant terms) of the NS equations:

\[
\frac{\partial p}{\partial r} \ll \frac{\partial p}{\partial x} \quad (v_r \text{ is a small quantity, } v_r \ll v_x)
\]

With $v_r \ll v_x$ and $R \ll L_x$ (for thin films or channels) one can show that

\[
\frac{\partial^2 v_x}{\partial x^2} \ll \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial v_x}{\partial r} \right) \quad \text{and} \quad v_x \frac{\partial v_x}{\partial x} \sim v_r \frac{\partial v_r}{\partial r} \quad (\text{two inertial terms are of the same order of magnitude})
\]
, which means that inertial term can be neglected if \( \text{Re} \left( \frac{R}{L_x} \right) \ll 1 \) where, \( \text{Re} = \frac{\nu_x R}{v} \) (This is not surprising considering the prevailing geometry and flow situations in hollow fibers of a membrane. This condition is also similar to that for creeping flow: \( \text{Re} \ll 1 \), with the characteristic length chosen as “R” or the radius of the sphere) Let us revert to the governing equation:

\[
\frac{\mu}{r} \frac{\partial}{\partial r} \left( r \frac{\partial v_x}{\partial r} \right) = \frac{dp}{dx} \tag{1}
\]

Integrate twice \( v_x(x, r) \) in \( r \) direction with \( \frac{dp}{dx} = \frac{dp}{dx} (x) \) with BCs. \( v_x(x, R) = 0 \) (no – slip), and

\[
v_x(x, 0) \text{ is finite (} \nabla v_x(x, 0) = 0 \text{): symmetric condition}
\]

\[
\frac{dp}{dx} = -\frac{8\mu \bar{v}_x(x)}{R^2} \quad \text{and} \quad v_x(x, r) = 2\bar{v}_x(x) \left( 1 - \frac{r^2}{R^2} \right) \tag{2a}
\]

Or simply, \( v_x(x, r) = -\left( \frac{dp}{dx} \right) \frac{R^2}{4\mu} \left( 1 - \frac{r^2}{R^2} \right) \quad \text{local mean velocity (r – averaged)} \)

Continuity: \( \frac{1}{r} \frac{\partial}{\partial r} \left( r v_r \right) = -\frac{\partial v_x}{\partial x} = -2 \frac{\partial \bar{v}_x(x)}{\partial x} \left( 1 - \frac{r^2}{R^2} \right) \tag{3} \)

Integrate eq. (3) along \( r \)-direction with condition @\( r = 0 \) \( \bar{v} v_r = 0 \) (symmetric)

\[
v_r(r, x) = -R \frac{\partial \bar{v}_x(x)}{dx} \left[ \left( \frac{r}{R} \right) - \frac{1}{2} \left( \frac{r}{R} \right)^3 \right] \tag{4}
\]

However, at \( r = R \), \( v_r(R, x) = v_\omega \text{(known)} \)

\[
\Rightarrow \frac{\partial \bar{v}_x(x)}{dx} = -\frac{2v_\omega}{R} \tag{5}
\]

Also, @\( x = 0 \) \( \bar{v} = v_0 \) (incoming velocity to tube). Integrate eq. (5) in \( x \)-direction to obtain

\[
\bar{v}_x(x) = v_0 - \frac{2v_\omega x}{R} \quad \left( \text{‘}x\text{’ cannot be long! It is a short tube} \right) \tag{6}
\]

On substitutions

\[
\begin{align*}
v_x(x, r) &= 2 \left( v_0 - \frac{2v_\omega x}{R} \right) \left( 1 - \frac{r^2}{R^2} \right) : \text{from eq. (2a)} \\
v_r(x, r) &= 2v_\omega \left( \frac{r}{R} - \frac{1}{2} \left( \frac{r}{R} \right)^3 \right) : \text{from eqs. (4) and (5)} \\
\frac{dp}{dx} &= -\frac{8\mu}{R^2} \left( v_0 - \frac{2v_\omega x}{R} \right) : \text{from eqs. (2a) and (6)}
\end{align*}
\]

Integrate the last equation to derive \( \bar{p}_1 - \bar{p}_2 = \frac{8\mu v_\omega L}{R^2} \left( 1 - \frac{v_\omega L}{v_\omega R} \right). \)

Note that if \( v_\omega = 0 \), the results expectedly reduce to those for an impermeable tube, i.e. Hagen-Poiseuille equation for pressure-drop in a straight cylindrical tube (with non-porous walls). Finally, you should also note that \( v_r(x, r) \) is \emph{approximately} zero but not \emph{exactly} zero, and the flow is \emph{approximately} 1D or unidirectional but not \emph{exactly} 1D or unidirectional. I leave it to you to plot the velocity and pressure profiles, and compare them with those for a straight tube.
Prototype examples 4-5: Heat/ Mass transfer in laminar flow in a circular tube

- The Graetz problem and The Graetz-Nusselt problem

Physical situation:

\[ v_z = v_z(\text{max}) \left( 1 - \frac{r^2}{R^2} \right) \] ; fully developed flow, \( Re < 2100 \) \( T = T_o \) (uniform at the inlet)

a) Graetz-Nusselt prescribes heat flux at the tube-wall when \( z > 0 \)

b) Graetz problem prescribes \( T_i \) at wall when \( z > 0 \)

Restrictions:

1. \( \mu, \rho = \text{const} \) \( C_p, k \equiv \text{avg} \) \( \Rightarrow \bar{\mu}, \bar{C}_p, \bar{k} \)
   - Coupling between momentum and heat/mass transport is one-way: velocity profile is superimposed on temp/concentration profiles & not vice-versa.
2. Fully-developed laminar flow
3. Negligible viscous dissipation (Brinkman number is small)
4. Radial and axial symmetry: \( v_r, v_\theta = 0 \)
5. SS

Energy equation:

\[ v_z \frac{\partial r}{\partial z} = \frac{k}{\rho C_p} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + \frac{\partial^2 T}{\partial z^2} \right) \]

Momentum/Continuity: \( \Rightarrow v_z(r) = v_z(\text{max}) \left( 1 - \frac{r^2}{R^2} \right) \)

(superimposed on temperature profiles or energy balance)

Prototype example 4: The Graetz-Nusselt problem (\( q_w \) or wall flux is prescribed)

BCs: 1. \( z = 0 \), \( T = T_o \)
2. \( z = L \), \( \frac{\partial T}{\partial z} = 0 \); long tube approx? (yet to be determined)
3. \( r = 0 \), \( T = \text{finite} \) \( \Rightarrow \frac{\partial T}{\partial r} = 0 \)
4. \( r = R \), \( -k \frac{\partial T}{\partial r} = q_w \) (heat supplied or removed: the numerical value of \( q_w \) will be \( \pm \))

Non-dimensionalize:
\[ \theta = \frac{T - T_o}{(\Delta T)_{\text{characteristic}}} = \frac{T - T_o}{(q_w R^2 / k)} \]

(Why not \( \theta = T / T_o \)? Because \( T_o \) is arbitrary; does not characterize heat-transport. On the other hand, \( q_w = -k \frac{\partial T}{\partial r} \approx -k \frac{\Delta T}{\Delta r} \), considering “\( R \)” is relatively smaller.)

\[ \xi = \frac{\tau}{R} , \ \ \psi = \frac{z}{z_c} \]

convective length \((Why \ not \ \psi = \frac{z}{L} ? \ flux. \ Because \ "L" \ is \ arbitrary, \ fluid-temperature \ keeps \ on \ increasing \ along \ the \ length \ no \ matter \ how \ small \ is \ the \ heat-flux \ at \ the \ wall)\)

\[ = \frac{z}{R Pe} ; z_c = R Pe; \ Pe = \frac{\text{convective effect}}{\text{conductive effect}} = Re Pr \ (R \ is \ the \ conductive \ length) \ (Pr \sim 1 \ for \ gas \ and \ \sim 1000 \ for \ liquid)\]

\[ v_z / v_{z_{\text{max}}} = (1 - \xi^2) \]

\[ (1 - \xi^2) \frac{\partial \theta}{\partial \psi} = \frac{1}{\xi} \frac{\partial}{\partial \xi} \xi \frac{\partial \theta}{\partial \xi} + \frac{1}{Pe^2} \frac{\partial^2 \theta}{\partial \psi^2} \]

If \( Re \) is large \( \gg 1 \), the 3\(^{rd} \) term is negligible compared (\(< 2100) \) to 1\(^{st} \) and 2\(^{nd} \) terms, i.e., conduction in \( z \) direction is negligible in comparison to convective heat transport.

That is, \( \frac{1}{Pe^2} \frac{\partial^2 \theta}{\partial \psi^2} \ll 1 \); On the other hand, radial conductive term is important \& retained.

Now,

\[ (1 - \xi^2) \frac{\partial \theta}{\partial \psi} = \frac{1}{\xi} \frac{\partial}{\partial \xi} \xi \frac{\partial \theta}{\partial \xi} \]

**BCs.**

1. \( \psi = 0 \ \ \ \ \theta = 0 \)
2. \( \xi = 0 \ \ \ \ \frac{\partial \theta}{\partial \xi} = 0 \)
3. \( \xi = 1 \ \ \ \ -\frac{\partial \theta}{\partial \xi} = 1 \)

**Note:** Parabolic on \( \psi \) (1\(^{st} \) order)

- Similarity transform is no good- it has a bounded domain.

- Separation of variable should work (homogeneous PDE), but BC-3 is non-homogeneous \( \Rightarrow \) We should first remove non-homogeneity in the boundary condition. Compare the situation with that of prototype example 2 where we had to remove non-homogeneity in the equation in order to apply “Separation of Variables” method.

**Propose:** \( \theta = \theta_{\infty}(\psi, \xi) - \theta_{\xi}(\psi, \xi) \)

Note that in the present case of constant heat flux at the wall, temperature will keep on increasing in the tube no matter how small is the flux value. However, a distinct temperature profile can be expected far (long distance) from the tube entrance. Also, similar to the previous prototype example, \( \phi(\tau, \xi) \) has been defined such that \( \phi_{\xi} \) gradually vanishes with increasing \( \psi \) or length, and
Limiting form: $\theta_{\infty}(\psi, \xi) = A(\psi) + B(\xi)$: (See BSL 10.8)

**Note that** $\nabla T \sim q_w$ remains constant at the wall throughout the tube length. Actual temperature also keeps on changing throughout the length. However, change in $\theta_{\infty}(\psi, \xi)$ (temperature at long distances in the tube) is similar. That is, a temperature profile is established in r-direction (shorter direction in the tube). Thus, although $T$ changes along the length, $\frac{\partial \theta_{\infty}}{\partial \psi}$ remains constant (invariant along the length) in the tube.

Plugging into equation:

$$\frac{dA}{d\psi} = \frac{1}{(1-\xi^2)} \frac{dB}{d\xi} = C_o$$

$f^n$ of $\psi$ only \quad $f^n$ of $\xi$ only

$A(\psi) = C_o \psi + C_0' \quad \& \quad \frac{1}{\xi} \frac{d}{d\xi} \frac{\xi dB}{d\xi} = C_o (1-\xi^2) \Rightarrow B(\xi) = C_o \frac{\xi^2}{4} - C_o \frac{\xi^4}{16} + C_1 \ln \xi + C_2'$

It yields,

$$\theta_{\infty}(\psi, \xi) = C_o \psi + C_o \left( \frac{\xi^2}{4} - \frac{\xi^4}{16} \right) + C_1 \ln \xi + C_2$$

BCs. $\xi = 0, \quad \theta_{\infty} = finite \Rightarrow C_1 = 0$

$$\xi = 1, \quad -\frac{\partial \theta_{\infty}}{\partial \xi} = 1 \Rightarrow C_o = -4$$

(can't use BC $\psi = 0 \Rightarrow \theta = 0$ because $\theta_{\infty}$ is valid only for large $\psi$). $C_2$ is yet to be determined.

**Make use of integral heat balance over the tube length whose end is far from the inlet**

$$-2\pi R q_w = 2\pi \int_0^R \rho C_p (T - T_o) v_z r dr$$

$$-\psi = \int_0^1 \theta_{\infty}(\psi, \xi)(1-\xi^2)\xi d\xi \rightarrow non-dimensionalize$$

(what happened to $\rho C_p$? It is there in $\psi = \frac{Z}{Z_c}$ or $\frac{Z}{RPe}$)
\[ \int_0^1 \left( -4\psi - 4\left( \frac{\xi^2}{4} - \frac{\xi^4}{16} \right) + C_2 \right)(1 - \xi^2)\xi d\xi \]
\[ = -\psi - \frac{7}{96} + C_2 \frac{1}{4} \Rightarrow C_2 = \frac{7}{24} \]

\[ \theta_\infty(\psi, \xi) = -4\psi - \left( \frac{\xi^2}{4} - \frac{\xi^4}{4} \right) + \frac{7}{24} \]

On \( \psi: \text{linear} \quad \xi: \text{parabolic temp profile} \)

As a homework, determine the bulk fluid temperature or mixed-cup temperature: \( \theta_b = -4\psi \) far from the tube-length (see Dean)

Also, show that in the present case of constant wall heat flux for a laminar, Newtonian flow, far from the tube entrance, the Nusselt number (based on the tube diameter), which is the dimensionless wall temperature gradient \( \left( \frac{\partial \theta}{\partial \xi} / (\theta - \theta_b) \right) \) evaluated \( @ \xi = 1 \) = 48/11 or 4.364

Revert:

\[ \theta(\psi, \xi) = -4\psi - \left( \frac{\xi^2}{4} - \frac{\xi^4}{4} \right) + \frac{7}{24} - \theta_\infty(\psi, \xi) \]

\( \theta_\infty \) must satisfy \( \left( 1 - \xi^2 \right) \frac{\partial \theta_\infty}{\partial \psi} = \frac{1}{\xi} \frac{\partial}{\partial \xi} \left( \xi \frac{\partial \theta_\infty}{\partial \xi} \right) \) (See BSL 12.2.1)

BCs:
\[
\begin{align*}
\xi &= 0 & \frac{\partial \theta_\infty}{\partial \psi} &= 0 \\
\xi &= 1 & \frac{\partial \theta_\infty}{\partial \xi} &= 0 \quad \left( \frac{\partial \theta_\infty}{\partial \xi} = \frac{\partial \theta_\infty}{\partial \psi} - \frac{\partial \theta}{\partial \psi} = 0 \right) \\
\psi &= 0 & \theta_t(0, \xi) &= \theta_\infty(0, \xi) = -\left( \frac{\xi^2}{4} - \frac{\xi^4}{4} \right) + \frac{7}{24} \\
\theta_t = \theta_\infty - \theta: & \text{apply BCs on } \theta \\
\end{align*}
\]

Now, apply Separation of variables (equation and BCs are all homogenous for \( \theta_t \))

\[ \theta_t(\psi, \xi) = T(\xi)Z(\psi) \]

\[ \frac{\partial Z(\psi)}{\partial \psi} = -c^2 Z \Rightarrow Z = Ae^{-c^2\psi} \quad (c^2 \equiv \text{separation const.}) \]

And \( \frac{1}{\xi} \frac{d}{d\xi} \xi \frac{dT}{d\xi} + c^2(1 - \xi^2)T = 0 \)
\[
\begin{align*}
\xi &= 0 & \frac{\partial T}{\partial \xi} &= 0 \\
\xi &= 1 & \frac{\partial T}{\partial \xi} &= 0 \quad \left( \frac{\partial T}{\partial \xi} = \frac{\partial T}{\partial \psi} - \frac{\partial \theta}{\partial \psi} = 0 \right) \\
\end{align*}
\]

This equation is a special form of Sturm-Liouville equation (and not Bessel equation):

\[ \frac{d}{dx}(r(x)y') + [q(x) + \lambda P(x)]y = 0 \quad : y(x) \]

BCs. \( a_1y(a) - a_2y'(a) = 0 \)
\[ b_1 y(b) - b_2 y'(b) = 0 \]

Solution assumes the form of \( y_n(x) \) on orthogonal function with weight function \( p(x) \) such that
\[
\int_a^b p(x)y_m(x)y_n(x) = 0 \quad m \neq n \\
\int_a^b p(x)y_m(x)y_n(x) = \frac{1}{(b-a)} \quad m = n
\]

There exists an infinite set of eigenfunction \( T(\xi) \) and eigenvalues \( c_i \), we can obtain by using the method of Frobenius, and deriving a series solution about \( \xi = 0 \). A recursive relationship allows us to get constants in the series in terms of two unknown constants. We will do later. For now,
\[
\phi(\psi, \xi) = \theta_\infty(\psi, \xi) - \sum_{i=1}^{\infty} B_i e^{-c_i \psi} T(\xi)
\]

where, \( B_i = \frac{\int_0^1 \theta_\infty(\xi, 0) T(\xi)(1-\xi^2)\xi d\xi}{\int_0^1 T(\xi)(1-\xi^2)\xi d\xi} \); \( T \equiv \text{Graetz function. See Siegel, Sparrow, Hallman App Sc. Res} \ A7(1958)386 - 392 \)

**Asymptotic solution for small distances (BSL 12.2.2)**

Explore temperature profiles near the walls; neglect curvature effects.

Assume fluid extends from \( S = 0 \) to \( S \to \infty \) (semi-infinite)

Also, velocity gradient near the wall is linear: \( v_z = \frac{v_o S}{R} \)

Energy equation becomes
\[
\nu_o \left( \frac{S}{R} \right) \frac{\partial \tau}{\partial Z} = \alpha \frac{\partial^2 \tau}{\partial S^2} = \left( \frac{k}{\rho c_p} \right) \frac{\partial^2 \tau}{\partial S^2} \quad \text{(Cartesian coordinate)}
\]

\[
\begin{align*}
Z = 0 & \quad T = T_o \\
S = 0 & \quad -k \frac{\partial T}{\partial S} = q_w; \quad S \to \infty \quad T = T_o
\end{align*}
\]

at the neighborhood of the walls

or \( \frac{v_o \partial T}{R \partial Z} = \alpha \frac{1}{S} \frac{\partial^2 T}{\partial S^2} \)

or \( \frac{v_o}{R} \frac{\partial^2 T}{S \partial S^2} = \alpha \frac{1}{S} \frac{\partial^2 T}{\partial S^2} \)

Asymptotic solution for small distances (BSL 12.2.2)
\[
\frac{v_o \partial q_s}{R \partial z} = \alpha \frac{1 \partial q_s}{S \partial S} \quad (\text{define } q_s = -k \frac{\partial T}{\partial S})
\]

**Non-dimensionalize:** \( \psi = \frac{q_s}{q_w}; \quad \eta = \frac{S}{R} \) substitute to get

\[
\lambda = \frac{Z}{\left( v_o R^2 / \alpha \right)} = \frac{Z}{Z_c} \quad (\text{Note the characteristic length } Z_c = v_o R^2 / \alpha)
\]

Therefore, \( \frac{\partial \psi}{\partial \lambda} = \frac{\partial}{\partial \eta} \left( \frac{1}{\eta} \frac{\partial \psi}{\partial \eta} \right) \)

**BCs** \( \lambda = 0, \quad \psi = 0 \)
\( \eta = 0, \quad \psi = 1; \quad \eta \to \infty \quad \psi = 0 \) \( \text{semi-infinite domain: The BC on } \lambda \)\( \text{collapses with one of the two BCs on } \eta, \text{i.e. } \eta \to \infty \)

**Similarity transform or Method of combination of variables:**

Use or derive \( Z = a \eta \lambda^b = \frac{\eta}{\sqrt{\eta \lambda}} \)

And \( Z \psi'' + (3Z^3 - 1)\psi' = 0 \)

\( Z = 0 \quad \psi = 1 \)
\( Z \to \infty \quad \psi = 0 \)

Solution is \( \psi = \frac{q_s}{q_w} = \int_Z^{\infty} Z e^{-z^3} dZ / \int_0^{\infty} Z e^{-z^3} dZ \)

\( = \frac{3}{\Gamma(2/3)} \int_Z^{\infty} Z e^{-z^3} dZ \)

But \( \int_T^{T_0} dT = -\frac{1}{k} \int_S^{\infty} q_s dS \) (at the neighborhood of the walls)

Therefore,

\[
\theta = \frac{T - T_o}{q_w R / K} = \frac{3}{\Gamma(2/3)} \int_Z^{\infty} \psi dZ \quad (\psi = \frac{q_s}{q_w})
\]

\[
\theta(\eta, \lambda) = \frac{3}{\Gamma(2/3)} \left[ e^{-z^3} / \Gamma(2/3) \right] - Z \left[ 1 - \frac{\Gamma(2/3)}{\Gamma(2/3)} \right] \quad \text{Incomplete function}
\]

\[
\theta(\eta, \lambda) = \frac{3}{\Gamma(2/3)} \left[ e^{-z^3} / \Gamma(2/3) \right] - Z \left[ 1 - \frac{\Gamma(2/3)}{\Gamma(2/3)} \right] \quad \text{Complete function}
\]

(There are tables to evaluate such mathematical functions including Graetz and gamma functions, for example in the book by Kreyszig)
Prototype example 5: Graetz Problem (wall temperature is prescribed)

The restrictions are the same as in example 4.

\[ \theta = \frac{T - T_w}{T_0 - T_w}, \quad \xi = \frac{r}{R}, \quad \psi = \frac{z}{R Pe} \] (characteristics variables are the same as in the previous case)

The governing equation is also the same as before

\[ (1 - \xi^2) \frac{\partial \theta}{\partial \phi} = \frac{1}{\xi} \frac{\partial \theta}{\partial \xi} \] (note that the axial conduction term is again neglected; Pe is large)

**BCs:**

\[ \theta(0, \xi) = 1; \]

\[ \theta(\psi, 0) = \text{finite or } \frac{\partial \theta}{\partial \xi} = 0; \]

\[ \theta(\psi, 1) = 0 \] (compare to the previous case when the BC was non-homogenous)

In this case, the equation is homogenous and the BCs on \( \psi \) are also homogenous. Separation of variables will now work without any mathematical manipulation.

**Separation of variables:**

\[ \theta = R(\xi)F(\psi) \]

\[ \frac{1}{F} \frac{dF}{d\psi} = \frac{1}{R(1 - \xi^2)} \frac{dR}{d\xi} = -B^2 \]

\( \Rightarrow F = Ae^{-B^2\psi} ; \)

\[ R: \frac{d}{d\xi} \left( \xi \frac{dR}{d\xi} \right) + B^2(1 - \xi^2)\xi R = 0 \]

\( \xi = 0 \Rightarrow \frac{dR}{d\xi} = 0 ; \quad \xi = 1 \Rightarrow R = 0 \) (use BCs on \( \theta \) to get BCs on \( R \))

Check to see if Sturm-Liouville equation applies

i.e. \( \frac{d}{dx} \left[ r(x)y' \right] + [q(x) + \lambda P(x)]y = 0 \)

**BCs**

\[ A_1 y(a) - A_2 y'(a) = 0 \]

\[ B_1 y(b) - B_2 y'(b) = 0 \]
Comparing the equations, 
\[ r(\xi) = \xi \quad q(\xi) = 0, \quad P(\xi) = \xi (1 - \xi^2) \] weighing function, 
\[ \lambda = B^2, \]

Comparing the BCs 
\[ a = 0 \quad A_1 = 0 \quad A_2 \neq 0 \]
\[ b = 1 \quad B_1 = 1 \quad B_2 = 0 \]

Hence, Sturm-Liouville equation form applies and
\[ \int_0^1 R_n R_m \xi (1 - \xi^2) d\xi = 0; \quad m \neq n \] (But types of function still unknown)
\[ = 1; \quad m = n \]

(This time, we will extensively discuss Graetz function):

Let \( U = \xi B \) to get
\[ \frac{d^2 R}{dU^2} + \frac{1}{U} \frac{dR}{dU} + \left[ 1 - \frac{U^2}{B^2} \right] R = 0 \]

\[ \Rightarrow \text{There is a singularity at } U = 0 \]

Propose solution of the form
\[ R = \sum_{n=0}^{\infty} C_n U^n \quad (\text{Frobenius series}) \]

Plug this to get
\[ \sum_{n=2}^{\infty} \left[ C_{n+2}(n+2)(n+1) + C_{n+2}(n+2) + C_n - \frac{C_{n-2}}{B^2} \right] U^n + C_1 U^{-1} + C_0 2 + C_3 3 U^1 + C_2 2 + C_3 3.2. U + C_0 + C_1 U^1 = 0 \]

Gather terms, 
\[ R = C_1 \sum_{n=0}^{\infty} B_{2n} U^{2n} + C_2 \sum_{n=0}^{\infty} B_{2n+1} U^{2n+1} \]

where, 
\[ B_{2n} = \frac{1}{(2n)^2} \left[ \frac{1}{B^2} B_{2n-4} - B_{2n-2} \right] \]
\[ B_{2n+1} = 0 \] identically

Therefore, to obtain complete solution identically, we use method of reduction of order where
\[ y_2(x) = y_1(x) \int \frac{\exp(-\int P_1(x) dx)}{[y_1(x)]^2} dx \quad \text{where, } y_1(x), \text{ and } y_2(x) \text{ are solution of} \]
\[ y'' + P_1(x)y' + P_2(x)y = 0; \quad P_1(x) = -\frac{1}{x} \text{ in the present case.} \]

And, 
\[ R(U) = C_1 R_1(U) + C_2 R_2(U) \]
\[ = C_1 \sum_{n=0}^{\infty} B_{2n} U^{2n} + C_2 \sum_{n=0}^{\infty} (R_1(U) \ln U - \sum dnU^n) \]
\[ R \text{ should be finite as } U \to \infty \Rightarrow C_2 = 0 \]
Hence, \( R(U) = C_1 \sum_{n=0}^\infty B_{2n} U^{2n} \)

\[ B_0 = 1, \quad B_2 = -\frac{1}{2^2}, \quad B_{2n} = \frac{1}{2n} \frac{1}{B_2} B_{2n-4} - B_{2n-2} \]

\[ \theta = \sum_{n=0}^\infty A_n e^{-\frac{B_{2n} \psi}{2}} R(B_n \xi) \quad \text{R is the Graetz function} \]

To get \( A_n \), we use orthogonality conditions at \( \psi = 0 \)

\[ A_n = \frac{\int_0^1 \theta(\xi) (1-\xi^2) R(B_n \xi) d\xi}{\int_0^1 (R(B_n \xi))^2 (1-\xi^2) d\xi} = \frac{I_U}{I_L} \]

\( I_U \) is evaluated using

\[ \int_0^1 \frac{d}{d\xi} \left( \xi \frac{d R(B_n \xi)}{d\xi} \right) d\xi = -B_n^2 \int_0^1 (1-\xi^2) \xi R(B_n \xi) d\xi \quad \text{from ODE} \]

Hence,

\[ \xi \frac{dR}{d\xi}(B_n \xi) \bigg|_{\xi=1} = 0 = B_n^2 \int_0^1 (1-\xi^2) \xi R(B_n \xi) d\xi \]

\[ I_u = -\frac{1}{B_n^2} \left( \frac{d R(B_n \xi)}{d\xi} \right) \bigg|_{\xi=1} \]

Also, \( I_L = \frac{1}{2B_n} \left( \frac{\partial R(B_n \xi)}{\partial B} \left( B_n \xi \right) \frac{\partial R(B_n \xi)}{\partial \xi} \right) \bigg|_{\xi=1} \)

\[ A_n = -\left[ \frac{2}{B_n \frac{\partial R(B_n \xi)}{\partial B} \bigg|_{\xi=1}} \right] \]

Therefore, \( \theta(\psi, \xi) = \sum_{n=0}^\infty -\frac{2}{\frac{\partial R(B_n \xi)}{\partial B} \bigg|_{\xi=1}} R(B_n \xi) e^{-\frac{B_{2n} \psi}{2}} \) (Check \( \psi \to \infty, \Theta \to 0 \) or \( T \to T_w \))

where, \( R(U) = \sum_{n=0}^\infty B_{2n} U^{2n} \)

\[ B_0 = 1, \quad B_2 = -\frac{1}{2^2}, \quad B_{2n} = \frac{1}{(2n)^2} \frac{1}{B_2} B_{2n-4} - B_{2n-2} \]

\( B_n \) are roots of \( R(B) = 0 \) \quad (See Jacob)

\[ B_0 = 2.705, \quad B_1 = 6.66, \quad B_2 = 10.3 \]

\[ \frac{\partial R}{\partial B_o} = 0.50082, \quad \frac{\partial R}{\partial B_1} = 0.371, \quad \frac{\partial R}{\partial B_2} = -0.505 \]

See ref. Graetz, L 1885, 25, #7, P22 Ann Dev Physik and Chem

Jacob, M 1953 V1, p 451 Heat Transfer
Graetz function is not easy to compute. Therefore, subsequent to the solutions provided by Graetz and Graetz-Nusselt, many attempts were made to fully solve the two cases in heat transfer: constant wall flux and constant wall temperature, especially for the extreme or far away from the entrance to the tube. The books by Kays, Crawford, and Weigand (2005, 4th Edition) and Kaka, Shah, and Aung (1987) have addressed/solved these cases slightly differently. The second case is indeed more computationally or mathematically complex than the first case. In the second case, Nusselt number for the far end of the tube is computed to be 3.657 (16% less than in the first case). Deen’s book has reported Nusselt numbers for both cases for the entire tube length, using the study of Shah and London (1978). In both cases, Nusselt numbers decrease along the tube length, and become constant at 4.364 and 3.657, respectively.

Kays, Crawford, and Weigand have used a general temperature profile for both cases (far from the tube length) which is outlined here:

$$\frac{\partial}{\partial x}\left(\frac{T - T_w}{T_b - T_w}\right) = 0,$$

which on differentiation gives:

$$\frac{\partial T}{\partial x} = \frac{dT_w}{dx} - \frac{(T - T_w)}{(T_b - T_w)} \frac{dT_w}{dx} + \frac{(T - T_w)}{(T_b - T_w)} \frac{dT_b}{dx}$$

**Constant wall flux:**

$$\frac{\partial T}{\partial x} = \frac{dT_w}{dx} = \frac{dT_b}{dx}$$

**Constant wall temperature:**

$$\frac{\partial T}{\partial x} = \left(\frac{T - T_w}{T_b - T_w}\right) \frac{dT_b}{dx}$$

A simple computation using the above different values for the temperature gradient gives $\text{Nu} = 4.364$ in the first case. Some additional computation (again involving Graetz function!) gives $\text{Nu} = 3.657$. The temperature variations with tube lengths for these two cases are as follows:

<table>
<thead>
<tr>
<th>T</th>
<th>Constant wall flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_w$</td>
<td>$T_b$</td>
</tr>
</tbody>
</table>

A schematic representation of variation in $T(z,r)$ in the constant wall temperature case is given below. $T_w$ remains constant along the length, but the wall flux or gradient varies. Far from the entrance, the entire fluid is at $T_w$. You should compare the temperature profiles to the previous case in which case the gradient at the tube walls remains constant along the length.
Prototype example 6: Brinkman problem (viscous heating)

Solve $T(r, z) = ? \Rightarrow$ Fluid-temperature increases because of viscous heating. Assume SS, fully developed laminar flow of a Newtonian, incompressible fluid. Note that the inlet and wall temperature are constant at $T_o$.

**Energy equation becomes**

$$\text{cal/s-cm}^3: \rho C_v v_z \frac{dT}{dz} = k \left[ \frac{1}{r \frac{dr}{dr}} r \frac{dT}{dr} + \frac{\partial^2 T}{\partial z^2} \right] + \mu \left( \frac{\partial v_z}{\partial r} \right)^2 (v_r, v_0 = 0)$$

Recall: $$\rho C_v \frac{dT}{dt} = -\nabla \cdot q - T \left( \frac{\partial P}{\partial T} \right)_V (\nabla V) - \xi : \nabla V$$

$$\xi : \nabla V = \mu \left[ \nabla V + \nabla V^T \right]: \nabla V = \phi_v (+ve)$$

If $P_e \gg 1$ axial conduction term can be neglected (similar to the previous case):

$$k \frac{\partial^2 T}{\partial z^2} \ll \rho C_v v_z \frac{dT}{dz} \quad \text{or} \quad \frac{1}{P_e^2} \frac{\partial^2 T}{\partial \psi^2} \ll 1$$

$$\rho C_v v_z \frac{dT}{dz} = k \left[ \frac{1}{r \frac{dr}{dr}} r \frac{dT}{dr} \right] + \mu \left( \frac{\partial v_z}{\partial r} \right)^2 \quad (1)$$

**BCs:** $T(0, r) = T_o \text{ for all } r \geq 0$  

$T(z, 0) = \text{finite or } \nabla T = 0,$ and  

$T(z, R) = T_o \text{ for all } z \geq 0$

Non-dimensionalize,

$$\theta = \frac{T-T_o}{T_o}, \quad \xi = \frac{r}{R}, \quad \psi = \frac{z}{R_P e} = \frac{z}{R_P e} = \frac{kz}{\rho C_p v_{\text{max}} R^2}$$

Substituting,

$$\left(1 - \xi^2 \right) \frac{\partial \theta}{\partial \psi} = \frac{1}{\xi} \frac{\partial}{\partial \xi} \left( \xi \frac{\partial \theta}{\partial \xi} \right) + 16B_r \xi^2 \quad (2)$$
where, $Br = \frac{\mu v^2_{\text{max}}}{4kT_0} \equiv \left( \frac{\text{rate of heat produced by viscous dissipation}}{\text{rate of heat-transport by conduction}} \right)$ in radial direction

**BCs:** $(0, \zeta) = 0$ for all $\zeta \geq 0$

$\theta(\psi, 0) = \text{finite or } \nabla \theta = 0$, and

$\theta(\psi, 1) = 0$ for all $\psi \geq 0$

$\Rightarrow$ The equation is non-homogeneous, linear 2nd order on $\zeta$. Non-homogeneity should be removed before applying the separation of variable method.

Try $\theta = \theta_\infty(\zeta) - \theta_t(\psi, \zeta)$ (3)

$a$ temperature profile is established in r-direction far from the tube-entrance, which is constant along tube length.

$\Rightarrow$ Viscous-heat generated in the fluid is removed from the wall; ‘gradient’ adjusts to keep the wall temperature constant at $T_0$

$$-(1 - \xi^2) \frac{\partial \theta_t}{\partial \psi} = -\frac{1}{\xi} \frac{\partial}{\partial \xi} (\xi \frac{\partial \theta_t}{\partial \xi}) + \frac{1}{\xi} \frac{\partial}{\partial \xi} \left( \xi \frac{\partial \theta_\infty}{\partial \xi} \right) + 16Br \xi^2$$

**On $\theta_\infty$:**

$$\frac{1}{\xi} \frac{d}{d\xi} \left( \xi \frac{d\theta_\infty}{d\xi} \right) + 16Br \xi^2 = 0$$

$\theta_\infty = -Br \xi^4 - C_1 \ln \xi + C_2$

**BCs:** $\theta_\infty(0) = \text{finite} \Rightarrow C_1 = 0$

$\theta_\infty(1) = 0 \Rightarrow C_2 = 1$

$\theta_\infty = Br(1 - \xi^4)$;

**And on $\theta_t$:**

$$(1 - \xi^2) \frac{\partial \theta_t}{\partial \psi} = \frac{1}{\xi} \frac{\partial}{\partial \xi} (\xi \frac{\partial \theta_t}{\partial \xi})$$

$$\frac{\partial \theta_t}{\partial \psi} = \frac{1}{\xi} \frac{\partial}{\partial \xi} (\xi \frac{\partial \theta_t}{\partial \xi})$$

**BCs:** $\theta_t(0, \zeta) = \theta_\infty \quad \text{see (3) above}$

$\theta_t(\psi, 0) = \text{finite or } \nabla \theta = 0$

$\theta_t(\psi, 1) = 0$

Separation of Variables, $\theta_t(\psi, \xi) = Z(\psi)F(\xi)$
On \( F(\xi) \): \[
\frac{\partial}{\partial \xi} \left[ \xi \frac{\partial F}{\partial \xi} \right] = a^2 \xi (1 - \xi^2) F
\]

\( F \) is solved in the same way as that for Graetz function! \( Z(\psi) \) is also evaluated the same way as before to solve

\[
\theta(\psi, \xi) \equiv Br(1 - \xi^4) - \sum_{n=0}^{\infty} A_n R(B_n, \xi) e^{-B_n^2 \psi}
\]

where, \( R(B_n, \xi) = \text{Graetz function} \)

\[
and A_n = -\frac{2 Br}{B_n} \left( \frac{\partial R}{\partial B_n} \right) \bigg|_{\xi=1} - \frac{1}{\Sigma_{n=0}^{\infty} B_n^2 B_n^2} = \frac{1}{(2n+6)(2n+8)} \frac{B_n^2 (\partial R / \partial B_n) dR/d\xi}_{\xi=1}
\]

1) \text{Large } \nabla V \text{ near the wall } \rightarrow \text{Maximum heat production} \text{ (see eqs. 1 and 2)}
2) \text{Temperature grad changes at the tube walls along the tube length but } \theta_w \text{ remains const at 0. At a far distance, gradient decreases to zero.}
3) \text{Temperature gradient is always zero at the center of the tube, as in the boundary condition.}

**You** should consider solving another case when the wall heat flux is zero (adiabatic). In this case, think of a solution in the form \( \theta_w(\psi, \xi) = A(\psi) + B(\xi) \). That is, the gradient at the wall is always zero. But, at a far distance, the radial temperature profile is established, and the temperature gradient \( \frac{\partial \theta_w}{\partial \psi} \) remains invariant along z-direction. See the problem 11B.2(c) of BSL.

**So far** we solved three prototype problems in heat transport: constant wall flux, constant wall temperature, and viscous heating in fluid flow. **Note that there can be analogous mass transport problems!** For example, consider the constant concentration \( C_0 \) of a reactant in a fluid mixture at the inlet of a tube. A \( n^{th} \) order reaction occurs at the wall, which means concentration gradient is constant at the wall. This is analogous to our prototype example 4. Follow the same procedure including an integral mass balance to solve for concentrations at short and long distances in the tube. Similarly, the analogous to viscous heating term is a chemical homogenous reaction in mass transport. Again, follow the same procedure as above. It is clear that, the non-dimensional forms of the conservation equations and BCs in heat and mass transport case should be the same or similar to obtain the identical or similar solutions.
Prototype example: 7 (Natural Convection: Coupling between hydrodynamic and energy)

Energy balance equation:
\[ \rho C_v \left[ \frac{\partial T}{\partial t} + v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} + v_z \frac{\partial T}{\partial z} \right] = k \left[ \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right] - \nabla \cdot \left( \frac{\partial p}{\partial T} \right) + \mu \nabla^2 T \]

Long vertical plate (\(-\infty \text{ to } +\infty\))
\text{explore steady-state temperature} & velocity profiles

Note: ⇒ Plates are infinitely long: \(-\infty \text{ to } +\infty\)
\[ \frac{\partial T}{\partial z} = \frac{\partial^2 T}{\partial z^2} = 0 \]
⇒ \(v_y = 0\) why? Apply continuity: \(\frac{\partial v_z}{\partial z} = 0\), \(v_z \neq 0\)

Thus, \(\nabla \cdot \vec{V} = 0\) yields \(v_y = 0\)
\(\left( \frac{\partial v_y}{\partial y} = 0 \right)\) (Also \(y\) momentum balance)

Check for \(\nabla p\) in \(y\) direction

Energy balance equation is now reduced to:
\[ \frac{\partial^2 T}{\partial y^2} = 0 \Rightarrow T = T_c @ y = +b \]
\[ T = T_h @ y = -b \]
\[ T = T_{mean} - \frac{1}{2} \Delta T \left( \frac{y}{b} \right) \text{ where, } T_{mean} = \frac{T_h + T_c}{2} \text{ and } \Delta T = (T_h - T_c): \text{ It is a linear profile.} \]

(Note that in this example, we have solved energy equation ahead of NS equation and temperature profiles superimposed on momentum balance equation)

Velocity profile:

Z-momentum balance equation is simplified as:
\[
\mu \frac{d^2 v_z}{dy^2} - \frac{dp}{dz} + \rho g = 0
\]

\[
\rho = \bar{\rho} - \bar{\rho} \beta (T - \bar{T}): \text{Taylor's series neglecting the higher order term. } \bar{T} \text{ is unknown. Revisit Lecture 6.}
\]

\[
\frac{dp}{dz} = \bar{\rho} g \text{ (if fluid were static). Or, } \frac{dp}{dz} = 0, \text{ where } p \text{ is the hydrodynamic pressure.}
\]

\[
\mu \frac{d^2 v_z}{dy^2} = -\bar{\rho} g \beta (T - \bar{T}) \tag{\rho \bar{T}, \bar{\rho} \bar{T}, \text{viz.} \text{ a warm fluid pocket at } T \text{ rises relatively to the cold bulk fluid at a temperature } \bar{T}. \text{ Is it a model?})
\]

**driving force for momentum in } y \text{ direction**}

\[
\mu \frac{d^2 v_z}{dy^2} = -\bar{\rho} g \beta \left[ (T_{\text{mean}} - \bar{T}) - \frac{1}{2} \Delta T \left( \frac{y}{b} \right) \right]: \text{ substitute from the previous solution for } T.
\]

**BCs.** \( y = \pm b, \ v_z = 0 \) (no - slip condition)

\[
v_z = \frac{\bar{\rho} \beta g b^2 \Delta T}{12 \mu} \left[ \left( \frac{y}{b} \right)^3 - A \left( \frac{y}{b} \right)^2 - \left( \frac{y}{b} \right) + A \right] \text{ where, } A = \frac{b(T_m - T)}{\Delta T}
\]

Note \( \bar{T} \) remains to be determined

Assume, Volume flow up = Volume flow down (it means that fluid is crossing over from left to right at \( + \infty \) and right to left at \( -\infty \); There cannot be an infinite source of fluid generation)

\[
\int_{-1}^{+1} v_z d \left( \frac{y}{b} \right) = 0 \text{ (Let net volumetric flow in the } z\text{-direction be 0). Note it is not a Continuity equation.}
\]

\[-\frac{2}{3} A + 2A = 0 \Rightarrow A = 0
\]

Therefore, \( \bar{T} = T_m = \frac{T_h + T_c}{2} \)

Thus, \( \bar{T} \) is specific to the problem (temperature profile)

\[
v_z = \frac{\bar{\rho} \beta g b^2 \Delta T}{12 \mu} \left[ \left( \frac{y}{b} \right)^3 - \left( \frac{y}{b} \right) \right]
\]

If \( \phi = \frac{b v_z \bar{\rho}}{\mu}, \eta = \left( \frac{y}{b} \right), \text{ } Gr = \frac{\bar{\rho}^2 \beta g b^2 \Delta T}{\mu^2} \)

\[
\phi = \frac{1}{12} Gr [\eta^3 - \eta]
\]

(Deen and BSL-latest edition) use \( \bar{T} = T_{\text{mean}} \) with the assumption that error is minimum in Taylor's series expansion for density changes if the expansion is around \( T_{\text{mean}} \) or around the density at \( T_{\text{mean}} \), and show that \( \frac{dp}{dz} = \bar{\rho} g \) or \( \frac{dp}{dz} = 0 \) where, \( p \) is the hydrodynamic pressure. The final answers are the same. These books have also addressed natural convection in an unconfined domain, but that requires boundary layer theory. Time permitting it will be solved later using Similarity Transform technique.
Prototype example 8: Steady-state diffusion through a stagnant gas film (Film Theory)

- Constant P and T; no chemical reaction.

A evaporates, diffuses upward because of the concentration gradient, and is carried or swept away by B. The species B diffuses in the opposite direction towards the liquid A also because of the concentration gradient. But B is insoluble in A. Therefore, there is no “sink” for B, and therefore, there should not be any concentration gradient of B at the liquid-vapor interface (\(J_B = -D_{AB} \nabla C_B\)). However, this scenario (finite concentration gradient) is possible if there is a ‘convective’ or “bulk-transport” of B induced in the positive z-direction so that the net flux of B at any horizontal plane including g-l interface is zero. Note that there is no pressure-driven (forced) convection or free (natural) convection in the film.

\[ \frac{\partial C_A}{\partial t} + \nabla \cdot N_A = R_A \] (moles/s – m³)

where, \(N_A = x_A (N_A + N_B) - \frac{C_{DAB}}{vC_A} \frac{dx_A}{dz} \) diffusion flux (non-convective flux)

\(\frac{\partial C_A}{\partial t} + \nabla \cdot C_A = D_{AB} \nabla^2 C_A + R_A \) (moles/s – m³): If the species conservation equation is written like this, there is a clear understanding of fluid velocity \(v\) in the forced convection, but what is the “velocity” in the present case?

Revert to eq. (1). For 1-D mass transfer, SS, no reaction,
\[
\frac{d}{dz} N_A = 0
\]

\[\rightarrow N_A = \text{constant} = N_A^0 \quad (z = z_1)\]

\[
\frac{d}{dz} \left( x_A (N_A + N_B) - \overline{C} D_{AB} \frac{dx_A}{dz} \right) = 0 \quad - (2)
\]

Also, \(\frac{d}{dz} N_B = 0\). Considering that B is insoluble in the liquid A, there should not be a finite or net flux of B at the A-B interface \(\rightarrow N_B^0 = 0\) at \(z = z_1\).

Therefore, \(N_B = N_B^0 = 0\) everywhere in the gas film \((z_1 \leq z \leq z_2)\)

Or, \(N_B = 0 = x_B (N_A + N_B) - \overline{C} D_{AB} \frac{dx_B}{dz} \quad vC_B\)

\[0 = x_B N_A - \overline{C} D_{AB} \frac{dx_B}{dz} \quad -- (3)\]

\[\text{now, we can explain the gradient at } z = 0 \text{ (interface)}\]

See the schematic below. \(J_A + J_B = 0\) or \(J_B = -J_A\) from the Fick’s first law of equimolar binary diffusion. There exists a concentration gradient of A from \(z = z_1\) to \(z_2\). In such case, a concentration gradient of B develops in the opposite direction from \(z_2\) to \(z_1\). Thus, at any horizontal plane there is a diffusion flux of B in the opposite direction of that of A. Also, note that there is a finite concentration gradient at the liquid-vapor interface for both species A and B. But, B is stagnant \((N_B = 0)\) anywhere along the diffusion path. Therefore, there is a bulk transport of B induced in the opposite direction of the diffusion flux to make the net flux or transport of B to be zero across any horizontal plane in the film. As stated earlier, there is no forced convection (no pump or external pressure applied) nor there is a free convection (constant temperature). Thus, it can be said that there is a diffusion of ‘A’ through the stagnant film of ‘B’.

Revert. Either (1), (2) or (3) will lead to

\[
N_A^0 \frac{dx_A}{dz} = \frac{d}{dz} \left( \overline{C} D_{AB} \frac{dx_A}{dz} \right) \quad (2^{nd} \text{ order ODE})
\]

Or,

\[
\frac{d}{dz} \left( \overline{C} D_{AB} \frac{dx_A}{dz} \right) = 0 \quad \left( \frac{dN_A}{dz} = 0 \right)
\]

Result is,

\[
\frac{1-x_A}{1-x_A_1} = \left[ \frac{1-x_A_2}{1-x_A_1} \right]^{\frac{z-z_1}{z_2-z_1}}
\]

Note that concentration gradients are non-linear.

**Note:** Slope of the concentration gradient for A is not constant but \(N_A\) is constant. Slope of the concentration gradient for B is also not constant, but \(N_B\) is zero.

\[
N_A = x_A (N_A + N_B) - \overline{C} D_{AB} \frac{dx_A}{dz} \quad \text{ (Both } x_A \text{ and } \frac{dx_A}{dz} \text{ vary along } z)
\]
\[ N_A = -\frac{CD_{AB}}{1-x_A} \frac{dx_A}{dz} \]

@ \( z = z_1 \) (or interface)

\[ N_A^0 = -\frac{CD_{AB}}{1-x_{A1}} \left( \frac{dx_A}{dz} \right) _{z=z_1} = \frac{CD_{AB}(x_{A1} - x_{A2})}{(z_2 - z_1) \log_{\text{mean}}(1-x_A)} \]

Defining \( k \) as the mass transfer coefficient: 

\[ J = k(C_A_0 - C_A_\infty) \equiv k(C_A_1 - C_A_2) \]

\[ k = \frac{D_{AB}}{(z_2-z_1) \log_{\text{max}}(x_B)} \text{ which is valid within Film theory} \]

\[ N_A = x_A N_A \]

\[ N_B = 0 = x_B N_A - CD_{AB} \frac{dx_B}{dz} \]

Most important: \( k \propto D_{AB} \) or \( \text{Sh} \propto \text{Sc} \) by Film theory.

Also, film theory can simulate (model) a slow moving film (boundary layer) past a surface in turbulent flow. Yet in such case, boundary layer theory is better to apply.

See Do’s book on adsorption. While determining diffusion coefficient of a binary mixture using a 'Stefan-tube', there is an error as high as 20% if \( N_A = x_A (N_A + N_B) - CD_{AB} \frac{dx_A}{dz} \) is approximated as \( N_A = -CD_{AB} \frac{dx_A}{dz} \), i.e. ignoring 'convective – flow'. Also, see BSL (2nd ed) 18B.2.

Before we conclude this lecture, let us look at the diffusion or transport in a spherical coordinate system from the perspective of mathematically writing the correct corresponding species conservation equation, for example in a spherical solid catalyst or a liquid droplet or an air bubble:

\[ N_A = x_A (N_A + N_B) - D_{AB} \frac{dC_A}{dr} \]

What does Continuity tell? \( \frac{1}{r^2} \frac{d}{dr}(r^2 N_A) = 0 \) (SS and no reaction)

Therefore, \( r^2 N_A = \text{constant} \); it follows that \( N_A \neq \text{constant} \), unlike in the previous Cartesian coordinate system \( N_A \) was \( \text{constant} \). All it means is that in the latter system both flux (moles/s-cm²) as well as the rate (moles/s) are constant; in the spherical or cylindrical system the rate is constant but not flux. There is a clear artifact of surface or interfacial area of the system under consideration:

\[ r \rightarrow r+\delta r: \text{CV} = 4\pi r^2 \delta r, \text{and } N_A = N_A(r) \]
Prototype type example 9: Diffusion into a falling film (Surface renewal theory)

Velocity profile:

\[ v_z = v_{\text{max}} \left( 1 - \frac{x^2}{\delta^2} \right) \]

(From NS equation)

\( x = \delta \ v_z = 0 \) (no-slip)

\( x = 0 \ \frac{dv_z}{dx} = 0 \) (\( v_z \) is maximum)

Species conservation equation:

\[
\frac{\partial C_A}{\partial t} + v_x \frac{\partial C_A}{\partial x} + v_z \frac{\partial C_A}{\partial z} = D_{AB} \left[ \frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial z^2} \right] + \ldots
\]

Note: \( \frac{\partial C_A}{\partial z} \neq 0 \); however \( \frac{\partial^2 C_A}{\partial z^2} \approx 0 \) because \( \text{Pe} \gg 1 \)

Non-dimensionalize \( x^* = \frac{x}{\delta} \) and \( z^* = \frac{z}{L_c} \), where \( L_c = \text{convective length} = \text{Pe} \delta \) (\( \delta \ll L_c \))

to show that \( \frac{1}{\text{Pe}^2} \frac{\partial^2 C_A}{\partial z^2} \ll 1 \) or \( v_z \frac{\partial C_A}{\partial z} \gg D_{AB} \frac{\partial^2 C_A}{\partial z^2} \) if \( \text{Pe} \gg 1 \)

Therefore, \( v_{\text{max}} \left( 1 - \left( \frac{x}{\delta} \right)^2 \right) \frac{\partial C_A}{\partial z} = D_{AB} \frac{\partial^2 C_A}{\partial x^2} \) \hspace{1cm} (1)

BCs. \( z = 0 \ C_A = 0 \) (pure liquid)

\( x = 0 \ C_A = C_{Ao} \) (solubility; in equilibrium with gas phase)

\( x = \delta \ -D_{AB} \frac{\partial C_A}{\partial x} = 0 \) (gas does not react with the solid surface; non-reactive surface)

Further simplifications – Slight penetration, short contact time for A in the liquid; A ‘sees’ liquid at velocity \( v_{\text{max}} \) and does not sense the presence of the wall far away. Penetration depth \( x \ll \delta \) the film thickness \( \delta \). The equation is modified as

\[ v_{\text{max}} \frac{\partial C_A}{\partial z} = D_{AB} \frac{\partial^2 C_A}{\partial x^2} \] \hspace{1cm} (1’)

The boundary condition \( x = \delta; -D_{AB} \frac{\partial C_A}{\partial x} = 0 \) is also simplified to \( x \to \infty \); \( C_A = 0 \) (Pigford (1941) has solved with the original boundary condition)
Gas is confined within the top layer (hatched) near the gas-liquid interface in the liquid (characteristic
time of diffusion of A in the liquid, i.e., \( \delta^2/D_{AB} \) is much greater than the residence time of the gas, i.e., \( L/V \).)

**Solution is sought using Similarity Transform method for a semi-infinite domain** (Recall 1st prototype
plate-jerk problem)

\[
\frac{C_A}{C_{Ao}} = 1 - erf \left( \frac{x}{\sqrt{4D_{AB}zv_{max}}} \right) \quad (2)
\]

(You must not re-solve the conservation eq. (1'). Just check that the non-dimensionalized conservation
momentum and mass species conservations equations and boundary conditions for both prototype
examples are identical)

You should also qualitatively plot \( C_A \) vs \( z \) for increasing \( x \) and \( C_A \) vs \( x \) for increasing \( z \).

**Mass flux from the concentration profiles (eq. 2):**

\[
N_A(z)|_{x=0} = -D_{AB} \frac{\partial C_A}{\partial x} |_{x=0} = C_{Ao} \sqrt{\frac{D_{AB}v_{max}}{\pi z}} \quad (You \ should \ also \ solve \ this \ as \ an \ exercise)
\]

Note that the flux decreases along the plate length, which is expected as the liquid is increasingly absorbed
with the gas.

(Make use of Leibniz rule in differentiating eq. 2:

If \( \phi(\alpha) = \int_{v_1(\alpha)}^{v_2(\alpha)} f(\eta, \alpha) \, d\eta \)

\[
\frac{d\phi}{d\alpha} = \int_{v_1}^{v_2} \frac{df}{d\alpha} \, d\eta + f(v_2, \alpha) \frac{dv_2}{d\alpha} - f(v_1, \alpha) \frac{dv_1}{d\alpha}
\]

In our case, \( f(\eta, \alpha) = e^{-\eta^2}, v_1 = 0, v_2 = \frac{x}{\sqrt{4D_{AB}zv_{max}}} \)

**Compare:**

\[
\alpha = x; \quad \frac{dv_2}{d\alpha} = \frac{1}{\sqrt{4D_{AB}zv_{max}}} \quad ; \quad \frac{dv_1}{d\alpha} = 0; \quad f(v_2, \alpha) = \frac{2}{\sqrt{\pi}} e^{-\eta^2}
\]
Total mass transfer per unit time,

\[ W_A \left( \text{mole}\text{s}^{-1} \right) = w \int_{0}^{L} N_A \big|_{x=0} dz = wC_{A0} \sqrt{ \frac{D_{AB}v_{\text{max}}}{\pi}} \int_{0}^{L} z^{-1/2} dz \]  
(integrated over the contact length L)

\[ = wL \frac{C_{A0}}{\pi L} \sqrt{\frac{4D_{AB}v_{\text{max}}}{\pi L}} \]

Under SS condition, you should be able to show (as an exercise/see BSL 18C.3) that the total mass transfer rate \( W_A \) over the film height \( L \) is the same as that convected across the horizontal plane at L, considering that a pure liquid enters the system from the top:

\[ = v_{\text{max}}w \int_{0}^{\infty} C_{A} \big|_{z=L} dx \]

Again, \( J = k(C_{A0} - 0) \), where \( k \) is the mass transfer coefficient

\[ k \propto \sqrt{\frac{4D_{AB}v_{\text{max}}}{\pi L}} \]

and \( k \propto \sqrt{\frac{v_{\text{max}}}{L}} \sim \sqrt{\frac{\text{surface renewal rate}}{\text{different from film theory}}} \) or \( \sqrt{\frac{1}{\tau}} \) where \( \tau \) is the contact time.

\[ k \propto \sqrt{D_{AB}} \text{ or } Sh \propto Sc^{1/2} \text{ : Surface renewal theory} \]

(Note: Film or Two – film or stagnant film theory predicts \( k \propto D_{AB} \))

Ex: Consider the example of diffusion from an air bubble moving upward, in a liquid (or a stationary bubble in a liquid flowing down past the air bubble). An equivalent example is also the absorption of a gas into the falling liquid droplet.

\[ \rightarrow \text{Pure liquid flows down past the bubble. Liquid flow induces circulation of gas inside the bubble through the interfacial shear force. The interfacial velocity is the same as } v_{\text{t}}, \text{terminal velocity of rising bubble.} \]
Levich has extensively discussed such mass transfer related problems, at least one of which will be later discussed in this course. BSL (18.5.1) and Deen (10.1) have also addressed such problems. Solving the problem requires first solving the velocity fields inside as well as outside the bubbles, and then solving the concentration profiles with the velocity profiles superimposed. The velocity fields are solved using streaming function. Concentration profiles have also been solved using stream functions.

In this lecture, we will restrict our discussion qualitatively. The first important thing to note is that this problem is mechanistically analogous to the falling film over the vertical plate discussed earlier. Why?

⇒ Surface is renewed continuously by the pure liquid flowing down past the bubble, as the circulating gas keeps the inside surface concentration constant. Thus, the boundary conditions are identical in two cases. It is a clear that a complex-looking problem has been solved or addressed by using a simple analogy!

Thus, one can show that

\[ k \propto \sqrt{D_{AB}} \text{ and } \]

\[ N_{Avg} = \sqrt{\frac{4D_{AB}v_L}{\pi D}} C_{Ao} \]

Surface is renewed @ rate \( \frac{v_L}{\sqrt{D}} \);  

\[ \text{Pure liquid,} \]

\[ CO_2 \quad L = \pi D \]

Here, surface is renewed @ rate \( \sqrt{\frac{v_{max}}{L}} \)

Similarly, consider the trickle flow of a liquid over a packed bed of spherical catalysts:

mass transfer rate \( \propto \sqrt{D_{AB}} \) and surface renewal rate \( \propto \sqrt{\frac{v_L}{D}} \).

To this end, note that there is also “penetration theory” similar to the film theory, or surface renewal theory, or boundary layer theory, to calculate mass transfer coefficient or mass transfer flux of a gas into liquid. Each of these theories is applicable to different hydrodynamic conditions. The penetration theory considers “eddies” randomly moving around in liquid flow under turbulent condition. Eddies reach the gas-liquid interface, come in contact with the gas for different times, and return to the bulk liquid. During this contact time, gas diffuses into eddies. In this case as well, the gas-liquid surface (interface) is renewed, and \( k \propto \sqrt{D_{AB}} \) or \( Sh \propto Sc^{1/2} \)

\[ \text{gas} \]

\[ \text{liquid} \]

(turbulent flow conditions)
Prototype example 10: Taylor Dispersion or Taylor – Aris Diffusion/Dispersion

- Taylor (1953, 1954) and Aris (1956) pioneered and extensively studied diffusion/dispersion in a laminar tubular flow.

- Consider a fully developed laminar flow ($Re < 2100$) in a long tube. A RTD or tracer experiment is performed by injecting a dose (‘$\delta$' function) of tracer at the inlet to the tube of radius R. We are interested in studying concentration profiles in the tube, in particular response at the exit of the tube.

Species balance equation:

$$\frac{\partial C}{\partial t} + V \cdot \nabla C = D_m \nabla^2 C + \left(\frac{V}{R_P}\right) \quad (Re < 2100), \quad (D_m \equiv \text{molecular diffusion})$$

Or

$$\frac{\partial C}{\partial t} + V_{max} \left(1 - \frac{r^2}{R^2}\right) \frac{\partial C}{\partial z} = D_m \frac{\partial^2 C}{\partial z^2} + \frac{D_m}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r}\right)$$

We have seen earlier that $D_m \frac{\partial^2 C}{\partial z^2} \ll V_{max} \left(1 - \frac{r^2}{R^2}\right) \frac{\partial C}{\partial z}$ if $Pe >> 1$. Recall the equation in the non-dimensionalized form when

$$\frac{1}{\rho C^2} \frac{\partial^2 C^*}{\partial \psi^2} \ll (1 - \xi^2) \frac{\partial C^*}{\partial \psi} \quad \text{(where} \ z_c \equiv \text{convective length} = RPe)$$

(Diffusion in axial direction $\ll$ Convection)

Introducing $\xi = \frac{r}{R}, \ \psi = \frac{z}{L}, \ C^* = \frac{C}{C_{Ao}}, \ \tau = \frac{t}{L/V_{max}}, \ \frac{V_{max}}{L}; C_{Ao} = \frac{M}{Q\Delta t} \ (\text{dose for short time})$

The time-dependent 2D ($z$-$r$) conservation equation is transformed as

$$\left(\frac{\partial^2 C^*}{\partial \xi^2} + \frac{1}{\xi} \frac{\partial C^*}{\partial \xi}\right) = \left(\frac{R^2 V_{max}}{D_m L}\right) \frac{\partial C^*}{\partial \tau} + \left(\frac{R^2 V_{max}^2}{D_m L^2}\right) \left(1 - \xi^2\right) \frac{\partial C^*}{\partial \psi}$$

IC: $C^* = 0$, for all $\xi$ and $\psi$. BCs. 1. $\xi = 0 \quad \frac{\partial C^*}{\partial \xi} = 0$

2. $\xi = 1 \quad \frac{\partial C^*}{\partial \xi} = 0$

3. $\psi = 0 \quad C^* = 1$ for a short time $\Delta t$; 0 otherwise; or $\psi \to \infty, \ C^* = 0$
Also note that \( z_c = RPe = R(ReSc) \)

\[
\begin{align*}
R &= \frac{R V_{max}}{v} = \frac{(R^2 V_{max})}{D_m}
\end{align*}
\]

, Or the term in the parenthesis of eq. (1) is nothing but \( \frac{z_c L}{L} \). Taylor sought a solution valid for long time, or when enough time has lapsed and pulse has travelled a distance \( l_p \) such that

\[
l_p / V_{max} \gg \frac{R^2}{(3.8)^2 D_m} \quad \text{(see BSL)}
\]

Plawsky in Transport Phenomena Fundamentals has provided the solution in details:

\[
\beta_D = \frac{R^2 V_{max}}{D_m L} = \frac{R^2 / D_m}{(L / V_{max})} = \frac{\text{diffusion time}}{\text{convection time}} \left( Pe \frac{R}{L} \right) \quad \text{(A)}
\]

If \( \beta_D \) is large, then diffusion is not important and dispersion or spreading is determined by convection alone and the tracer spreads in radial direction similar to the velocity profile:

If \( \beta_D \) is small, then diffusion will wipe out or remove radial gradient in concentration, in which case diffusion is important. To determine when diffusion is important, revisit equation (1) but neglect convection,

\[
\beta_D \frac{\partial C^*}{\partial \tau} = \left( \frac{\partial^2 C^*}{\partial \xi^2} + \frac{1}{\xi} \frac{\partial C^*}{\partial \xi} \right)
\]

Recall previous prototype equations for which the method of separation of variable were used to solve.

\[
C^* = e^{-\alpha \tau} J_0 \sqrt{\beta_D \alpha \xi} \quad (\alpha \equiv \text{const. of integration})
\]

Applying BC 2, \( J_1(\sqrt{\beta_D \alpha}) = 0 \). There are multiple roots, but consider first root only as the Bessel function decays fast.

\[
\sqrt{\beta_D \alpha} = 3.8 \quad \text{(Recall Bessel functions)}
\]

This solution represents the time it takes for any radial variation in concentration to decrease to \( \frac{1}{e} \) of the
original value, i.e., for longer times or larger distance in the tube. Therefore, for diffusion to be important $\beta_D \ll (3.8)^2$;

Let us address now **diffusion-controlled response or spreading.**

The solution is sought by switching over to Lagrangian co-ordinate in which case the observer or coordinate system moves with the average speed $\frac{V_{\text{max}}}{2}$ of the flow; $\bar{z} = z - \bar{v}_z(t)$ or $\zeta = \psi - \frac{\tau}{2}$ ($\tau$ is the dimensionless time $t/\frac{L}{V_{\text{max}}}$) and $\psi$ is the dimensionless distance $(\bar{z}/L)$. The modified equation is

$$\left(\frac{\partial^2 C^*}{\partial \xi^2} + \frac{1}{\xi} \frac{\partial C^*}{\partial \xi}\right) = \beta_D \left(\frac{1}{2} - \xi^2\right) \frac{\partial C^*}{\partial \zeta}$$

Or

$$\frac{1}{\xi} \frac{\partial}{\partial \xi} \left(\xi \frac{\partial C^*}{\partial \xi}\right) = \beta_D \left(\frac{1}{2} - \xi^2\right) \frac{\partial C^*}{\partial \zeta}$$

Under the present case, when diffusion controls the spreading, or the spreading is rapid after a sufficiently long time (Eulerian approach), or after the pulse has travelled a large distance in the tube (Lagrangian approach), $\frac{\partial C^*}{\partial \zeta}$ may be assumed to be constant along $z$ or $\psi$ direction, as $\frac{\partial C}{\partial \zeta}$:

$$\frac{1}{\xi} \frac{\partial}{\partial \xi} \left(\xi \frac{\partial C^*}{\partial \xi}\right) = \beta_D \left(\frac{1}{2} - \xi^2\right) \frac{\partial C^*}{\partial \zeta}$$

(recall similar scenario in prototype example on constant wall heat flux)

Applying method of separation of variables and integrating

$$C^* = C_o + \frac{\beta_D}{8} \left(\xi^2 - \frac{1}{2} \xi^4\right) \frac{\partial C}{\partial \zeta}$$

$(C^* = C_o \quad \zeta = 0 \text{ or } \psi = \tau/2)$

Thus, the average mass or molar flux across the tube cross-section as seen by the observer moving with the mean velocity:

$$N_A \sim -2V_{\text{max}} \int_0^1 C^* \left(\frac{1}{2} - \xi^2\right) \xi d\xi$$

(integral term equivalent to $\int_0^R C(r, z) \left(1 - \frac{r^2}{R^2}\right) 2\pi r dr$)

Substituting $C^*$ in the above equation with $\beta_D$ from (A),

$$N_A \sim -\frac{R^2V_{\text{max}}^2}{192D_m} \frac{\partial C}{\partial \zeta}$$

$$\sim -K \frac{\partial C}{\partial \zeta}$$

where, $K = \text{dispersion coefficient} = \frac{R^2V_{\text{max}}^2}{192D_m}$

(Axial change in concentration as seen by the observer is approximated by the radially averaged concentration, as a sufficient spreading has occurred in the radial direction)

The above flux-equation implies that the 2D concentration distributions in a parabolic tubular flow can be approximated as a 1D (axial) concentration distribution in a flow having a radially flat velocity profile with the mean average velocity $\bar{V} = \frac{V_{\text{max}}}{2}$, and axial dispersion coefficient as $K$. In other words, the general 2D species balance equation (1) written for a tracer movement in a parabolic flow is replaced with
\[
\frac{\partial C}{\partial t} + \vec{V} \frac{\partial C}{\partial z} = K \frac{\partial^2 C}{\partial z^2} - (2) \quad \text{where,} \quad K = \frac{R^2 V_{\text{max}}^2}{192 D_m}
\]

Later, Aris modified the expression for \( K \) for the full time domain: \( K = D_m + \frac{R^2 V_{\text{max}}^2}{192 D_m} \)

**Some notes:**

(1) \( K \) can be expressed as \( J = -K \frac{\partial C}{\partial z} \) where, \( K \) is the **Taylor-Aris dispersion coefficient** for \( \text{Re} < 2100 \). Note that ‘\( K \)’ is not a physical or thermodynamic property like ‘\( D_m \)’, and the value clearly depends on \( V_{\text{max}} \& D_m \).

(2) If \( D_m \) increases, ‘dispersion’ decreases, or vice-versa, which seems to be weird. But this is the way, ‘Taylor dispersion’ behaves. In general, “diffusion” is responsible for creating a concentration gradient; it is the convection which wipes out the gradient. In this case, however, convection or the radially parabolic velocity profile in the tube smears the radially flat concentration of the dose (input) at the tube-inlet to the parabolic profile; diffusion wipes out the gradient later in the tube.

(3) Equation (2) represents the following scenario:

<table>
<thead>
<tr>
<th>( \delta(t) )</th>
<th>( \bar{V} = \frac{V_{\text{max}}}{2} ) (plug flow! but Reynolds number is less than 2100!!)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Axial dispersion (} K \text{)} )</td>
<td>( C(t,z) = ? )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( \text{1st} )</th>
<th>( \text{2nd} )</th>
<th>( \text{3rd} )</th>
<th>( \text{4th} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Turbulent flow (eddies)} )</td>
<td>( \text{Re} = \frac{Vd}{v} )</td>
<td>( K = D_m + \frac{R^2 V_{\text{max}}^2}{192 D_m} )</td>
<td></td>
</tr>
</tbody>
</table>

For the region ‘2’, a commonly asked question is: why does axial dispersion coefficient (\( D_L \) or \( K \)) exceed molecular coefficient (\( D_m \)) even if \( \text{Re} < 2100 \)?

**The answer is:** We are referring to Taylor dispersion, when the parabolic velocity profile can be replaced with a plug flow profile, with the radial concentration removed, but the axial ‘dispersion’ included. The total mass is conserved with the radially distributed amount of the solute redistributed along ‘\( z \)’ or axial direction; thus \( K \) or \( D_L \) increases with increasing velocity or Reynolds number.
Lecture #16

Prototype example 11: Strained diffusion-controlled reaction

⇒ Consider a strained diffusion-controlled reaction. Specifically, we are discussing here the unmixed combustion of a fuel in a one-step irreversible reaction in a laminar diffusion flame formed by the axisymmetric planer counter flows.

\[
\begin{align*}
\text{Reaction is, } & A + \nu B \rightarrow C \quad \Rightarrow \quad r_1 = \nu r_2 \\
& (2) \quad (1) \quad (3) \quad r_B = \nu r_A \\
& (r_1 - \nu r_2 = 0)
\end{align*}
\]

**General case concentration profiles:**

**Solution:** All convection has done is to create a stagnation plane/zone (small velocities) in which diffusion is important.

**Velocity field** (imposed from outside)

\[ v_x = \epsilon x \]  
Assume \( \rho = \text{constant} \]
\[ v_y = -\epsilon y \quad \epsilon \equiv \text{strained rate} \sim v_\infty - 0 \left( \frac{d v_y}{d x} \right) \]

Depending on \( \epsilon \) or \( \epsilon(t) \), the ‘zone’ of small velocities will be different. Solve for mass fraction profiles: \( \omega_1(y) \), \( \omega_2(y) \neq x \) (x is the distance in an infinitely long plate)

(If reaction is very fast zone will be of zero-thickness, viz. plane/sheet)

\[ \Rightarrow \text{Continuity} \quad \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 \quad \text{check:} \quad \begin{cases} v_x = \epsilon x \\ v_y = -\epsilon y \end{cases} \]

\( y \) – momentum balance is not required although pressure increases from \( P_\infty \) to \( P_0 \) (stagnation plane) as velocity \( v_y \) decreases from \( v_\infty \) to \( 0 \): \( \rho v_\infty^2 \sim \Delta p \)

**Species:**

1. \[ \frac{\partial \omega_1}{\partial t} + v_x \frac{\partial \omega_1}{\partial x} + v_y \frac{\partial \omega_1}{\partial y} = \frac{1}{\rho} \frac{\partial}{\partial y} \left( \rho D \frac{\partial \omega_1}{\partial y} \right) + r_1 \]
2. \[ \frac{\partial \omega_2}{\partial t} + \epsilon x \frac{\partial \omega_2}{\partial x} - \epsilon y \frac{\partial \omega_2}{\partial y} = \frac{1}{\rho} \frac{\partial}{\partial y} \left( \rho D \frac{\partial \omega_2}{\partial y} \right) + r_2 \]

\( t = 0 \) reaction zone will be at stagnation zone, and \( t > 0 \) reaction zone moves.

\( t = 0 \) \( \omega_1 = 1 \quad \omega_2 = 0 \) \( y > 0 \)
\( \omega_2 = 0 \) \( y < 0 \)

\( t > 0 \) \( y \rightarrow \infty \) \( \omega_1 = 1, \omega_2 = 0 \)
\( y \rightarrow -\infty \) \( \omega_2 = 1, \omega_1 = 0 \)

From (1) & (2) with \( r_1 - \nu r_2 = 0 \)

\[ \frac{\partial (\omega_1 - \nu \omega_2)}{\partial t} - \epsilon y \frac{\partial}{\partial y} (\omega_1 - \nu \omega_2) = \frac{\partial}{\partial y} D \frac{\partial}{\partial y} (\omega_1 - \nu \omega_2) \]

Let \( k = (\omega_1 - \nu \omega_2) \)

\[ \frac{\partial k}{\partial t} - \epsilon y \frac{\partial k}{\partial y} - \frac{\partial}{\partial y} D \frac{\partial}{\partial y} (D \frac{\partial k}{\partial y}) = 0 \]

(reaction can be slow or fast)

**Note:** If the reaction is very fast, zone will be of zero thickness, and at the reaction zone/plane, \( \omega_1 = \omega_2 = 0 \) (species A, B will be destroyed completely & instantaneously, leaving behind the product C only) \( \Rightarrow \) This is what a flame (a torch of a burner) does!

**Solution:** Try \( \eta = y f(t) \)

Recall the Stoke's 1st problem.

Solution by Similarity transform

(Combination of variables)

\[ \frac{\partial k}{\partial t} = \frac{dk}{d\eta} \frac{d\eta}{dt} = y f' \frac{dk}{d\eta} = \eta f' \frac{dk}{d\eta} \]
\[
\frac{\partial k}{\partial y} = f \frac{dk}{d\eta}, \quad \frac{\partial^2 k}{\partial y^2} = f \frac{d^2 k}{d\eta^2}
\]

The equation becomes,
\[
\left(\frac{\eta f' dk}{d\eta} - \epsilon \frac{\eta f \partial k}{\partial \eta} - D f \frac{d^2 k}{d\eta^2}\right) = 0
\]
\[
\left(\frac{1}{f}(f' - \epsilon) \frac{dk}{d\eta} - D \frac{d^2 k}{d\eta^2}\right) = 0 \quad - (3)
\]

\(f(t)\) must disappear for the method of combination to work!

\[
\frac{1}{f}(f' - \epsilon) = \text{constant} = 2 \quad (\text{assume}) \quad - (4)
\]

\(f' - \epsilon f - 2f^2 = 0\)

\[
f(t) \Rightarrow f = \left(\frac{1}{2\epsilon} (1 - e^{-2\epsilon t})\right)^{-1/2} \quad (5)
\]

Therefore, \(\eta = yf(t) = y \left(\frac{1}{2\epsilon} (1 - e^{-2\epsilon t})\right)^{-1/2} \quad (6)\)

\((y \text{ and } t \text{ have been combined to } \eta)\)

Put (4) in (3); we are now solving (without ‘D’)

\[2\eta \frac{dk}{d\eta} - \frac{d^2 k}{d\eta^2} = 0 \quad \text{where, } \eta = \eta(y, t) \text{ from (6)} \quad - (7)\]

\(\Rightarrow 2 \text{ BCs are required for } k(\eta)\)

**BCs:**
\[
t = 0 \quad \text{for} \quad y > 0 \quad \omega_1 = 1, \omega_2 = 0 \quad \{ \equiv \eta > 0 \quad k = 1 \}
\]
\[
y < 0 \quad \omega_2 = 1, \omega_1 = 0 \quad \{ \equiv \eta < 0 \quad k = -\nu \}
\]

\(\text{for all } t > 0 \quad y \rightarrow -\infty \quad \omega_1 \rightarrow 1, \omega_2 = 0 \quad \{ \equiv \eta \rightarrow -\infty \quad k = -\nu \}
\]
\[k = A + B \text{ erf}(\eta)\]
\[
1 = A + B
\]
\[
-\nu = A - B \quad \text{BCs} \Rightarrow
\]
\[
k = \omega_1 - \nu \omega_2 = \frac{1}{2}(1 - \nu) + \frac{1}{2}(1 + \nu) \text{ erf}(\eta) \quad - (8)
\]
Now, let us ask where is the flame? Where is the reaction zone?

@ Reaction zone/flame: \( k = 0 \)  (fast kinetics)

\[ (See\ BCs: -v \leq k \leq 1) \quad (k = \omega_1 - \nu \omega_2) \quad (\omega_1 = \omega_2 = 0) \]

Try locating the movement of flame.

\[ \eta = \eta_{flame}(y, t) \text{ at } k = 0 \]

Therefore,

\[ \text{erf}(\eta_F) = -\frac{(1-v)}{(1+v)} \]

\[ \eta_F = \text{erf}^{-1}\{-(\frac{1-v}{1+v})\} = y_F f(t) \]

**Time-consideration of flame movement:**

\[ y_F = \left\{ \frac{1}{2} (1 - e^{-2\epsilon t}) \right\}^{1/2} \text{erf}^{-1}\{-(\frac{1-v}{1+v})\} \quad (9) \text{ from eq. (5)} \]

Check \( t = 0, \ y = 0 \) reaction zone is at stagnation plane

\( t > 0, \ y \) can move up or down depending upon sign of

\[ \text{erf}^{-1}\{-(\frac{1-v}{1+v})\} \text{ i.e. if } \]

\( v > 1 \) \( y \) is + ve plane moves up

\( v < 1 \) \( y \) is - ve plane moves down

\( i.e. \quad v > 1 \quad B \) is getting consumed faster, flame moves towards B (up in the present case)

\( v < 1 \quad A \) is getting consumed faster, flame moves towards A (down in the present case)

Plane moves from stagnation plane at \( y = 0 \) to \( y_1(t_1) \) to \( y_2(t_2) \) to a SS level, given by equation (6).

For small \( t \),

\[ 1 - e^{-2\epsilon t} \approx 2\epsilon t + \cdots \text{ expand it} \]

Therefore,

\[ y_F \approx \sqrt{t} \text{erf}^{-1}\left\{-(\frac{1-v}{1+v})\right\} \quad \text{and} \quad \eta_F \approx \frac{y_F}{\sqrt{t}} \quad (10) \]
With D incorporated, \( \eta = yf(t) = \frac{y}{\sqrt{Dt}} \left( \frac{1}{2\epsilon} (1 - e^{-2\epsilon t}) \right)^{-1/2} \) \( (6') \)

\[
y_F = 2\sqrt{D} \left( \frac{1}{2\epsilon} (1 - e^{-2\epsilon t}) \right)^{1/2} \text{erf}^{-1} \left\{ -\frac{(1 - \nu)}{(1 + \nu)} \right\} = (9')
\]

And approximated equations: \( y_F \approx 2\sqrt{Dt} \text{erf}^{-1} \left\{ -\frac{(1 - \nu)}{(1 + \nu)} \right\} \) and \( \eta_F \approx \frac{y_F}{2\sqrt{Dt}} \) \( ---- (10') \)

Fuel consumption rate,

\[
m = \rho D \frac{\partial \omega_1}{\partial y} \text{ (at flame)} = \rho \frac{D e}{2\pi (1-e^{-2\epsilon t})^{1/2}} \cdot (1 + \nu) e^{-\eta_F^2}
\]

**Note:** \( t \to \infty \) \( y_F \to \text{finite} \) \( \text{SS (generally) at } t > 1/\epsilon \)

(Fuel consumption is large to begin with; decreases to a SS value at SS or \( t \to \infty \) or \( y_F \) at \( t \to \infty \))

- Convection has created **diffusion-limitation condition**
- The *straining* of the flame is physically significant because it **increases the rate of reactant consumption**, not only by increasing the interfacial exposure of fuel to oxidant, but also by convecting additional reactant to the flame. (SIAM J. APPL. MATH. VOL. 28, No. 2, 1975)
- Flame creates a **reaction-plane** away from the **hydrodynamic-stagnation** plane, where the reaction is very fast \( (\omega_1 = \omega_2 = 0) \)
- **Similarity Method** was used to solve 'k' or track the movement of flame.
Lecture #17

Prototype example 12: Simultaneous momentum, heat, and mass transport

\[ \rightarrow \text{Condensation of steam in the presence of an inert gas (air) on a vertical surface (plate):} \]

The example below will show that the effect of air mixed in steam is to reduce the condensation heat transfer coefficient, possibly by one-order of magnitude. This considerable decrease in \( 'h' \) can occur at the air quality as low as 0.1, implying that the condensers must be designed/operated with a proper venting arrangement so that the non-condensable gas is instantly removed from the system. It is never safe to assume that non-condensable gas will not be present. See *In Boiling, Condensation and Gas-liquid flow by Whalley*, for details.

Before analysing the condensation of steam in the presence of air, let us begin with that of a saturated steam without air:

One can write down the continuity \& NS equation or momentum balance equation in \( x \)-direction with suitable BCs and approximation. And, the velocity profile of liquid in the film (condensate), assuming laminar flow, can be derived as

\[
v_x(y) = \frac{g(\rho_f - \rho_v)\delta_f^3}{2\mu_f} \left[ 2 \left( \frac{y}{\delta_f} \right) - \left( \frac{y}{\delta_f} \right)^2 \right] \left[ \delta_f = \delta_f(x) \right] \quad \text{(This is another homework problem)}
\]

See Koh et.al (1961), Int J Heat & Mass transfer for detailed analysis. You can also check the book by McCabe-Smith or Kern. In general, acceleration term can be neglected assuming fully developed laminar flow regime \( \frac{\partial v_x}{\partial x} \sim 0 \). From the velocity profile \( v_x(y) \), \( \dot{m}(x) \) or local mass flow rate \( \left( \frac{kg}{s} \right) \) can be calculated as

\[
\dot{m}(x) = \int_0^{\delta_f} \rho_f v_x(y) dy = \frac{g(\rho_f - \rho_v)d^3(x)}{3\mu_f} \quad \text{(1)} \quad (0 \leq y \leq \delta_f)
\]

Energy equation can also be written for the film to determine variation in the film thickness along the length, viz. \( \delta_f(x) \), and define \( \text{Nu}_x \) or \( h_x \):

**Energy equation:** \( \frac{d^2 T_f}{dy^2} = 0 \quad (SS, \frac{\partial T}{\partial x} \sim 0) \)

With suitable BCs, on integration,
\[ T_f = T_w + (T_{sat} - T_w) \left( \frac{y}{\delta_f(x)} \right) \]  

(2)

Therefore, \( q_w = -k_f \left. \frac{dT}{dy} \right|_{y=0} = k_f \frac{(T_{sat} - T_w)}{\delta_f} = h(T_{sat} - T_w) \): definition for 'h' (not "truly" a thermal boundary layer; here, we have a physical film of condensate)

Still, we have one more conservation equation (macroscopic mass & energy balances) to use:

\[ \Rightarrow \lambda \left( \frac{d\dot{m}}{dx} \right) = g \rho_f (\rho_f - \rho_v) \delta f(x) \frac{d\delta f}{dx} = k_f (T_{sat} - T_w) \]  

(3)

Combining (1) & (2) & integrating (3) with BC, \( x = 0, \ \delta_f = 0 \)

\[ \delta f(x) = \left[ \frac{4k_f \mu_f (T_{sat} - T_w)x}{g \rho_f (\rho_f - \rho_v) \lambda} \right]^{1/4} \]  

\( h_f(x) \sim \frac{k_f}{\delta_f(x)} \)

From (2) \( h_f(x) \) is calculated as

\[ \left[ \frac{g \rho_f (\rho_f - \rho_v) \lambda k_f^3}{4 \mu_f (T_{sat} - T_w)x} \right]^{1/4} \]

Local heat transfer coefficient

\[ Nu(x) = \frac{h_f x}{k_f} = \left[ \frac{g \rho_f (\rho_f - \rho_v) \lambda k_f^3}{4 \mu_f (T_{sat} - T_w)x} \right]^{1/4} \]  

(It can be shown that the average heat transfer coefficient at \( x = L \) is \( 4/3h_f) \)

\Rightarrow Revert to condensation in the presence of air or a non-condensing gas (mass transfer effects):
Notes: 1. There is no $\prime k_g \gamma$ if pure component (no air)

2. $\prime h_g \gamma$ must be corrected for the effect of diffusion flux onto the condensate-layer.

- Ackerman correction factor.

See Browers in AIChE J (1995) 41 (7) for details. Briefly the traditional stagnation film model is modified by considering “convective velocity”, “bulk transport” or “Stephan flow” or “Induced velocity”. Recall the prototype diffusion-in-stagnant film example/equation:

$$N_A = (N_A + N_B) \frac{CA}{C} + J_A$$

$$= (N_A + N_B) \frac{CA}{C} - D_{AB} \frac{dCA}{dy}$$

$$N_A = \frac{N_A}{N_A + N_B} \frac{CD_{AB}}{\delta_f} \ln \left[ \frac{N_A}{N_A + N_B} - x_{A2} \right] \frac{N_A}{N_A + N_B} - x_{A1}$$

with $N_B = 0$ (air is stagnant)

$$= k_g (p_{A1} - p_{A2})$$ or $k_x (x_{A1} - x_{A2})$: definition for $k_g$ or $k_x$

**Heat transfer coefficient (modified)**

$$q_S = h_g \left( -\frac{dT}{dy} \right) z_f + N_A C_p (T - T_s)$$ (within air-vapor film)

- diffusion length/air--vapor film
- mass flux towards condensate film

$$\int_{T_s}^{T_1} \frac{dT}{q_s - N_A C_p (T - T_s)} = \frac{1}{h_g z_f} \int_0^0 dy$$ (integrated over diffusion length; not condensate-film)

$$q_s = \left( \frac{h_g (N_A C_p)}{1 - \exp(-\frac{N_A C_p}{h_g})} \right) (T_1 - T_s);$$

$$= h_g C (T_1 - T_s) \Rightarrow \quad C \equiv \text{Ackerman correction factor} = \left( \frac{\epsilon}{1 - e^{-\epsilon}} \right); \quad \epsilon = \frac{N_A C_p}{h_g}$$

$h_g$ may be considered as heat transfer coefficient w/o mass transfer similar to Dittus-Boelter equation:

$$h_g = 0.023 Re^{0.8} Pr^{\frac{1}{3}}$$

In summary, the effect of mass transfer (diffusion) is to modify $\prime h_g \gamma$ through an additional resistance:

$$h_g' = h_g \left( \frac{\epsilon}{1 - e^{-\epsilon}} \right). \text{ Note that if } N_A = 0, C = 1, h'_g = h_g \text{ (same as that for a pure or single component)}$$

$\Rightarrow$ The remaining model equations for the design of a heat exchanger (condenser) are straight forward:

(1) **Air (gas) phase heat balance:**

\[ GC_p \frac{dT_g}{dx} = -h_g \frac{e}{1-e^{-e}} (T_g - T_s) \left( \frac{cal}{s} \right) \ (h_g' = h_g \frac{e}{1-e^{-e}}) \]

@ \( x = 0 \) \( T_g = T_{g,\text{inlet}} \)

(2) **Mass transfer:** \( n_A = -k_{g,A} (p_{g,A} - p_{s,A}) \); \( p_{s,A} = f(T_s) \) (Antoin's correlation)

\[ p_{g,A} = \left( \frac{n_A}{n_{A+n_B}} \right) p_{\text{Total}} \]

\[ \frac{dn_A}{dx} = -k_{g,A} (p_{g,A} - p_{s,A}) \]

@ \( x = 0 \) \( n_A = n_{A,\text{inlet}} = G_{\text{inlet}} \times y_{A,\text{inlet}} \left( \frac{\text{moles}}{s} \right) \)

**Note:** \( n_B = \text{const} = G_{\text{inlet}} \times (1 - y_{A,\text{inlet}}) \)

throughout the height or \( \frac{dn_B}{dx} = 0 \)

(3) **Heat Balance in coolant:**

\[ q_w = \dot{w_C} c_p \frac{dT_c}{dx} = GC_p \frac{dT_g}{dx} + \lambda A \frac{dn_A}{dx} \] (total heat transferred across the film/wall)

\[ = h_g \frac{e}{1-e^{-e}} (T_g - T_s) + \lambda A \frac{dn_A}{dx} \] (assume unit width of plate)

@ \( x = 0 \) \( T_c = T_{c,\text{inlet}} \)

There are three variables, namely, \( T_g, T_c \) and \( n_A \), and as many number of equations (ODEs) to solve for the condenser length required for \( n_A \) to decrease from the inlet value \( (n_{A,\text{inlet}}) \) to some prescribed value at the bottom of the condenser. See Gupta and Verma (2002) Chem Eng Sci 57 (14), 2679-2696, for detailed calculations.

**Correlations:**

- a. \( h_g = 0.023 \text{Re}^{0.8} \text{Pr}^{1/3} \) : gas - side
- b. \( h_c = 0.36 \text{Re}^{0.55} \text{Pr}^{1/3} \) : coolant side
- c. \[ \frac{k_g \text{Pr}^{M_A}}{G} \text{Sc}^{2/3} = 0.023 \times \text{Re}^{-0.17} \]

\[ \frac{1}{h_{oc}} = \frac{1}{h_g} + \frac{1}{h_c} + \frac{1}{h_f} \] overall 'h_{oc}' can also be defined as
Lecture #18

Introduction to the 2nd part of the course (Advanced topics??)
(High Reynolds number-flow, Boundary layer theory, Turbulence, Flow at large Peclet number)

So far, we studied a total of 12 prototype examples: 3 on momentum transport, namely, Stoke’s first problem, start-up flow, and flow in a permeable tube or bundles of hollow fibers (lubrication approximation); 4 on heat transport, namely, Nusselt problem, Graetz-Nusselt problem, Brinkman problem, and free convection in confined flow; and 4 on mass transport, namely, diffusion in a stagnant fluid (film theory), diffusion in a flow past a vertical plate (surface renewal theory), Talyor-Aris dispersion in a laminar tubular flow, and diffusion-strained reaction. The last example was related to the simultaneous momentum, heat and mass transport; in particular we addressed condensation of steam over a vertical plate, from a mixture of air and steam. If you objectively re-look at these examples, you can say that we have indirectly studied 3 additional examples on mass transport. How? By making an analogy with heat transport, each of the 4 prototype examples can have an analogous situation in mass transport. Thus, temperature gradients at the walls can have an analogous concentration gradients at the reactive walls, viz. heterogeneous reaction, and the homogenous source of heat generation (viscous heating) can have an analogous homogeneous chemical reactions in fluid flow. Similarly, Grashoff number based on temperature difference can also be defined based on concentration difference, implying there can be free convection in a non-uniform concentration field under isothermal condition.

Here, the main point to be considered is that, apart from the common assumptions of an incompressible fluid, NF, and laminar flow (low Reynolds number), all examples had unidirectional or approximately unidirectional flow. It also implies that these problems were simple to solve, and basic mathematical methods or techniques (Combination of variables and/or Separation of variables) sufficed to exactly solve the governing conservation equations. Another common feature of these examples was that there was no reference to “boundary layer” or “boundary layer theory”, which is rather a common feature of most of fluid flows in chemical engineering applications. Also, note that we did not use heat transfer coefficient, or mass transfer coefficient, or drag coefficient, or friction factor, nor we used Nusselt number or Sherwood number to calculate heat/mass transfer coefficients. It was not necessary. Why not? Because the velocity, temperature, or concentration profiles were all analytically solved from the conservation equations. Once these profiles are solved, one can calculate the respective gradients on a solid surface, and then calculate momentum flux or drag or pressure drop, as well as heat conduction and diffusion flux. Of course, once the flux is calculated, heat or mass transfer coefficient can be defined or calculated per say. Similarly, once drag or pressure drop is determined, one can define/calculate drag coefficient or friction factor.

Situation is, however, completely different at high Reynolds numbers or flow under turbulent conditions. Here, mathematical complexity is significantly high, and the problems are not easy to
solve. In other words, velocity, temperature, and concentration fields are not easy to resolve, and the respective wall gradients or flux cannot be analytically determined or calculated. Therefore, there are transport models and theories to solve/address such problems. From engineering calculation point of view, drag coefficients, friction factor, mass and heat transfer coefficients must be determined empirically or experimentally, of course with assistance from theory. In some cases, special mathematical techniques are required to solve the conservation equations, even if the flow is at low Reynolds numbers (e.g. creeping flow). In these contexts, we start new topics (Advanced?) in this course.

**Streamlines and Stream functions (incompressible fluid)**
(laminar flow can be characterized by streamlines)

(1) Define streamlines direction $\mathbf{ds}$ given by $\mathbf{ds} \times \mathbf{V} = 0$ (i.e. parallel to velocity vector, or velocity vector is tangent to streamline at all points in the flow field)

If 2-dimensions,

$$
\begin{vmatrix}
  i & j & k \\
  dx_x & dy_y & dz_z \\
  v_x & v_y & v_z \\
\end{vmatrix} = 0 \Rightarrow (v_y dx_x - v_x dy_y) \mathbf{k} = 0 \quad (\perp \text{to } d\mathbf{s} \text{ & } \mathbf{V})
$$

Or, $\frac{dy_y}{dx_x} = \frac{v_y}{v_x}$

(note that particle path and streamlines are identical under SS; Streak lines $\Rightarrow$ dye continuously put in & tracing every lines. Particle lines $\Rightarrow$ one dye)

(2) **Stream function** $\psi(x, y)$ defined as

$$d\psi = \left. \frac{\partial \psi}{\partial x} \right|_y dx + \left. \frac{\partial \psi}{\partial y} \right|_x dy$$

with $\left. \frac{\partial \psi}{\partial x} \right|_y = -v_y \quad \& \quad \left. \frac{\partial \psi}{\partial y} \right|_x = v_x \quad - (1)$

Then, $d\psi = -v_y dx + v_x dy$, and when equation (1) holds good, $\nabla \cdot \mathbf{V} = 0$ (check).

Alternatively, for an incompressible fluid-flow, there exists '$\psi(x, y)$' with the constraints

$$v_x = \left. \frac{\partial \psi}{\partial y} \right|_x \quad \text{and} \quad v_y = -\left. \frac{\partial \psi}{\partial x} \right|_y$$

(3) **Streamlines are given by** $d\psi = 0 \quad \text{or} \quad \psi(x, y) = \text{constant, } c$ (from 1 and 2)

Or, $\frac{dy}{dx} = \frac{v_y}{v_x} \quad \Rightarrow \quad \psi(x, y) = \text{constant}$ represents a streamline

Streamlines:

$$\psi = c_1$$
$$\psi = c_2$$
$$\psi = c_3$$

defines a surface of streamlines having different values, $c_1, c_2, c_3$, etc.

$\psi$ is constant along a streamline
Some physical significances of $\psi$:

1. $v_x$ and $v_y = 0$ at solid boundary because of no-slip condition, implying $\psi(x, y) = 0$ represents a solid boundary.

2. Two streamlines cannot cross each other, otherwise there will be two velocities. Mass cannot transfer across the streamlines.

3. A class of flow fields can be solved using $'\psi'$ relatively easier rather than $v_x$ & $v_y$. In other words, we have $\nabla^2 \psi = 0$ in stead of $\nabla \vec{V} = 0$ for an incompressible 2D fluid flow. Similarly, the viscous $\nabla^2 V$ term in NS equation can be easily transformed to $\nabla^4 \psi = (\frac{\partial^4}{\partial x^4} + 2 \frac{\partial^4}{\partial x^2 \partial y^2} + \frac{\partial^4}{\partial y^4}) \psi$. See BSL Table 4.2.1.

4) For creeping flow past a sphere (Re $\to 0$, viscous term $\gg$ inertial term) $\nabla^4 \psi = 0$...easy to solve $\psi$. Once $\psi$ is solved, determine $v_r$ & $v_\theta \to \nabla \vec{V}$ (strain tensor) $\to \tau$ and $\sigma$ (stresses) at the solid surface $\to$ determine forces along the flow $\to$ direction $\to$ integrate over the entire sphere to obtain the world famous Stokes law (1851) $= 6\pi \mu c_\infty R$. Re-solve Deen’s example 7.4.2 as a home work.

**Inviscid fluid-flow and irrotational flow**

Are they different? Can a flow of an inviscid fluid be rotational? Can a creeping flow (low Reynolds number when viscose effect is dominant) around a sphere be irrotational? Does $\mu = 0$ represent the same flow field of an inviscid fluid as that of a fluid having $\vec{\omega} = \nabla \times \vec{V} = 0$? See Deen’s book.

Some definitions (and some occasional mix-up): Inviscid fluid: $\mu = 0$

- Ideal fluid: $\rho = c$, $\mu = 0$
- Irrotational flow: $\vec{\omega}$ (vorticity vector) $= \nabla \times \vec{V} = 0$
- Potential flow: $\rho = c$, $\mu = 0$ and $\nabla \times \vec{V} = 0$

⇒ Let us start with the flow of an ideal fluid: ($\rho = c, \mu = 0$ or Re $\to \infty$)

NS equation: $\rho \frac{D \vec{V}}{Dt} = \rho \left( \frac{\partial \vec{V}}{\partial t} + \vec{V} \cdot \nabla \vec{V} \right) = -\nabla P + \rho \vec{g}$ (neglecting the viscous term; better known as Euler equation)

$$\rho \vec{V} \cdot \nabla \vec{V} = -\nabla P \quad \text{(under SS)} \quad - (1)$$

$$\vec{V} \cdot \nabla \vec{V} = \nabla \left( \frac{\vec{V}^2}{2} \right) - \vec{V} \times \left( \nabla \times \vec{V} \right) \quad : \text{vector algebra} \quad - (2)$$

Take dot product with $\vec{V}$ on both sides:

$$\vec{V} \cdot (\vec{V} \cdot \nabla \vec{V}) = \vec{V} \cdot \nabla \left( \frac{\vec{V}^2}{2} \right) - \vec{V} \cdot [\nabla \times (\nabla \times \vec{V})] = \vec{V} \cdot \nabla \left( \frac{\vec{V}^2}{2} \right)$$

(Note $\vec{V} \cdot [\nabla \times (\nabla \times \vec{V})] = 0$; use Dean Table A 1 to show this. The assumption of $\nabla \times \vec{V} = 0$ is not required!)
Accordingly, \( \vec{V} \cdot \nabla \left( \frac{V^2}{2} \right) = - \left( \frac{V \cdot \nabla \rho}{\rho} \right) = -V \cdot \nabla \left( \frac{p + gh}{\rho} \right) \); here \( h \) is the height above some horizontal reference plane.

Or, \( \vec{V} \cdot \nabla \left( \frac{V^2}{2} + \frac{p}{\rho} + gh \right) = 0 \)

Recall that \( \vec{V} \) is parallel to streamline \( \vec{a} \). Therefore, \( \vec{V} \cdot b \), where \( b \) is some scalar quantity, represents the rate of change of the scalar \( b \) along a streamline, which is equivalent to writing

\[
\Delta \left( \frac{V^2}{2} + \frac{p}{\rho} + gh \right) = 0; \text{Bernoulli's equation (conservation of K.E. + P.E. + pressure Energy)}
\]

where, the term in the parenthesis is the scalar quantity, \( b \), and \( \Delta \) refers to any two points along the same streamline of an ideal fluid.

\( \Rightarrow \) Let us now start with an irrotational flow \( \vec{\omega} = \nabla \times \vec{V} = 0 \) of an ideal fluid \( \rho = c, \mu = 0 \):

By taking the curl of each term in the NS equation, we get

\[
\frac{D\vec{\omega}}{Dt} = \vec{\omega} \cdot \nabla \vec{V} \quad \text{where, } \vec{\omega} = \nabla \times \vec{V}
\]

Therefore, if \( \vec{\omega} = 0 \) anywhere in the flow field, then \( \frac{D\vec{\omega}}{Dt} = 0 \text{ everywhere.} \) It means that if the vorticity is zero anywhere in a fluid (e.g. uniform and unperturbed flow) which is frictionless or inviscid, that fluid remains irrotational forever.

Now, revisit the previous equations (1) & (2) for \( \mu = 0 \) and insert \( \nabla \times \vec{V} = 0 \) to obtain

\[
\nabla \left( \frac{V^2}{2} + \frac{p}{\rho} + gh \right) = 0
\]

Thus, the same Bernoulli's equation is obtained where the sum in the parenthesis is constant everywhere in the fluid (i.e. the same for all streamlines)! Thus, Bernoulli's equation is valid for potential flow \( (\rho = c, \mu = 0 \text{ & } \nabla \times \vec{V} = 0) \) everywhere in the flow field, not necessarily along a streamline as in the previous case of the flow of an ideal fluid!! Deen also mentions that this contrasts the creeping flow past a sphere of a viscous fluid \( (\text{Re} \to 0) \), where \( \nabla \times \vec{V} = 0 \) (irrotational) only at far distances from the sphere!!

If \( \nabla \times \vec{V} = 0 \), there is a potential function \( \phi \) such that

\[
v_x = \frac{\partial \phi}{\partial x} \quad \text{and} \quad v_y = \frac{\partial \phi}{\partial y} \text{ (check) or } \vec{V} = \nabla \phi \text{ and } \nabla^2 \phi = 0. \text{ Thus, we have,}
\]

\[
\begin{align*}
\nabla \cdot \vec{V} &= 0 \Rightarrow \nabla^2 \psi = 0 \quad (\rho = c) \\
\n\nabla \times \vec{V} &= 0 \Rightarrow \nabla^2 \phi = 0 \quad (\text{irrotation flow})
\end{align*}
\]

These represent kinematic solutions to a class of flow field problems, without reference to NS equation.

Also, \( v_x = \frac{\partial \psi}{\partial y} = \frac{\partial \phi}{\partial x} \).
\[ v_y = -\frac{\partial \psi}{\partial x} = \frac{\partial \phi}{\partial y} \]  

You should recall that these are Cauchy Riemann conditions.

Consider an analytic function of a complex variable \( z \): \( w(z) = \phi + i \psi \), where \( z = x + iy \). It can be shown that the function has real & imaginary parts that are each solution to Laplace equations:

\[ \nabla^2 \phi = \nabla^2 \psi = 0 \]

Therefore, any analytic function \( w(z) \) represents potential function & stream function, and thus velocity field of an ideal irrotational flow or simply potential flow \((\rho = c, \nabla \times \vec{V} = 0, \mu = 0)\).

**Ex.** \( w(z) = iz^2 = i(x + iy)^2 = -z^2 + i(x^2 - y^2) \) (in Cartesian coordinates)

Verify \( \nabla^2 \phi = \nabla^2 \psi = 0 \), i.e. the real part is potential function and imaginary part is stream function. In other words, any complex analytic function \( w(z) = \phi + i \psi \) will satisfy \( \nabla^2 \psi = \nabla^2 \phi = 0 \), and describe some potential flow, although it may not be the one you want!

**Ex.** Very often it is convenient to work on polar coordinates \((r, \Theta)\):

\[
\begin{align*}
  w(z) &= Az^n = Ar^n e^{i n \Theta} = Ar^n (\cos n \Theta + i \sin n \Theta) \\
  \phi &= Ar^n \cos n \Theta; \quad \psi = Ar^n \sin n \Theta
\end{align*}
\]

Verify \( \nabla^2 \phi = \nabla^2 \psi = 0 \) (Note that the polar representation of \( \nabla^2 \equiv \frac{\partial}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \Theta^2} \))

Define, complex velocity \( C = v_x - iv_y \) in Cartesian coordinates, where \( v_x = \frac{\partial \phi}{\partial x}; \quad \text{and} \quad v_y = -\frac{\partial \psi}{\partial x} \)

Therefore, \( C = \frac{\partial \psi}{\partial x} + i \frac{\partial \phi}{\partial x} = \frac{\partial w}{\partial x} = \frac{\partial w}{\partial z} = \frac{\partial w}{\partial z} \) (note \( \frac{\partial z}{\partial x} = 1 \))

In polar coordinate system \( C = |v| e^{-i\alpha}, \) where \( |v| = \sqrt{v_r^2 + v_\theta^2} \), \( \alpha = \angle v_x \) & \( v_y \)

And two coordinate systems are related as:

\[
\begin{align*}
  v_x &= v_r \cos \Theta - v_\theta \sin \Theta \\
  v_y &= v_r \sin \Theta + v_\theta \cos \Theta \\
  C &= [v_r(r, \Theta) - iv_\theta(r, \Theta)] e^{-i\Theta}
\end{align*}
\]

**Ex:** Let \( w(z) = u e^{-i\alpha} z \)

\[
C = \frac{dw}{dz} = u e^{-i\alpha} = u(\cos \alpha - i \sin \alpha). \) Therefore, \( u_x = u \cos \alpha, \ u_y = u \sin \alpha \) and the flow field is

![Diagram](diagram.png)

**Ex.** Revert to \( w = Az^n, \) \( C = \frac{dw}{dz} = nAz^{n-1} = nAr^{n-1} e^{i n \Theta} e^{-i \Theta} = nAr^{n-1} (\cos n \Theta + i \sin n \Theta) e^{-i \Theta} \)

\( v_r = nAr^{n-1} \cos n \Theta, \ v_\theta = -nAr^{n-1} \sin n \Theta; \) Also \( \phi = Ar^n \cos n \Theta, \ \psi = Ar^n \sin n \Theta \)
If $\theta = \frac{k\pi}{n}$, $k = 1, 2, 3 ...; v_r = (-1)^knAr^{n-1}$, $v_\theta = 0$

**Velocity fields are,**

$n = \frac{1}{2}:

\begin{align*}
&\begin{array}{c}
\text{Velocity field 1} \\
\end{array} \\
\end{align*}

\frac{1}{2} < n < 1:

\begin{align*}
&\begin{array}{c}
\text{Velocity field 2} \\
\end{array} \\
\end{align*}

$n: 3:

\begin{align*}
&\begin{array}{c}
\text{Velocity field 3} \\
\end{array} \\
\end{align*}

$n: 2:

\begin{align*}
&\begin{array}{c}
\text{Velocity field 2} \\
\end{array} \\
\end{align*}

**Source/Sink:** $w(z) = k \ln z = k \ln (re^{i\theta}) = k \ln r + ik\theta$

\begin{align*}
\phi &= k \ln r, \quad \psi = k\theta \\
C &= \frac{k}{z} = \frac{k}{r}e^{-i\theta}
\end{align*}

const. potential ($v_r = k/r, v_\theta = 0$)

$k = -ve.$

$m = \int_0^{2\pi} v_r r d\theta = \int_0^{2\pi} kd\theta = 2\pi k \Rightarrow k = \frac{m}{2\pi};$

$w = \frac{m}{2\pi} \ln z \rightarrow \text{source} \; \text{or} \; -\frac{m}{2\pi} \ln z \Rightarrow \text{sink}$

**Vortex** $w(z) = -\frac{i\Gamma}{2\pi} \ln z$

Check and plot:

$\Gamma = \oint \mathbf{U} \cdot d\mathbf{l} = \int_0^{2\pi} v_\theta r d\theta$

$v_r = 0$

$v_\theta = \frac{\Gamma}{2\pi r}$

**Doublet (Source + Sink)**

superimposition yields

Streamlines, constant potential

$\psi_s$
\[ w = \frac{\mu}{z} (\text{check by adding/superposition}) = \frac{\mu}{x + iy} = \left( \frac{x - iy}{x^2 + y^2} \right) \Rightarrow \psi = -\frac{\mu y}{x^2 + y^2} \]

\[ \Rightarrow x^2 + y^2 + \frac{\mu y}{\psi} = 0 \Rightarrow x^2 + \left( y + \frac{\mu}{2\psi_1} \right)^2 = \left( \frac{\mu}{2\psi_1} \right)^2 \]

Centre: \( \left( 0, -\frac{\mu}{2\psi_1} \right) \) & \( r = \frac{\mu}{2\psi_1} \)

\[ C(z) = -\frac{\mu}{z^2} = -\frac{\mu}{R^2} e^{-2i\theta} = -\frac{\mu}{R^2} (\cos\theta - i\sin\theta) e^{-i\theta} \]

\[ \uparrow \quad \uparrow \]

\[ U_r \quad U_\theta \]
Before we introduce BLT, let us continue with one more example of potential flow:

**Flow around cylinder without circulation:**

\[
\psi = (Ua - Ua)\sin \theta = 0 \rightarrow \text{cylinder (radius } a)\]

From stream function, calculate \( v_x = v_\infty(1 - \frac{r^2}{a^2}\cos 2\theta) \), \( v_y = -v_\infty\left(\frac{a^2}{r^2}\sin 2\theta\right) \) to show that \( \psi = 0 \) at \( r = a \)

\( v^2 = 4v_\infty^2 sin^2 \Theta \). Where is the no-slip condition at the solid surface (except at the two stagnation points)? Apply Bernoulli equation between the points far away from the cylinder and on the cylinder to show that \( p - p_\infty = \frac{1}{2}\rho v_\infty^2(1 - 4\sin^2 \Theta) \). See example 4.3.1 of BSL (Cartesian coordinate system) or 8.3-1 of Dean (polar coordinate system). The pressure distribution is symmetric about x-axis (flow direction), which means that there is no form drag on the cylinder! It is called d’Alembert’s paradox, with the potential theory predicting zero drag on the cylinder.

So far we can solve

1. Laminar viscous flow \( \Rightarrow \) low/moderate Reynolds nos including \( Re \rightarrow 0 \) (creeping flow)
2. Potential flow \( \Rightarrow \) high Reynolds nos.
But, this gives rise to d’Alembert’s paradox (predicts that drag on a plate in a flow field is 0, because $\mu = 0$ and/or $\nabla \times \vec{V} = 0$).

Potential flow is important because there exists a theorem which states that if the vorticity is zero anywhere in a fluid which is frictionless then that fluid remains irrotational forever.

For $\rho = c \Rightarrow \frac{D\vec{\omega}}{Dt} = (\vec{\omega} \cdot \nabla) \vec{V} \quad (\vec{\omega} = \nabla \times \vec{V})$

If $\vec{\omega} = 0$, then $\frac{D\vec{\omega}}{Dt} = 0$ everywhere.

Supercooled liquid He has zero $\mu \Rightarrow$ Helmholtz theorem suggests potential flow should be very common in nature for low viscosity fluids. **Reality is different: even low $\mu$-fluids have friction which is important.** You need a transfer pump to deliver or supply liquid He in a pipe.

Revisit NS equation: ($Re \to \infty$)

$$\rho \frac{\partial \vec{V}}{\partial t} + \rho(\vec{V} \cdot \nabla) \vec{V} = -\nabla p + \mu \nabla^2 \vec{V} + \rho \vec{g}$$

$$\mu \to 0, \mu \nabla^2 \vec{V} \text{ drops out,}$$

(Highest order derivative was dropped out)

Non-dimensionalize: $\frac{DV^*}{Dt^*} = -\nabla^* p^* + \frac{1}{Re} \nabla^* V^* + \frac{1}{Fr} g^*_r$

Term drops out as $Re \to \infty$

One BC is removed! $V_x = 0$ at surface! ⇒ It reduces the order of differential equation; removes the cylinder (solid surface) from consideration!

- This is not feasible. All it implies is that non-dimensionalization procedure was not correct.
  - $x^* = \frac{x}{L} \Rightarrow L$ characterizes $x$
  - $y^* = \frac{y}{L} \Rightarrow L^*$ cannot characterize $y^*$, if $Re \uparrow$

One should realize that characteristic distance in $y$ direction is much-much smaller than $L$: $\delta \ll L \Rightarrow y^* = \frac{y}{L}$ or $\frac{\delta}{L} \ll 1; \ y^* = \frac{y}{\delta}$ & $x^* = \frac{x}{L}$
\[ \frac{\delta}{L} \ll 1 \] is the basic assumption of (Prandtl) Boundary layer Theory.

Consider flow around a cylinder:

Flow field is divided in two regimes:

I. Close to the surface: viscous term is important, no matter how high is \( Re \); inertial flow is also important. 
\[ \frac{\delta}{L} \ll 1 \] or characteristic distance in \( y \) direction is much less than that in \( x \) direction.

II. Away from the surface: Potential flow; \( x, y \) – characteristic lengths are \( \sim \) the same. If \( Re \rightarrow \infty \) then the viscous term \( \rightarrow 0 \)

**NS equations in region I** (See Schlichting chapter 3-5):

\[
\begin{align*}
\rho \left[ \frac{\partial V_x}{\partial t} + V_x \frac{\partial V_x}{\partial x} + V_y \frac{\partial V_x}{\partial y} \right] &= -\frac{\partial p}{\partial x} + \mu \left[ \frac{\partial^2 V_x}{\partial x^2} + \frac{\partial^2 V_x}{\partial y^2} \right] \\
\rho \left[ \frac{\partial V_y}{\partial t} + V_x \frac{\partial V_y}{\partial x} + V_y \frac{\partial V_y}{\partial y} \right] &= -\frac{\partial p}{\partial y} + \mu \left[ \frac{\partial^2 V_y}{\partial x^2} + \frac{\partial^2 V_y}{\partial y^2} \right]
\end{align*}
\]

Note: \( V_x^* = \frac{V_x}{U_\infty} \), \( V_y^* = \frac{V_y}{V_c} \) \((V = \?\), \( x^* = \frac{x}{L} \), \( y^* = \frac{y}{\delta} \)

**Continuity:** \( \frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} = 0 \)

\[ \Rightarrow \frac{U_\infty}{L} \frac{\partial V_x^*}{\partial x^*} + V_c \frac{\partial V_y^*}{\partial y^*} = 0 \quad \text{If} \quad \frac{\partial V_y^*}{\partial y^*} \neq 0 \Rightarrow \frac{\partial V_y^*}{\partial y^*} \neq 0 \]

or \( \frac{U_\infty}{L} \approx \frac{V_c}{\delta} \Rightarrow V_c \approx U_\infty \left( \frac{\delta}{L} \right) \)

\[ \delta \ll L \quad V_c \ll U_\infty \quad \text{but it is not zero (finite)} \]

\[ V_y^* = \frac{V_y}{U_\infty \left( \frac{\delta}{L} \right)} \quad t^* = \frac{t}{L/U_\infty} \]

Boundary layer theory does predict \( V_y \neq 0 \) as \( \frac{\partial V_y^*}{\partial x^*} \neq 0 \Rightarrow \) There is deceleration in \( x \) – direction.

**Non-dimensionalize:**

\[
\rho \left[ \frac{\partial V_x^*}{\partial t^*} + V_x^* \frac{\partial V_x^*}{\partial x^*} + V_y^* \frac{\partial V_x^*}{\partial y^*} \right] + \rho \frac{U_\infty^2}{L} V_x^* \frac{\partial V_x^*}{\partial x^*} + \rho U_\infty^2 \left( \frac{\delta}{L} \right) V_y^* \frac{\partial V_x^*}{\partial y^*} = -\rho \frac{U_\infty^2}{L} \frac{\partial p^*}{\partial x^*} + \mu \left[ \frac{\partial^2 V_x^*}{\partial x^2} \right]
\]

Or \( \frac{\partial V_x^*}{\partial t^*} + V_x^* \frac{\partial V_x^*}{\partial x^*} + V_y^* \frac{\partial V_x^*}{\partial y^*} = -\frac{\partial p^*}{\partial x^*} + \frac{1}{Re} \left[ \frac{\partial^2 V_x^*}{\partial x^2} + \left( \frac{1}{\delta} \right)^2 \frac{\partial^2 V_x^*}{\partial y^2} \right] \)

\[
\left( \begin{array}{c}
0 - 1 \\
(0 - 1)
\end{array} \right)
\]
Each term is of the order one except \( \delta \ll L \) or \( L \gg \delta \) and \( Re \uparrow \uparrow \)

Therefore, \( \frac{1}{Re} \frac{\partial^2 V_x}{\partial x^2} \rightarrow 0 \) and \( \frac{1}{Re} \left( \frac{L}{\delta} \right)^2 \frac{\partial^2 V_y}{\partial y^2} \rightarrow ? \)

\[
= -\frac{\partial p}{\partial x^*} + \frac{1}{Re} \left( \frac{L}{\delta} \right)^2 \frac{\partial^2 V_y}{\partial y^2} \quad \text{(Re is high, so is \( \left( \frac{L}{\delta} \right)^2 \))}
\]

Among the three possibilities, \( \frac{1}{Re} \left( \frac{L}{\delta} \right)^2 \gg 1 \) or \( 1 \ll \delta \approx 1 \), the first two are ruled out because both viscous and inertial terms must to be retained, or they are important, to avoid the paradox. Only last condition holds good:

\[
\frac{1}{Re} \left( \frac{L}{\delta} \right)^2 \approx 1 \quad \text{or} \quad \frac{\delta}{L} \approx \frac{1}{\sqrt{Re}} \quad \text{(Re \uparrow boundary layer thickness \( \delta \) decreases)}
\]

NS dimensionless equation in BL becomes:

\[
\frac{\partial V_x}{\partial t^*} + V_x \frac{\partial V_x}{\partial x^*} + V_y \frac{\partial V_y}{\partial y^*} = -\frac{\partial p}{\partial x^*} + \frac{\partial^2 V_y}{\partial y^2} \quad \Rightarrow \text{Re has disappeared. It is embedded in the equation.}
\]

\[
y^* = f(\delta)
\]

\[
\frac{\delta}{L} \approx \frac{1}{\sqrt{Re}} \ll 1 \quad \text{if} \ Re \rightarrow \infty \quad (~100)
\]

**Boundary Layer Theory:**

\[
\begin{aligned}
\mu \frac{\partial^2 V_x}{\partial y^2} & \quad \text{must be retained in NS equation. Mathematically,} \ \delta \ll L \ \text{or} \ y_c \ll x_c. \\
\text{The theory will predict finite drag on a solid surface. On the other hand,} \\
\text{both terms can be dropped (or} \ y_c \approx y_c \text{in potential flow (Re \rightarrow \infty), away from} \\
\text{a solid surface.}
\end{aligned}
\]

**What about NS in \( y \)-direction?**

Non-dimensionalize the \( y \) - direction momentum equation using the correct/appropriate characteristic variables:

\[
V_x = V_x U_\infty, \quad x = x^*L, \quad y = y^* \delta, \quad V_y = V_y^* U_\infty \frac{\delta}{L} \quad \text{(from continuity)}:
\]

\[
\frac{\partial V_x}{\partial x^*} + \frac{\partial V_y}{\partial y^*} = 0 \Rightarrow \left( V_x^* \right)_{c} = \left( V_x^* \right)_{c} \frac{\delta}{L} ; \quad p = p^* \rho U_\infty^2
\]

Substitute,

\[
\rho \left( \frac{U_\infty^2}{L} \right) \left( \frac{\delta^2}{L} \right) V_x^* \frac{\partial V_x^*}{\partial x^*} + \rho \left( \frac{U_\infty^2}{L} \right) V_y^* \frac{\partial V_y^*}{\partial y^*} = -\rho \left( \frac{U_\infty^2}{L} \right) \frac{\partial p^*}{\partial y^*} + \mu \left( \frac{U_\infty^2}{L} \right) \left( \frac{\delta^2}{L} \right) \frac{\partial^2 V_y^*}{\partial y^2} + \frac{U_\infty^2}{L} \left( \frac{\delta}{L} \right) \frac{\partial^2 V_y^*}{\partial y^2}
\]

\[
V_x^* \frac{\partial V_x^*}{\partial x^*} + V_y^* \frac{\partial V_y^*}{\partial y^*} = -\left( \frac{U_\infty^2}{L} \right) \frac{\partial p^*}{\partial y^*} + \left( \frac{\mu^2}{\delta^2} \frac{U_\infty^2}{L} \right) \frac{\delta^2}{L} \frac{\partial^2 V_y^*}{\partial y^2} \quad \Rightarrow \text{drops out}
\]

\[
\frac{1}{Re} \left( \frac{L}{\delta} \right)^2 \approx 1
\]

Therefore, \( \frac{\partial p^*}{\partial y^*} = 0 \quad p \neq p(y) \quad \rightarrow \text{No pressure-drop in} \ y \text{direction in BL, which implies that potential flow/} \text{regime impresses its pressure all the way to the surface.}
**Summary:** Governing equations in BL (Prandtl BL):

Continuity: \( \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 \)

\( x \)-momentum: \( \frac{\partial v_z}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = -\frac{1}{\rho} \frac{dp}{dx} + \nu \frac{\partial^2 v_x}{\partial y^2} \)

\( y \)-momentum: \( \frac{\partial p}{\partial y} = 0 \)

BC. 1 \( y = 0 \) \( V_x = V_y = 0 \) (no slip)

2. \( y \to \infty \) \( V_x = U(x, t) \) (free stream velocity)

3. \( x = 0 \) \( V_x = U_\infty \) (approach velocity)
Lecture #20

Blasius Solution to BL Equations

Flow over a flat plate:

\[
\begin{aligned}
\delta \sim \frac{1}{\sqrt{Re_x}} = \sqrt{\frac{\mu}{\rho v_x x}} \\
\delta \sim \sqrt{\frac{\mu x}{\rho v_\infty}}
\end{aligned}
\]

X: Momentum:

\[
\frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = -\frac{1}{\rho} \frac{dp}{dx} + \nu \frac{\partial^2 v_x}{\partial y^2}
\]

SS: \(\frac{\partial v_x}{\partial t} = 0; \frac{dp}{dx} = 0; \frac{\partial v_x}{\partial x} \neq 0;\) semi-infinite domain;

Why? Because \(\frac{dp}{dy} = 0\) and potential regime imposes its uniform pressure \(P_\infty\) to BL.

Using stream function:

\[
\frac{\partial \psi}{\partial y} = f'(\eta)g(x) \sqrt{\frac{v_\infty}{v_x}}
\]

BC 2: \(y \to \delta(x)\) is replaced with \(y \to \infty\). Why? This was Blasius’ approach to solving PBL equations. Conceptually, two regimes (potential and BL) approach each other asymptotically. A person swimming in the BL does not see the potential flow regime, or vice versa, no matter how high is Re. Two theories stand apart. Also, potential flow is first solved, and the pressure and velocity solutions (conditions) are imposed at the top edge of the BL.

Let \(\eta = \frac{y}{\delta(x)} = y \sqrt{\frac{v_\infty}{v_x}}\); \(\psi = \psi(x, y)\)

Revert to solving the momentum equations:

\[
\psi = f(\eta)g(x) \quad \text{(replacing } y \text{ with } \eta \text{ and } x)\]

\[
\frac{\partial \psi}{\partial y} = f'(\eta)g(x) \frac{\partial \eta}{\partial y} = f'(\eta)g(x) \sqrt{\frac{v_\infty}{v_x}}
\]

BC 2: \(v_\infty = f'(\eta)g(x) \sqrt{\frac{v_\infty}{v_x}}\)
Therefore, \( f'(\eta) = 1, \quad g(x) = \sqrt{v_\infty v_x} \) (take it arbitrary)

\[
\begin{align*}
v_x &= \psi_y = g f'/\delta = v_\infty f' \\
-v_y &= \psi_x = g f - \frac{gf'y}{2x\delta} = -\frac{1}{2} \sqrt{\frac{v_\infty}{x}} (\eta f' - f)
\end{align*}
\]

\[
\psi_{xy} = \frac{g f'}{\delta} - \frac{gf' y}{2x\delta^2} - \frac{gf'}{2x\delta}; \quad \psi_{yy} = \frac{g f''}{\delta^2}; \quad \psi_{y \gamma} = \frac{g f'''}{\delta^3} \quad \text{(check all these calculations)}
\]

**BCs.** on \( \psi \):

1. \( y = 0 \quad v_x = 0 \quad \frac{\partial \psi}{\partial y} = 0 \)
2. \( v_y = 0 \quad \frac{\partial \psi}{\partial x} = 0 \)
3. \( y \to \infty \quad v_x = v_\infty \quad \frac{\partial \psi}{\partial y} = v_\infty \)

**BCs.** on \( f \):

1. \( \eta = 0 \quad f' = 0 \)
2. \( \eta = 0 \quad f = 0 \)
3. \( \eta \to \infty \quad (y \to \infty) \quad f' = 1 \)

Plugging,

\[
\frac{g f'}{\delta} \left( \frac{g f'}{\delta} - \frac{gf' y}{2x\delta^2} - \frac{gf'}{2x\delta} \right) - \left( g f' - \frac{gf' y}{2x\delta} \right) \frac{g f''}{\delta^2} = v \frac{g f'''}{\delta^3}
\]

Recall \( g = v_\infty \delta \) and \( g' = v_\infty \frac{\delta}{2x} \) (Recall \( \delta \sim \frac{\mu x}{\sqrt{\rho v_\infty}} \))

\[ff'' + 2f''' = 0\]

BC. (1-2) \( \eta = 0 \quad f' = f = 0 \) and (3) \( \eta \to \infty \quad f' = 1 \)

\[
\frac{df''}{d\eta} = -\frac{1}{2} ff''
\]

\[
\int \frac{df''}{f'''} = -\frac{1}{2} \int f d\eta
\]

\[
f'' = \exp \left( -\frac{1}{2} \int_0^\eta f d\eta \right) / \int_0^\infty \exp \left( -\frac{1}{2} \int_0^\eta f d\eta \right) \Rightarrow f' = \int_0^\eta f'' d\eta
\]

\[
f = \int_0^\eta f' d\eta = \frac{\int_0^\eta \exp \left( -\frac{1}{2} \int_0^\eta f d\eta \right) d\eta}{\int_0^\infty \exp \left( -\frac{1}{2} \int_0^\eta f d\eta \right) d\eta}
\]

Recall \( v_x = v_\infty f'(\eta) \)

\[
v_y = \frac{1}{2} \sqrt{\frac{v_\infty}{v_x}} (\eta f' - f)
\]

\[
\eta = \sqrt{\frac{v_\infty}{v_x}}
\]

**Blasius Solution (1908 - 10):**

For small values of \( \eta \) (close to plate):
\[ f(\eta) = A_0 + A_1\eta + \frac{A_2}{2!}\eta^2 + \frac{A_3}{3!}\eta^3 + \cdots \text{ (convergence for } \eta < 1) \]

**Plug in ODE:**

\[ f = \sum_{n=0}^{\infty} \left( -\frac{1}{2} \right)^n \frac{a^{n+1}c_n}{3n+2!} \eta^{3n+2} \]

where, \( C_0 = 1, C_1 = 1, C_2 = 11, C_3 = 375, C_4 = 27897, C_5 = 3,817,137 \)

What is \( \alpha \)? \( \Rightarrow \alpha = f''(0) \); Blasius ‘patched’ a series of small \( \eta \) to an asymptotic series for large \( \eta \). Best procedure is to use numerical integration to match \( \eta = \infty \) at BC. This yields \( \alpha = 0.332 \). \( f''(x) \) is an important variable to calculate. Check: it is nothing but the velocity gradient at the wall! Therefore, wall drag can be calculated from \( f''(x) \), shown later.

Once \( f(\eta) \) is known & \( g(x) = v_\infty \delta(x) \)

\[ \psi = g(x)f(\eta) = v_\infty \delta(x)f(\eta) \]

Therefore, \( v_x = \frac{\partial \psi}{\partial y} \), \( v_y = -\frac{\partial \psi}{\partial x} \) (so \( t^n \))

For small \( \eta \) (close to plate)

\[ v_x = \frac{1.33}{4} v_\infty \frac{v_\infty}{v_x} y \approx \frac{v_\infty y}{\delta(x)} \quad (y \ll \delta) \]
\[ \left( \frac{\partial v_x}{\partial y}\right)\text{close to plate} = \frac{v_\infty}{\delta(x)} \]

\[ v_y = \frac{1.33v_\infty^{3/2}}{16v^{1/2}x^{3/2}} y^2 \approx \frac{v_y^2}{\delta(x)} \quad (\text{Note } v_y \ll v_x) \]

**BL thickness is defined as the distance from the wall where**

\[ \frac{v_x}{v_\infty} = f'(\eta) = 0.99 \]

This occurs at \( \eta = 5 \) or \( y = 5 \frac{v_x}{v_\infty} \)

\[ \frac{y}{x} = 5 \frac{1}{\sqrt{Re_x}} \rightarrow \frac{\delta(x)}{x} = \frac{5}{\sqrt{Re_x}} \]
Fluid gets slowed down as $x \rightarrow$ increases; Hence, it displaces the potential flow in $y - direction$. The distance by which the external potential flow field is displaced outwards as a consequence of the decrease in velocity in the boundary layer is determined by

$$v_\infty \delta^* = \int_0^\infty (v_\infty - v_x) dy$$

decrease in volume flow due to BL.

The book by Kayes et al. mentions that “there is some ambiguity in speaking of the boundary layer thickness if what is meant is the region in which velocity changes from $v_\infty$ to 0”. $\delta^*$ is a measure of the displacement of the main stream resulting from the presence of the flat plate and its BL. The book by Schlitching attributes the “displacement” to the difference between the $y$-component of the velocities of BL and potential regime at the outer edge of the BL, which was not considered in calculations, but was considered for $x$-component: $y \text{ at } \delta \text{ or } y \rightarrow \infty$, $v_x = v_\infty$. Revert to calculation

$$\delta^* = \int_0^\infty \left(1 - \frac{v_x}{v_\infty}\right) dy$$

$$= \frac{\sqrt{v_x}}{v_\infty} \int_0^\infty (1 - f'(\eta)) d\eta = \frac{\sqrt{v_x}}{v_\infty} (\eta_1 - f(\eta_1)) = 1.72 \frac{\sqrt{v_x}}{v_\infty} \ll 5 \frac{\sqrt{v_x}}{v_\infty}$$

where, $\eta_1$ denotes point/location outside BL.

Thus, $\delta^* = 1.72 \frac{\sqrt{v_x}}{v_\infty}$; compare to $\delta = 5 \frac{\sqrt{v_x}}{v_\infty} \rightarrow \delta^* \approx 1/3 \delta$

‘$\delta^*$’ means $\frac{dp}{dx} \neq 0$ which was zero in potential flow and superimposed on BL because $\frac{dp}{dy} = 0$, as assumed in Blausius solution. Therefore, because of ‘displacement’, a new $\frac{dp}{dx}$ in potential flow (Bernoulli’s theorem) should be considered in BL theory/solution as a correction $\rightarrow 2^{nd}$ order BL.

**Skin Friction:** (Potential theory cannot predict skin friction/drag)-

$$D = b \int_0^l \tau_0 dx \quad (b \equiv \text{width of plate})$$

$$\tau_0(x) = \mu \frac{dv_x}{dy}\bigg|_{y=0} \quad \text{where } v_x = v_\infty f'(\eta)$$
\[ = \mu v_\infty \sqrt{\frac{v_\infty}{v_x}} f''(0) \quad (\tau = +\mu \frac{dv_x}{dy}) \text{ on plate} = 0.332\mu v_\infty \sqrt{\frac{v_\infty}{v_x}} \]

\[ D = b\mu 0.332 \frac{v_\infty^{3/2}}{\sqrt{v}} \int_0^l \frac{1}{\sqrt{x}} dx \]

\[ D = 2 \times 0.332 \times b v_\infty \sqrt{\mu l v_\infty} \rightarrow \text{No adjustable constant} \]

\[ C_D = \frac{\tau_o(x)}{\rho v_\infty^2} = 0.332 \sqrt{\frac{v}{v_\infty}} = 0.332 \sqrt{\frac{v}{Re_x}} \text{ (compare it with } C_D \text{ for creeping flow, calculated analytically!)} \]

**Momentum thickness** is also defined by slowing down of fluid:

\[ \rho v_\infty^2 \theta = \rho \int_0^\infty v_x (v_\infty - v_x) dy \]

\[ \theta = \int_0^\infty \frac{v_x}{v_\infty} (1 - \frac{v_x}{v_\infty}) dy = \sqrt{\frac{v_x}{v_\infty}} \int_0^\infty f' (1 - f') d\eta = 0.664 \sqrt{\frac{v_x}{v_\infty}} \]

Recall that Blasius solved BL equation using a similarity transform with

\[ \frac{dp}{dx} = 0: v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = -\frac{dp}{dx} \text{outerflow} + v \frac{\partial^2 v_x}{\partial y^2} \]

In many cases, \( \frac{dp}{dx} \neq 0 \) curved solid surface

**BL Separation:**

Flow past a sphere or cylinder shows such features.

\[ \Rightarrow 1f \frac{dp}{dx} \neq 0; \text{ it is difficult to solve NS in BL with the } v_x \frac{\partial v_x}{\partial x} \text{ non-linear term.} \]

\[ \Rightarrow \text{Same flow problems with } \frac{dp}{dx} \neq 0 \text{ have been solved assuming } \frac{dp}{dx} = e^x, \text{ but without similarity transform.} \]

\[ \Rightarrow \text{Falkner & Skin showed that if } V_\infty \approx x^m, \text{ then similarity transform solution is possible (} \eta \text{ exists).} \]

→ **Boundary layer theory** has been extensively studied using numerous methods including more popular von Karman momentum balance and Karman-Pohlhausen method. In the same context (BL), many different types of flow situations including boundary layer separation, flow past bluff bodies and blunt objects, positive pressure gradient, solid curvature effect, streamline bodies, air foil, movement of golf and cricket balls, unsteady-state flow, and flow instabilities, etc, have been studied in depth. The books authored by Schlitching, and also, Deen have a detailed coverage of some of these advanced topics related to hydrodynamics. We will skip these topics and instead move to the concentration and thermal boundary layers in the next lecture.
Consider diffusion only (Levich “Physicochemical Hydrodynamics”):

\[ \delta_m \left( \frac{v_x}{v_\infty} \approx 0.99 \right) \]

\[ \delta_c \left( \frac{C}{C_\infty} \approx 0.99 \right) \]

Consider two cases: \( Sc \approx 1000 \) (liquids) & \( \approx 1 \) (gases)

\[ \downarrow \frac{v}{D} \]

**Case 1:** \( \delta_m \gg \delta_c \) or \( v \gg D \) (liquids) (mass boundary layer is within momentum boundary layer)

Momentum transfer occurs over \( \delta_m \gg \delta_c \) (mass boundary layer is within momentum boundary layer)

**BL equation for species:**

\[ v_x \frac{\partial C}{\partial x} + v_y \frac{\partial C}{\partial y} = D \frac{\partial^2 C}{\partial y^2} + (\text{terms neglected}) \]

\[ \frac{\partial C}{\partial x} \approx \frac{C_\infty}{\delta_c} ; \quad \frac{\partial C}{\partial y} \approx \frac{\partial^2 C}{\partial x^2} \approx \frac{\partial^2 C}{\partial y^2} \approx \frac{C_\infty}{\delta_c^2} \]

\[ v_y \frac{\partial C}{\partial y} \approx v_y \frac{C_\infty}{\delta_c} \quad (y \approx \delta_c \text{ and not } \delta_m) \]

Recall \( v_y \) (near the plate) = \( \frac{1.33 v_\infty^{3/2} y^2}{16v^{1/2} x^{3/2}} \approx \frac{v y^2}{\delta_m^3} \) (see previous lectures)

Therefore, \( v_y \frac{\partial C}{\partial y} \approx \frac{v \delta_c^2 C_\infty}{\delta_m^3} \frac{\partial \delta_c}{\partial y^2} \) and \( D \frac{\partial^2 C}{\partial y^2} \approx D \frac{C_\infty}{\delta_c^2} \)

\[ v \frac{\delta_c}{\delta_m} C_\infty \approx D \frac{C_\infty}{\delta_c^2} \Rightarrow \left( \frac{\delta_c}{\delta_m} \right)^3 \approx \frac{1}{(v/D)} \]

Or \( \delta_c \approx \frac{\delta_m}{S_c^{1/3}} \) (Note: \( Sc \uparrow \) or \( \delta_m \gg \delta_c \))

**Similarly, \( \delta_T \) (heat transfer) \approx \frac{\delta_m}{Pr^{1/3}} \) (analogy with mass transfer)

\[ \delta_c \approx \left( \frac{Pr}{Sc} \right)^{1/3} \quad \text{or} \quad \delta_c \approx \delta_T \]

See last lectures:

\[ \frac{\delta_m}{x} \approx \left( \frac{v}{v_\infty x} \right)^{1/2} \]

\[ \frac{\delta_c}{x} \approx \left( \frac{v}{v_\infty x} \right)^{1/2} \left( \frac{D}{v} \right)^{1/3} \]
\[ \Rightarrow \delta_c \approx D \frac{1}{2} v \frac{x}{v_\infty} \]

If \( N = -D \frac{\partial C}{\partial y}, \) \( N \approx \frac{D(C_\infty - C_s)}{\delta_c(x)} \approx \frac{D(C_\infty - C_s)}{\frac{1}{2} \sqrt{\frac{1}{2} x^2}} \)

Or \( N \left( \text{flux, } \text{moles/cm}^2s \right) = \left( \frac{D^{2/3} v_\infty^{1/2}}{v_\infty^{1/2} x^{3/2}} \right) (C_\infty - C_s) \)

- \( k_m \) (mass transfer coefficient) \( \sim D^{3} v^{-\frac{1}{6}} v_\infty^{\frac{1}{3}} x^{-\frac{1}{2}} \) liquid – solid
- Compare to film theory \( k_m \sim D \) (SS, 1D, stagnant film)
- Compare to surface renewal theory \( k_m \sim D^{\frac{1}{2}} v_{\text{max}}^{\frac{1}{2}} x^{-\frac{1}{2}} \) (gas-liquid surface is renewed)

Case 2: Consider \( \delta_c \approx o(1) \) ⇒ gas

(momentum transfer \( \approx \) molecular transfer: \( \delta_m \approx \delta_c \))

Now \( y \ll \delta_m \): close to plate

Momentum equation:
\[ v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = n \frac{\partial^2 v_x}{\partial y^2} \]

Species Balance:
\[ v_x \frac{\partial C}{\partial x} + v_y \frac{\partial C}{\partial y} = D \frac{\partial^2 C}{\partial y^2} \]

Recall:
\[ v_x^* \frac{\partial v_x^*}{\partial x} + v_y^* \frac{\partial v_x^*}{\partial y^*} = n \frac{\partial^2 v_x^*}{\partial y^*^2} \] (momentum balance)
\[ v_x^* \frac{\partial C^*}{\partial x} + v_y^* \frac{\partial C^*}{\partial y^*} = \frac{\partial^2 C^*}{\partial y^*^2} \] (species balance)

(\( \text{Peclet no or ReSc is hidden as } Re \text{ in NS equation} \))

\( ReSc = Pe \approx o \left( \frac{1}{\delta^2 \delta_c} \right) \)

\( \delta_c \approx \frac{1}{\sqrt{ReSc}} \)

\( \frac{\delta_c}{\delta_m} \approx \frac{1}{\sqrt{ReSc}} \approx 1/\sqrt{Sc} \Rightarrow \text{gases } \sim 0(1) \)

Compare for liquids:
\[ \frac{\delta_c}{\delta_m} \approx \frac{1}{Sc \delta_c} \]

Thermal boundary layer: replace \( Sc \) by \( Pr \) \( \{ \text{liquids } Pr \approx 1000 \}
\( \text{gases } Pr \approx 1 \) and \( \delta_c \) by \( \delta_h \) (analogy between mass and heat transport). Similarly, \( k_m \) by \( h \) and \( Sh \) number by \( Nu \) number.
Turbulence: A feature of fluid flow at high Reynolds number

(1) Structure of turbulence
(2) Reynold’s mathematical description of turbulent flow.

- Laminar flow is characterized by streamlines; dye-test with digital photographs can be used to track the path of the particle, and streamlines can be plotted.
- Leave transience flow regime between laminar and turbulence, all flows which are not laminar are turbulent, and vice versa! Thus, fluid flow can be categorized in these two categories.
- Most of real world applications including industrial are based on turbulent flows.

Nature/characteristics of turbulence

(1) $Re$ is large ($Re > 2100$ for tubular flow)
(2) Irregularity in flow (dye test or visual or video can be used to check such feature)
(3) “Diffusivity” increases; thus mixing is high.
(4) Rotational
(5) Dissipation of heat/energy
(6) Inertial effects dominate the viscous effects
(7) Not a feature of fluids but of flow.
(8) Not amenable to mathematical analysis; rely heavily on models, theories, and experimental measurements. Turbulent flow can be mathematically perceived as an instability in flow, arising due to perturbation in laminar-turbulent flow regime. The prototype examples 1-12 all considered laminar flow and could be solved relatively easily. Situation here is different.
(9) The most closest pictorial or visual description of a turbulent flow could be “violent swirling” flow, termed “eddies” (not to be mixed up with streamlines having angular velocity ($v_0$) in the regular or common laminar flow).
(10) Yet, we are referring to continuum (and not molecular).

⇒ One approach is to model “smoothed” behaviour only ⇒ Reynold’s approach using time-averaged quantities (to be discussed in the next lecture)
⇒ Another approach is to model the fluctuations, but non-linearity in $NS$ theorem leads to “chaotic” behaviour which is extremely sensitive to initial conditions.

Mathematically describe turbulence:

Consider velocity fluctuations

$$
\bar{v} = \bar{v} + v' \quad ; \quad \bar{v}' = 0 \quad (averaged \ \text{wrt \ time}) \quad \Rightarrow \frac{(v')^2}{\bar{v}'} \neq 0
$$

If $\bar{v}' \neq 0$, then it is no good for analysis.
Homogeneous Turbulence: \( \sqrt{(v_x')^2} \) rms of fluctuation is constant over entire turbulence but \( \sqrt{(v_y')^2} \neq \sqrt{(v_z')^2} \).

\( \Rightarrow \) Isotropic turbulence is homogeneous turbulence with the addition of \( \sqrt{(v_x')^2} = \sqrt{(v_y')^2} = \sqrt{(v_z')^2} \).

(fluctuations in the direction of flow \( \approx \perp r \) to the flow)

Mathematic description of isotropic turbulence is possible. However, it exists only in the absence of mean velocity gradients, far from walls – which is not much of application! We are interested in the flow near the surface.

\( \Rightarrow \) Shear turbulence – very common: \( v_x'(x,t) \)

\( \Rightarrow \) Scale of turbulence – is determined by distance over which correlated motion exists, eg. One might look at the correlation tensor:

\[
Q_{ij}(\vec{r}) = \overline{v_i'(x)v_j'(x+r)} \neq 0
\]

\( \Rightarrow \) Intensity of turbulence: \( v_i^{(e)} = \sqrt{\overline{(v_i')^2}} / \bar{v}_i \);

Correlation:

What is the smallest eddy size possible? Smallest scale of turbulence?

Kolmogorov (1941) proposed Universal Equilibrium Theory. Suppose we have large eddies of length \( 'l_0' \) and velocity \( v_o = \left( \overline{v'^2} \right)^{\frac{1}{2}} \), with Reynolds number based on \( Re_o = \frac{v_o'l_o}{\nu} \gg 1 \).

In general, these eddies are unstable and break down to small eddies when subjected to a disturbance:

\[
\text{Length scale } l, v; \quad l_o \gg l_1 \gg l_e \gg \cdots \quad l_n \uparrow \quad \text{Re is approaching 1 (viscous term is becoming important)}
\]

Assume:

1. Characteristic time for an eddy is one turn over time.
2. Kinetic energy transfer rate:

\[
\epsilon_o = \frac{d}{dt} \left( \frac{1}{2} \overline{v'^2} \right) \approx \frac{v_o^2}{\epsilon} = \frac{v_o^2}{l_o/v_o} = \frac{v_o^2}{l_o} \quad \uparrow \quad \text{turnover time}
\]

Note: Taylor microscale:

\[
\epsilon = \frac{15\nu^2}{l_t^2} \quad v_t = \left( \overline{v'^2} \right)^{\frac{1}{2}}
\]
3. $\epsilon$ is independent of eddy size

Large eddy $\rightarrow$ Small eddy $\rightarrow$ Kolmogorov eddy (smallest sized eddy)

Viscous dissipation is same everywhere ($\epsilon_n = \frac{v_n^2}{l_n} = \frac{v_o^2}{l_o} = \epsilon_o$)

Ref. Book by Tennekes and Lumley

**Dimensional analysis:** Parameters determining small scale motion will depend on $\epsilon \ (cm^2/s^3)$ and $\nu \ (cm^2/s)$ (rate of dissipation & kinematic viscosity which is also a rate)

In (Kolmogorov eddy) $l_n = f(\epsilon, \nu) \approx \left(\frac{\nu^3}{\epsilon}\right)^{1/4}$; check dimensions

constant parameters

$v_n = (\nu \epsilon)^{1/4}; \tau_n = (\nu \epsilon)^{1/2}; \text{Re}_n = \frac{l_n v_n}{\nu} \approx 1$ (similarly, define the other variables)

Local Reynolds number, $\text{Re}_n = \frac{l_n v_n}{\nu} = \frac{(\nu^3/\epsilon)^{1/4}(\nu \epsilon)^{1/4}}{\nu} = 1$ (hence proven!)

$$l_n = \left(\frac{\nu^3}{\epsilon}\right)^{1/4} = \left(\frac{\nu^3}{\nu_o^3}\right)^{1/4} = \left(\frac{\nu^3}{\nu_o^3}\right)^{1/4}$$

$$\Rightarrow \frac{l_n}{l_o} = \left(\frac{\text{smallest}}{\text{largest}}\right) = \left(\frac{\nu^3}{\nu_o^3}\right)^{1/4} \frac{1}{l_o} = \left(\frac{\nu^3}{\nu_o^3}\right)^{1/4} = \frac{1}{\text{Re}_o^{3/4}}$$

**Kolmogorov Scale**

$$\frac{l_n}{l_o} = \frac{1}{\text{Re}_o^{3/4}}; \frac{v_n}{l_o} = \frac{1}{\text{Re}_o^{3/4}}; \frac{\tau_n}{l_o} = \frac{1}{\text{Re}_o^{1/2}}$$

(check these equalities)

Ex. $\text{Re}_n = \frac{\rho l_n v_n}{\mu} = 1 \Rightarrow v_n = \frac{\mu}{\rho l_n} ; v_o = \frac{\mu}{\rho l_o} \text{Re}_o \quad (\text{Re}_o \neq 1)$

Therefore, $\frac{v_n}{v_o} = \left(\frac{l_o}{l_n}\right) \frac{1}{\text{Re}_o} = \text{Re}_o^{3/4} \text{Re}_o^{-1} = \text{Re}_o^{-1/4}$

$$\Rightarrow \frac{v_n}{v_o} = \frac{1}{\text{Re}_o^{1/4}}$$

Stack:

Jet:

$$\frac{l_n}{l_o} = \frac{\text{Re}_o^{-3/4}}{\text{Re}_o^{-1/2}}$$

based on wind velocity
Lecture #22

Turbulent flow: Some mathematical analysis

**Reynold's decomposition:** \( \mathbf{v} = \overline{\mathbf{v}} + \mathbf{v}' \) *(fluctuations, small time - scale)*

\( \mathbf{v}' \) is defined such that \( \overline{\mathbf{v}'} = 0 \)

**Continuity:** \( \nabla.(\overline{\mathbf{v}} + \mathbf{v}') = 0 \) (all notions are vector) Take time-average \( \nabla.\overline{\mathbf{v}} = 0 \)

**NS:** \( \rho \frac{\partial}{\partial t} (\overline{\mathbf{v}} + \mathbf{v}') + [(\overline{\mathbf{v}} + \mathbf{v}'), \nabla](\overline{\mathbf{v}} + \mathbf{v}') = -\nabla(\overline{\rho} + \mathbf{p}') + \mu \nabla^2 (\overline{\mathbf{v}} + \mathbf{v}') \)

Recall: \( \nabla.(\overline{\mathbf{v}} \mathbf{v}') = (\overline{\mathbf{v}} \nabla)\overline{\mathbf{v}} + \overline{\mathbf{v}} (\nabla\overline{\mathbf{v}}) \)

Therefore, \( [(\overline{\mathbf{v}} + \mathbf{v}'), \nabla](\overline{\mathbf{v}} + \mathbf{v}') = \nabla.[(\overline{\mathbf{v}} + \mathbf{v}')(\overline{\mathbf{v}} + \mathbf{v}')] \)

\[
\begin{align*}
= \nabla \left( \begin{array}{ccc}
(\overline{\mathbf{v}}_x + v'_x)^2 & (\overline{\mathbf{v}}_x + v'_x)(\overline{\mathbf{v}}_y + v'_y) & (\overline{\mathbf{v}}_x + v'_x)(\overline{\mathbf{v}}_z + v'_z) \\
(\overline{\mathbf{v}}_x + v'_x)(\overline{\mathbf{v}}_y + v'_y) & (\overline{\mathbf{v}}_y + v'_y)^2 & (\overline{\mathbf{v}}_y + v'_y)(\overline{\mathbf{v}}_z + v'_z) \\
(\overline{\mathbf{v}}_x + v'_x)(\overline{\mathbf{v}}_z + v'_z) & (\overline{\mathbf{v}}_y + v'_y)(\overline{\mathbf{v}}_z + v'_z) & (\overline{\mathbf{v}}_z + v'_z)^2
\end{array} \right)
\end{align*}
\]

Noting that \( \overline{v_x'^2} + 2\overline{v_x'v_z'} + \overline{v_z'^2} = \overline{v_x'^2} + \overline{v_z'^2} \), and similarly, the time averaged \( \overline{\mathbf{p}'} = \overline{\mathbf{v}'} = 0 \), take the time average of the entire NS equation:

\[
\rho \frac{\partial\overline{\mathbf{v}}}{\partial t} + \nabla.\overline{\mathbf{v}\overline{\mathbf{v}}} + \nabla\overline{\mathbf{v}^2} = -\nabla\overline{\rho} + \mu \nabla^2 \overline{\mathbf{v}} \quad (\text{Note: } \overline{\mathbf{v}^2} \neq 0; \overline{\mathbf{v}'} = 0)
\]

where, \( \overline{\mathbf{v}^2} = \left( \begin{array}{ccc}
\overline{v_x'^2} & \overline{v_x'v_y'} & \overline{v_x'v_z'} \\
\overline{v_x'v_y'} & \overline{v_y'^2} & \overline{v_y'v_z'} \\
\overline{v_x'v_z'} & \overline{v_y'v_z'} & \overline{v_z'^2}
\end{array} \right) \) or \( \rho \overline{\mathbf{v}^2} \equiv \text{Reynold stresses } \left( \frac{N}{m^2} \right) \)

\[
\rho \frac{\partial\overline{\mathbf{v}}}{\partial t} = -\nabla\overline{\rho} - \nabla.\mathbf{t} - \nabla\overline{\rho\mathbf{v}^2} \quad (\text{Note that an extra term has arisen on time-averaging})
\]
Thus, \( \nabla \rho \vec{v}^2 = \nabla \cdot \tau \) (define shear stress in turbulent flow)

\[
\frac{D \vec{v}}{Dt} = -\nabla p - \nabla \cdot \tau - \nabla \cdot \tau^t
\]

\( \tau^t = -\rho \vec{v}' \vec{v}' \); an extra source of momentum generation

Component-wise:

\[
\rho \left( \frac{\partial \vec{v}_x}{\partial t} + \vec{v}_x \frac{\partial \vec{v}_x}{\partial x} + \vec{v}_y \frac{\partial \vec{v}_x}{\partial y} + \vec{v}_z \frac{\partial \vec{v}_x}{\partial z} \right)
\]

\[
- \frac{\partial p}{\partial x} + \mu \left( \frac{\partial^2 \vec{v}_x}{\partial x^2} + \frac{\partial^2 \vec{v}_x}{\partial y^2} + \frac{\partial^2 \vec{v}_x}{\partial z^2} \right) - \rho \left( \frac{\partial}{\partial x} \left( \vec{v}_x' \vec{v}_x' \right) + \frac{\partial}{\partial y} \left( \vec{v}_x' \vec{v}_y' \right) + \frac{\partial}{\partial z} \left( \vec{v}_x' \vec{v}_z' \right) \right)
\]

⇒ See the difference between the NS equation for Laminar flow and turbulent flow – an extra term arising on the RHS which describes an extra source (rate) of momentum generation or transport attributed to ‘eddies’ formation/generation, apart from the time-averaged quantities for all variables \( \vec{v} \) and \( \bar{p} \). The mathematical analysis is consistent with the experimental (photographic) observation of the flow structure of the boundary layer at the plate surface. Even in turbulent boundary layer, there is a region close to the surface that resembles the ‘laminar’ boundary layer, hence called the laminar sub layer or viscous layer, discussed later.
**Boussinesq model**: \( \tau^t = -\rho \overline{v v^t} = -\mu^t \frac{\partial \overline{v_x}}{\partial y} \) analogous to \( \tau^l = -\mu \frac{\partial \overline{v_x}}{\partial y} \) (1D)

(\( \mu^t \) is eddy viscosity; property of flow. It is not a physical property of fluid)

So that \( \tau^{total} = (\nu^l + \nu^t) \frac{\partial \overline{v_x}}{\partial y} \) \( (\nu^t \gg \nu^l) \)

All three eddy viscosity components in the \( x - direction \) are written as

\[ \overline{r_{xx}} = -\rho \overline{(v_x^t v_x^t)} = -\mu_{xx} \frac{\partial \overline{v_x}}{\partial x} \]

\[ \overline{r_{yx}} = -\rho \overline{(v_y^t v_x^t)} = -\mu_{yx} \frac{\partial \overline{v_x}}{\partial y} \]

\[ \overline{r_{zx}} = -\rho \overline{(v_z^t v_x^t)} = -\mu_{zx} \frac{\partial \overline{v_x}}{\partial z} \]

Similarly, \( J_{h}^t = -\alpha^t \frac{\partial (\rho C_p \overline{v_x^t})}{\partial y} \) : energy (rate) carried by eddy in \( y \) direction

\[ J_{m}^t = -D^t \frac{\partial \overline{C}}{\partial y} = -\overline{(v_y^t C^t)} \) : concentration (rate) carried by eddy in \( y - direction \)

Also, \( Pr^t = \frac{\nu^t}{a^t} \); \( Sc^t = \frac{\nu^t}{D^t} \) (analogy with the laminar cases)

Thus, energy and species balance equations derived for laminar flow are also time-averaged for turbulent flows, resulting in an extra source term for eddy transport for energy/species:

\[ \rho C_p \frac{D T}{D t} = \nabla (\alpha^t + \alpha^t) \frac{\partial (\rho C_p \overline{v_x^t})}{\partial y} \]

\[ \frac{D \overline{C}}{D t} = \nabla (D^t + D^t) \frac{\partial \overline{C}}{\partial y} \]

where, time-averaged quantities are defined: \( T = \overline{T} + T' \) and \( C = \overline{C} + C' \), such that \( \overline{T'} = 0, \overline{C'} = 0 \), and there is an extra source term for energy and concentration in the conservation equations.

**k-ε model** (two parameters model):

\( k = \frac{\nu^2}{2} \); \( \epsilon = dissipation \ of \ k \); by dimensional analysis \( \nu^t = c \frac{k^2}{\epsilon} \) \( (c = 0.009) \)

**Prandtl’s Mixing Layer Theory**:

- **Reynold stresses** expressed in terms of the mean velocity by defining a characteristic length scale of the turbulences, called as the **Prandtl’s mixing length** (\( l \)), which is the length of the travel of an eddy before mixing itself with a neighboring eddy; a concept/approach analogous to ‘\( \lambda \)’ (mean free path) used in the kinetic theory.

\[
\text{Difference in velocities:}
\begin{align*}
\Delta \overline{V}_{x,1} &= \overline{V}_x(y + l) - \overline{V}_x(y - l) &= l \left( \frac{\partial \overline{V}_x}{\partial y} \right)_{1} \\
\Delta \overline{V}_{x,2} &= \overline{V}_x(y + l) - \overline{V}_x(y) &= l \left( \frac{\partial \overline{V}_x}{\partial y} \right)_{2}
\end{align*}
\]

Therefore, \( |V_x'| = \frac{1}{2} (|\Delta \overline{V}_x|_1 + |\Delta \overline{V}_x|_2) = l \left( \frac{\partial \overline{V}_x}{\partial y} \right) \) (definition for fluctuating velocity component)

Assuming isotropic:

\[ |V_y'| = c |V_x'| = c l \left( \frac{\partial \overline{V}_x}{\partial y} \right) \rightarrow \textbf{Reynold stresses} \ ho \overline{V_x^t V_y'} = -\rho l^2 \left( \frac{\partial \overline{V}_x}{\partial y} \right)^2 \]

\[ \tau_t \equiv -\rho l^2 \left| \frac{\partial \overline{V}_x}{\partial y} \right| \frac{\partial \overline{V}_x}{\partial y} \] (easy to work, one parameter (\( l \) model)
- There are other theories: Taylor Vorticity Transport Theory, Von-Karman’s similarity Hypothesis

**Example: “The law of the wall” (BSL P162, old edition)**

\[
\frac{\rho \mathbf{V}}{d\ell} = -\nabla p - \nabla \cdot \left( \tau^l + \tau^t \right) + \rho \mathbf{g}
\]

\[
0 = -\frac{d \bar{p}}{dz} - \frac{1}{r} \frac{d}{dr} r \left( \tau^l_r + \tau^t_r \right)
\]

**BCs:**
\[
\begin{align*}
\tau^l &= 0 \quad \text{at } r = 0 \quad \text{(symmetric)} \\
\tau^t &= 0 \quad \text{at } r = 0 \quad \text{(symmetric)} \quad \text{(Note } \tau^t \text{ is also 0; } r = R) \\
\end{align*}
\]

Integrate, \( \tau^l + \tau^t = -\frac{d \bar{p}}{dz} \left( \frac{d \mathbf{V}}{dr} \right)^2 \)

At the wall \( \tau_{total,w} = \tau_o = -\frac{d \bar{p}}{dz} \) laminar turbulent components

\( \tau^l + \tau^t = \tau_o \frac{r}{R} \) (1) (\( \tau_o \) is the wall shear stress)

\[
\tau^l_r = -\rho \mathbf{l}^2 \left| \frac{d \mathbf{V}}{dr} \right| \frac{d \mathbf{V}}{dr} \quad \text{(turbulent flow, away from the wall)}
\]

*let l = k.s* (An eddy cannot be larger than its distance from the walls in a thin BL)*

Also, \( s = R - r \) or \( ds = -dr \)

Therefore, \( \tau_r^l = \rho l^2 s^2 \left| \frac{d \mathbf{V}}{dr} \right| \frac{d \mathbf{V}}{dr} = \tau_o \frac{R - s}{R} \) from (1) (neglecting ‘laminar’/viscous sub-layer; \( \tau^t \gg \tau^l \) far from wall)

Also, \( \frac{s}{R} \ll 1 \) close to wall \( \approx \tau_o(1 - 0) = \tau_o \)

*(There is a contradiction in mathematical analysis; physically, Prandtl theory is non-defensible)*

\[
\text{Or } \frac{d \mathbf{V}}{ds} = \pm \frac{1}{k_1 s} \sqrt{\frac{\tau_o}{\rho}} \tag{2}
\]

Let us define **friction velocity**, \( V^+ = \sqrt{\frac{\tau_o}{\rho}} \)

Plug in outside buffer zone and integrate, \( \bar{V}_z = \frac{V^+}{k_1} \ln s + c_1 \)

\[
\bar{V}_z - \bar{V}_{z1} = \frac{V^+}{k_1} \ln \left( \frac{s}{s_1} \right)
\]

Define, \( V^+ = \frac{g}{V^*}, s^* = \frac{s V^* \rho}{\mu} \) (dimensionless #); Therefore, \( V^+ - V_{z1}^+ = \frac{1}{k_1} \ln \left( \frac{s^*}{s_{11}^*} \right) \)

(not close to wall/not close to center either in turbulent core)
For $R_e > 20,000$ \[ V^+ = 3.8 + \frac{1}{0.36} \ln s^+ ; \quad s^+ > 26 \text{ (experimental measurements)} \]

In laminar sub-layer $V^+ = s^+$ (velocity profile is linear, same as in the laminar flow case). Using these equations, a universal velocity profile is plotted for tubular turbulent flow, including the buffer layer (see BSL for the universal velocity profile plot).

**Takeaway message:** There is a viscous sub-layer near the tube wall even in the turbulent flow, which is consistent with the BL postulate that at least one viscous term must be retained in the BL equation, no matter how high is Reynolds number or how small the fluid viscosity is. As we move away from the surface, the fluctuating velocity components increase rapidly and the Reynolds stresses are much larger than the viscous stresses.

We conclude the 2nd part of the course and take up some prototype examples in the next lectures. It is clear that apart from the first introductory lectures 1-7 covered on the basics of transport phenomena for an incompressible Newtonian fluid, mainly setting up conservation equations, the next course materials can be broadly categorized into two types of flows: one at low Reynolds numbers and the other at high Reynolds numbers. A schematic representation of the different situations covered in this course can be described as follows:

**Transport Phenomena (momentum transport?)**

### Low Reynolds number
- Laminar or streamline flows
- Viscous term in the conservation equation is retained.
- In some cases, inertial term may be neglected.
- Common examples are Stoke’s first problem
  - Start-up tubular flow, Poiseuille’s flow,
  - Nusselt and Graetz-Nusselt problems,
  - Free convection in confined flow, Mass transport considering diffusion in a stagnant fluid, Surface renewal theory,
  - Creeping flow or Stoke’s law.
- Often exact (analytical) solutions

### High Reynolds number

**Potential theory**
- Potential flow, inviscid fluid, $\mu \to 0$, irrotational flow, $\nabla \cdot \tau = 0$, $\nabla \times \vec{V} = 0$, Euler equation, Bernoulli’s equation, source/sink, doublet, vortex, D’Alembert’s paradox, flow away from the solid surface.

**Boundary layer theory**: Prandtl’s boundary layer, drag, Blasius solution, boundary layer thickness, momentum displacement, drag coefficient, skin friction, thermal and mass boundary layers, heat and mass transfer coefficients, bluff bodies, boundary layer separation, higher order boundary layers, streamline bodies, airfoil.

**Turbulent flow (feature of fluid-flow)**
- Fluctuations in velocity, irregularities in flow, eddies, wakes, large mixing rate, time-averaged quantities, Reynolds stresses, eddy diffusivities, Prandtl’s mixing length, universal velocity profiles, Law of the wall.

**Keywords (buzz):**
- Potential theory
- Boundary layer theory
- Turbulent flow
Prototype example 13: Reduction of BL convection – diffusion equation (for a flow over solid surface) to heat conduction (Levich: Physicochemical Hydrodynamics)

Emphasis is on BL: Liquids ($Sc$ is high ~ 1000)

\[ \nu_x \frac{\partial c}{\partial x} + \nu_y \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2} : \text{concentration BL} \]

**Note:** \( \frac{\partial^2 c}{\partial x^2} \ll \frac{\partial^2 c}{\partial y^2} \) and \( \nu_y \ll \nu_x \) but \( \frac{\partial c}{\partial y} \gg \frac{\partial c}{\partial x} \)

\[ \frac{\partial \nu_x}{\partial x} + \frac{\partial \nu_y}{\partial y} = 0 : \text{Continuity} \]

Replace independent variable \((x, y)\) by \((x, \psi)\), where \(\psi = \psi(x, y)\)

\[ \Rightarrow \left. \frac{\partial c(x, y)}{\partial x} \right|_y = \left( \frac{\partial c}{\partial x} \right)_\psi + \left( \frac{\partial c}{\partial \psi} \right)_x \frac{\partial \psi}{\partial x} = \left( \frac{\partial c}{\partial x} \right)_\psi - \left( \frac{\partial c}{\partial \psi} \right)_x \nu_y \]

(Recall: \(\nu_x = \frac{\partial \psi}{\partial y}, \nu_y = -\frac{\partial \psi}{\partial x}\))

\[ \frac{\partial c}{\partial y} = \left. \frac{\partial c}{\partial \psi} \right|_x \frac{\partial \psi}{\partial y} = v_x \left. \frac{\partial c}{\partial \psi} \right|_x \]

\[ \frac{\partial^2 c(x, y)}{\partial y^2} = \frac{\partial \psi}{\partial y} \left. \frac{\partial}{\partial \psi} \left( v_x \frac{\partial c}{\partial \psi} \right) \right|_x = v_x \frac{\partial}{\partial \psi} \left( v_x \frac{\partial c}{\partial \psi} \right) \]

Substitute in BL equation:

\[ \nu_x \left( \frac{\partial c}{\partial \psi} \right)_x - \nu_x v_x \left. \frac{\partial c}{\partial \psi} \right|_x + v_x \nu_y \left. \frac{\partial c}{\partial \psi} \right|_x = D v_x \frac{\partial}{\partial \psi} \left( v_x \frac{\partial c}{\partial \psi} \right) \]

**BCs.**

\[ \begin{align*}
C &= C_\infty \quad \psi \to \infty \quad (1) \\
C &= 0 \quad \psi \to 0 \quad (2) \\
C &= \text{finite} \quad x \to 0 \quad (3)
\end{align*} \]

**Note:** BC. 2 implies \(\psi = 0\) or \(v_x = v_y = 0\) at \(y = 0\) \((No - slip \ condition)\)

BC. 3 implies that 'C' has no singularity at the entrance of the fluid over the flat surface

\[ \left\{ \begin{array}{c}
\frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( K(x, t) \frac{\partial T}{\partial x} \right) \\
(2^{nd} \text{law of Fourier's heat equation}) \end{array} \right\} \]

See the book by Carslaw and Jaeger

Let us revert to diffusion equation for the flow over a surface, and pay attention to the region close to the surface where concentration changes within the BL.
Recall the hydrodynamic BL solutions of Blasius:

\[ v_x = \frac{v_o y}{\delta_m} ; \quad v_y = \frac{v y^2}{\delta_m^3} \] (close to plate)

Also, for small values of \( \psi \):

\[
\begin{align*}
\psi &= \sqrt{v v_0 x} f'(\eta) \\
\eta &= \frac{v_o}{v x y}
\end{align*}
\]

Also, Blasius series:

\[
f = \frac{\psi}{\sqrt{v v_0 x}} = \alpha \frac{\eta^2}{2} + \ldots
\]

\[
f' = \alpha \eta \Rightarrow v_x = \frac{1}{2} v_o \alpha \eta = \frac{1}{2} v_o \alpha \sqrt{\frac{2 \psi}{\alpha} (v v_0 x)^{-1/4}}
\]

**Diffusion equation:**

\[
\frac{\partial C}{\partial x} \bigg|_\psi = D \frac{\partial}{\partial \psi} \left( \frac{1}{2} v_o \alpha \sqrt{\frac{2 \psi}{\alpha}} (v v_0 x)^{-1/4} \frac{\partial C}{\partial \psi} \right) \quad (v_x \text{ is repalced})
\]

\[
= D \frac{1}{2} v_o \alpha \sqrt{\frac{2}{\alpha}} (v v_0 x)^{-1/4} \frac{\partial}{\partial \psi} \left( \psi^{1/2} \frac{\partial C}{\partial \psi} \right)
\]

Therefore,

\[
\frac{1}{x^4} \frac{\partial C}{\partial x} \bigg|_\psi = \beta \frac{\partial}{\partial \psi} (\sqrt{\psi} \frac{\partial C}{\partial \psi}) \quad \text{where, \( \beta = \frac{D (\alpha/2)^{1/2} v_o^{3/4}}{v^{1/4}} \)}
\]

**Momentum**

\[ v_o \]

\[ C_o \]

\[ \delta_m \]

\[ \psi \]

\[ v_x \]

\[ v_y \]

**Concentration**

\[ \delta_c \ll \delta_m \text{ Sc } \uparrow \uparrow \]

BCs. \( C = C_o \quad \psi \rightarrow \infty \)

\( C = 0 \quad \psi \rightarrow 0 \)

\( C = C_o \quad x \rightarrow 0 \)

(Note: Semi-infinite domain & one BC on \( x \) collapses with the other BC on \( \psi \))

- Similarity Transform (or combination of variable)

\[
\eta' = \text{another } \eta \, ? = \frac{1}{\psi^2} \left( \frac{\alpha}{2} \right)^{1/2} (v v_0 x)^{1/4}
\]

But, BCs are different

\[
\eta' = \eta'(\psi, x)
\]
\[
\frac{\partial C}{\partial x} = \frac{\partial C}{\partial \eta} \frac{\partial \eta}{\partial x} = -\frac{\psi^{1/2}}{4x^{3/4}} \left( \frac{\alpha/2}{(\nu v_o)^{1/4}} \right) \frac{1}{d\eta} \frac{dC}{d\eta} \\
\frac{\partial C}{\partial \psi} = \frac{\partial C}{\partial \eta} \frac{\partial \eta}{\partial \psi} = \frac{1}{2} x^{1/4} \psi^{1/2} \left( \frac{\alpha/2}{(\nu v_o)^{1/4}} \right) \frac{1}{d\eta} \frac{dC}{d\eta}
\]

On substitution,
\[
\frac{d^2 C}{d\eta^2} + \frac{\alpha v}{2 D \eta^2} \frac{dC}{d\eta} = 0
\]

Integration,
\[
C = C_1 \int_0^\eta \exp \left( -\frac{\alpha v}{2 D} \frac{z^3}{3} \right) dz + C_2
\]

Some algebra and BC fitting:
\[
C(x, y) = C_1 \int_0^{\eta_0} \frac{\nu_0 x}{v} \exp(-0.22 Sc z^3) dz \\
\int_0^\infty \exp(-0.22 Sc z^3) dz = \frac{\int_0^\infty e^{-t^3/3} dt}{(0.22 Sc)^{1/3}} \approx \frac{1}{(0.22 Sc)^{1/3}} \approx 0.89
\]

\[
C(x, y) = \frac{(0.22 Sc)^{1/3} C_1}{0.89} \int_0^{\eta_0} \frac{\nu_0 x z^3}{v x} \exp(-0.22 Sc z^3) dz
\]

**Graphical Solution**:

For a given value of \(x\), the concentration increases rapidly with increasing \(y\), and attains, at a distance \(\delta_c\) from the plate, a value that is almost (99%) equal to the concentration \(C_o\) in the bulk of the liquid, where
\[
\delta_c = 3 \left( \frac{D}{v} \right)^{1/3} \frac{\nu x}{\nu_o}
\]

**Flux (mass transfer)** \(J_m = D \left( \frac{\partial C}{\partial y} \right) \bigg|_{y=0}\) (moles/s-cm²)
\[
J_m = \frac{Dc_o(0.22 Sc)^{1/3}}{1.78} \frac{\nu_o}{\nu x} \frac{v x}{v_o}
\]
\[
J_m = 0.34 \frac{Dc_o(0.22 Sc)^{1/3}}{1.78} \frac{v x}{v_o} \left( \frac{v}{D} \right)^{1/3} \quad (\text{Note } \frac{v}{D} = Sc, \; Re_x = \frac{v o x}{v})
\]
\[ \approx D \frac{c_o}{\delta_c} \text{ (gradient is linear near the plate): from here, mass transfer coefficient can also be estimated)} \]

Therefore, \( \delta_c = \frac{D c_o J_m}{3} \left( \frac{D}{V} \right)^{\frac{1}{3}} \sqrt{\frac{v}{v_o}} = 0.6 \left( \frac{D}{V} \right)^{\frac{1}{3}} \delta_m \) (same as before)

\[ \left( \delta_m = \frac{5x}{\sqrt{Re_x}} \right) \]

\[ \Rightarrow \text{Assumptions in derivation: (1) } Re \gg 1 \text{ (2) } Sc \gg 1 \text{ or } \delta_c \ll \delta_m \]

\[ \Rightarrow \text{Total amount diffusing to the plate surface can be calculated by integrating:} \]

\[ W_{total} \text{ (moles/s)} = \int J_m dx. b \text{ (moles/s)} \]

\[ = 0.68 D c_o b (Sc)^{\frac{1}{3}} (Re)^{\frac{1}{2}} \quad (b \equiv \text{width of plate}) \]

\[ (Re = \frac{v_o L}{v}) \quad (L \equiv \text{length of the plate}) \]

**Prototype example 14: Flow over a plate with uniform suction**

Consider the flow of an incompressible fluid over a plate with uniform suction, often used to prevent or delay boundary layer separation, or simply, reduce drag. Such situation (negative y-component velocity) may also be prevalent in a flow over a porous surface including membranes, at low Reynolds number. In either case, the amount of fluid removed by suction is small compared to the free stream velocity \( U_\infty \). This does not mean that it can be totally neglected. Write the boundary layer equations for this flow. What are the boundary conditions? What is the difference between this problem and the flow over a flat plate without suction? A simple exact solution can be obtained for the case in which the velocity in the direction of flow is independent of length. The suction velocity must be of such a magnitude as to make this assumption correct. Assume steady state and solve for the normally defined boundary layer thickness.
• Free stream velocity $U_\infty$
• Due to suction at plate, the velocity in $y$—direction is negative as fluid is being constantly removed with the suction velocity, $v_o$.

**Momentum boundary layer equation:**

1) $\frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = -\frac{1}{\rho} \frac{dp}{dx} + \nu \frac{\partial^2 v_x}{\partial x^2} + \nu \frac{\partial^2 v_x}{\partial y^2}$ (x—direction momentum)
2) $\frac{\partial p}{\partial y} = 0$ (y—direction momentum)
3) Continuity: $\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0$

**BCs:**

<table>
<thead>
<tr>
<th>$v_x$</th>
<th>$v_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_x = U_\infty$</td>
<td>$v_y = -v_o$</td>
</tr>
<tr>
<td>$v_x = 0$</td>
<td>$v_y = 0$</td>
</tr>
<tr>
<td>$v_y = 0$</td>
<td>$v_x = 0$</td>
</tr>
<tr>
<td>$v_y \to \infty$</td>
<td>$v_x \to \infty$</td>
</tr>
</tbody>
</table>

**Exact solution:**

**Assumptions:** Steady state: $\frac{\partial v_x}{\partial t} = 0$ (1)

Flow over flat plate (semi-infinite zone) $\frac{dp}{dx} = 0$ (2)

Velocity in the direction of flow is independent of length: $\frac{\partial v_x}{\partial x} \sim 0$ (3)

(Note that the last term was expectedly non-zero in the Prandtl BL; here suction velocity mitigates the slowing down of the fluid in x-direction)

**Continuity:** $\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0$

\[ \frac{\partial v_y}{\partial y} = 0 \Rightarrow v_y \text{ is constant along } y — \text{ direction} \]

$\Rightarrow \boxed{v_y = -v_o}$ (close to plate)

**Motion:** $v_y \frac{\partial v_x}{\partial y} = \nu \frac{\partial^2 v_x}{\partial y^2}$

$\Rightarrow -v_o \frac{\partial v_x}{\partial y} = \nu \frac{\partial^2 v_x}{\partial y^2}$

Put $\frac{\partial v_x}{\partial y} = z$

$-v_o z = \nu \frac{\partial z}{\partial y} \Rightarrow z = A e^{-\frac{v_o y}{\nu}}$

$\Rightarrow \frac{\partial v}{\partial y} = A e^{-\frac{v_o y}{\nu}}$
\[ v_x = A' e^{-\frac{y_0 x}{v}} + B \]

\( y = 0, \quad v_x = 0 \Rightarrow B = -A' \)

\( y = \infty, \quad v_x = U_\infty \Rightarrow B = U_\infty \)

\[ v_x = U_\infty \left( 1 - e^{-\frac{y_0 y}{v}} \right) \quad \text{(close to plate)} \]

**Boundary Layer Theory:** \( v_x = 0.99 \ U_\infty \) at \( y = \delta_m \)

\[ \Rightarrow 0.99 \ U_\infty = U_\infty \left( 1 - e^{-\left(\frac{y_0}{v}\right) \delta_m} \right) \]

\[ e^{-\left(\frac{y_0}{v}\right) \delta_m} = 1 - 0.99 = 0.01 \]

Or \( \left(\frac{y_0}{v}\right) \delta_m = 4.6 \Rightarrow \frac{\delta_m}{\nu} = \frac{4.6v}{\nu_0} : \text{Boundary layer thickness is constant in the case of suction.} \)

Compare with \( \delta_m (\text{without suction}) = \frac{5x}{\sqrt{Re_x}} = 5 \sqrt{\frac{xv}{U_\infty}} \)

**Diffusion boundary layer thickness (High or Low Sc)**

\[ v_x \frac{\partial C}{\partial x} + v_y \frac{\partial C}{\partial y} = D \frac{\partial^2 C}{\partial y^2} + D \frac{\partial^2 C}{\partial x^2} \]

\[ \frac{\partial C}{\partial x} + \frac{v_0}{\nu} \frac{\partial C}{\partial y} = D \frac{\partial^2 C}{\partial y^2} \]

\[ \left[ v_0 \frac{\partial C}{\partial y} \right] = \left[ D \frac{\partial^2 C}{\partial y^2} \right] \Rightarrow \frac{v_0 C_\infty}{\delta_C} = D \frac{C_\infty}{\delta_C^2} \]

Therefore, \( \delta_C = D/v_0 \)

Or, \( \delta_C = 0.217 \frac{D}{v} \delta_m \quad \left( \delta_m = \frac{4.6v}{\nu_0} \right) \)

\[ = 0.217 \ Sc^{-1} \delta_m \]

\[ \delta_C \approx \frac{\delta_m}{Sc} \quad \text{Compare} \quad \left\{ \begin{array}{l} \delta_C \approx \frac{\delta_m}{\sqrt{Sc}} \quad \text{for liquids} \quad \text{Sc} \uparrow \uparrow \quad \text{without suction} \\ \approx \frac{\delta_m}{\sqrt{Sc}} \quad \text{for gases} \quad \text{Sc} \downarrow \downarrow \end{array} \right. \]

Since, \( v_y \) is same everywhere in flow, net suction \( \delta_C \) thickness is uniform at high or low Sc.

Similarly, \( \delta_{thermal} \approx \frac{\delta_m}{Pr} \). Once you have an estimate for boundary layer thicknesses, mass or heat transfer coefficients can be calculated or estimated: \( k_m \approx D/\delta_m \) and \( h \approx k/\delta_h \).
Prototype example 15: Diffusion to free falling solid particles (Levich)

\[ Re = \frac{vd\rho}{\nu} \ll 1 \] : Creeping flow (Stoke’s law is applicable). However, note that momentum BL does not exist in this case, and therefore, the BL theory is not valid. Yet is it possible that the concentration BL exists even though \( Re < 1 \)? Yes, if \( Pe_m \gg 1 \) or \( Sc \gg 1 \). So, we are discussing liquids.

\[
\begin{align*}
S_	ext{SS}, \\
\frac{\partial C}{\partial z} = 0
\end{align*}
\]

\[ BL \text{ only for concentration} \]
\[ (\delta_c \text{ only and no } \delta_m) \]

Concentration diffusion equation:

\[

\begin{align*}
& v_r \frac{\partial C}{\partial r} + v_\theta \frac{\partial C}{\partial \theta} = D \left( \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) + \left\{ \begin{array}{l}
\text{No } \phi \text{ -- dependence term or angular term}
\end{array} \right.
\end{align*}
\]

\[ \Rightarrow \text{velocity profiles should be superimposed from hydrodynamics:} \]

Recall creeping flow (See BSL or any other book on TP: Flow past a sphere at low Re < 1)

NS equation using stream function: \( \nu \nabla^2 \psi = 0 \) (from \( \mu \nabla^2 \vec{V} = 0 \) by retaining only viscous term only, as inertial term is negligible; \( Re \to 0 \) or \( \ll 1 \))

In spherical co-ordinates,

\[
\left[ \frac{\partial^2}{\partial r^2} + \frac{\sin \theta}{r^2} \frac{\partial}{\partial \theta} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \right) \right]^2 \psi = 0 \quad (\psi = \psi(r, \theta)) \text{ and } \nabla \cdot \vec{V} = 0
\]

BC 1: \( r = R \quad v_r = \frac{1}{r^2 \sin \theta} \frac{\partial \psi}{\partial \theta} = 0 \quad \text{no - slip condition at the sphere surface,} \)

2. \( r = R \quad v_\theta = -\frac{1}{r \sin \theta} \frac{\partial \psi}{\partial r} = 0 \)

3. \( r \to \infty \quad \psi = -\frac{1}{2} \nu_\infty r^2 \sin^2 \theta \quad (v_\infty \text{ is free - stream velocity}) \)

\( \text{(BC 3: consistent with } v_r = v_\infty \cos \theta \text{ & } v_\theta = -v_\infty \sin \theta \text{ far from the sphere, as } v_z \to v_\infty \text{ at } r \to \infty ) \)

Use similarity transform,

\[ \psi = f(r) \sin^2 \theta \quad : \text{Why? You have some clue from BC 3.} \]
On substitution in the conservation (NS) equation on $\psi$ above,
\[
\left(\frac{d^2}{dr^2} - \frac{2}{r^2}\right)\left(\frac{d^2}{dr^2} - \frac{2}{r^2}\right) f = 0
\]

Assuming $f(r) = C r^n$
And, substituting in the above equations, $n$ can assume the values of $-1, 1, 2,$ and $4$, in which case $f(r)$ has the form: $f(r) = C_1 r^{-1} + C_2 r + C_3 r^2 + C_4 r^4$

BC 3 yields $C_4 = 0$ and $C_3 = -\frac{v_\infty}{2}$.

Thus, $\psi(r, \theta) = \left(C_1 r^{-1} + C_2 r - \frac{1}{2} v_\infty r^2\right) \sin^2 \theta$

And, $v_r = \frac{1}{r^2 \sin \theta} \frac{\partial \psi}{\partial \theta} = \left(v_\infty - 2 \frac{C_2}{r} - 2 \frac{C_1}{r^3}\right) \cos \theta$
$v_\theta = -\frac{1}{r \sin \theta} \frac{\partial \psi}{\partial r} = \left(-v_\infty + \frac{C_2}{r} - \frac{C_1}{r^3}\right) \sin \theta$

BCs 1 & 2 yield $C_1 = -\frac{1}{4} v_\infty R^3$ and $C_2 = \frac{3}{4} v_\infty R$ so that

\[
\psi(r, \theta) = -\frac{v_\infty}{2} \sin^2 \theta \left(r^2 - \frac{3}{2} R r + \frac{1}{2} R^3\right)
\]

\[
\begin{align*}
v_r &= v_\infty \left(1 - \frac{3}{2} \left(\frac{R}{r}\right) + \frac{1}{2} \left(\frac{R}{r}\right)^3\right) \cos \theta \\
v_\theta &= -v_\infty \left(1 - \frac{3}{4} \left(\frac{R}{r}\right) + \frac{1}{4} \left(\frac{R}{r}\right)^3\right) \sin \theta
\end{align*}
\]

(From here onwards, one can derive the expressions for pressure distributions in the flow field, and also the famous Stoke’s law, $F_k = 6\pi \mu v_\infty R$ by sequentially determining strain tensors, stress tensors, and then, stress components in the direction of flow, at the sphere surface ($r = R$), and integrating them around ($\theta - direction$) over the surface. See BSL chapters 2 and 4. Note that there are two components in Stoke’s drag force: $4\pi \mu v_\infty R$ from the viscous and $2\pi \mu v_\infty R$ from normal stresses.)

⇒ Revert to the present example of diffusion to free falling solid particle at velocity, $v_o$

\[
\psi(r, \theta) = f(r) \sin^2 \theta
\]

\[
= -\frac{v_o}{2} \sin^2 \theta \left(r^2 - \frac{3}{2} R r + \frac{1}{2} R^3\right)
\]

Let $r = R + y$ or $y = r - R$: (pseudo – Cartesian geometry, when $y \ll R$ or when we are looking at values of $y$ close to solid surface)

\[
\psi = -\frac{v_o}{2} \sin^2 \theta \left((R+y)^2 - \frac{3}{2} R(R+y) + \frac{1}{2} R^3\right)
\]

\[
\approx -\frac{3}{4} v_o y^2 \sin^2 \theta \quad \text{(close to surface or small distance from the surface of)}
\]
\[ v_\theta = -\frac{1}{r \sin \theta} \frac{\partial \psi}{\partial y} \]

\[ \approx -\frac{1}{R \sin \theta} \frac{\partial \psi}{\partial y} \quad \text{close to the surface and} \quad \left( \frac{\partial \psi}{\partial r} = \frac{\partial \psi}{\partial y} \right) \]

\[ = \frac{3}{2} \frac{v_o}{R} \sin \theta \]

\[ v_\theta = \frac{\sqrt{-3v_o\psi}}{R} \quad - (1) \quad \text{(What about} \ v_r? \ It \ is \ cancelled \ out. \ See \ later) \]

Now, the diffusion equation is modified as

\[ v_r \frac{\partial C}{\partial r} + v_\theta \frac{\partial C}{\partial \theta} = D \left( \frac{\partial^2 C}{\partial r^2} + \frac{\partial^2 C}{\partial \theta^2} \right) \quad - (2) \quad \text{(for relatively large} \ R: \ \frac{\partial^2 C}{\partial r^2} \gg \frac{\partial^2 C}{\partial \theta^2} \)

Transform \( C(r, \theta) \rightarrow C(\psi, \theta) \) (Recall: in many BL examples, switch from \((x, y)\) to \((x, \psi)\))

\[ \frac{\partial C}{\partial r} = \frac{\partial C}{\partial \psi} \frac{\partial \psi}{\partial r} = \frac{\partial C}{\partial \psi} \left( R \sin \theta \ v_\theta \right) \quad (r \sim R, \text{when you substitute} \ C(r, \theta) \text{with} \ C(\psi, \theta)) \]

as \( v_r = -\frac{1}{r^2 \sin \theta} \frac{\partial \psi}{\partial r}; \ v_\theta = +\frac{1}{r \sin \theta} \frac{\partial \psi}{\partial r} \quad - (3) \)

Therefore,

\[ \frac{\partial C}{\partial \theta} \bigg|_r = \frac{\partial C}{\partial \theta} \bigg|_\psi + \frac{\partial C}{\partial \psi} \frac{\partial \psi}{\partial r} \bigg|_\psi - r^2 \sin \theta v_r \frac{\partial C}{\partial \psi} \bigg|_\theta \quad - (4) \]

\[ \frac{\partial^2 C}{\partial r^2} = \frac{\partial}{\partial \psi} \left( \frac{\partial R \sin \theta v_\theta}{\partial R} \right) \]

\[ = v_\theta \! R \sin \theta \frac{\partial}{\partial \psi} \left( v_\theta \! R \sin \theta \frac{\partial C}{\partial \psi} \right) \quad - (5) \]

Plug (3), (4), & (5) in (2)

\[ v_r \left( R \sin \theta \frac{\partial C}{\partial \psi} \right) + v_\theta \left( \frac{\partial C}{\partial \theta} - R^2 \sin \theta v_r \frac{\partial C}{\partial \psi} \right) = D v_\theta \! R \sin \theta \frac{\partial}{\partial \psi} \left( v_\theta \! R \sin \theta \frac{\partial C}{\partial \psi} \right) \]

\[ \frac{\partial C}{\partial \theta} = DR^3 \sin^2 \theta \frac{\partial}{\partial \psi} \left( v_\theta \frac{\partial C}{\partial \psi} \right) \]

Plug \( v_\theta \) from (1)

\[ \frac{\partial C}{\partial \theta} = DR^2 \sin^2 \theta \sqrt{3v_o} \frac{\partial}{\partial \psi} \left( \sqrt{-\psi} \frac{\partial C}{\partial \psi} \right) \quad - (6) : C(\psi, \theta) \]

BC. 1. \( \psi = 0 \quad C = 0 \quad : \text{surface} \)

2. \( \psi \rightarrow -\infty \quad C = C_o \quad (y \rightarrow \infty) \)

3. \( \theta = 0 \quad \psi = 0 \quad C = C_o \quad : \text{surface} \)

The last BC means: at \( \theta = 0 \), where there is the stagnation point, concentration at the surface is the same as bulk phase concentration. The species have reached the surface by diffusion, undisturbed by convection.
Let \( t = DR^2 \sqrt{3v_o} \int sin^2 \theta \, d\theta = DR^2 \sqrt{3v_o} \left( \frac{\theta}{2} - \frac{\sin 2\theta}{4} \right) + a_1 \) (now switch to \( C(\psi, t) \))

Put in (6)

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial \psi} \left( \sqrt{-\psi} \frac{\partial C}{\partial \psi} \right) \quad - (7) : C(\psi, t)
\]

You have a semi-infinite zone; apply again the method of combination of variables,

\( \eta = -\frac{\psi}{t^{2/3}} \) (See Levich for arriving at this combination)

\[-\frac{2}{3} \eta \frac{dC}{d\eta} = \frac{d}{d\eta} \left( \sqrt{\eta} \frac{dC}{d\eta} \right) \quad \begin{cases} \psi \to \lambda \psi' \\
t \to \mu t' \\
eq \text{remains unchanged if} \\
\mu = \lambda^{3/2} \end{cases}
\]

Introduce \( z = \sqrt{\eta} \)

\[
\Rightarrow \frac{\partial^2 C}{\partial z^2} + \frac{4}{3} z \frac{dC}{dz} = 0
\]

Integrate to derive \( C(z) = C_1 \int_0^z \exp \left( -\frac{4}{9} z^3 \right) \, dz + C_2 \)

where, \( z = \sqrt{\frac{3v_o}{4}} \, y \sin \theta \sqrt{DR^2 \sqrt{\frac{3v_o}{4}} \left( \theta - \frac{\sin 2\theta}{2} \right) + a_1} \)

BC. 1. \( \Rightarrow C_2 = 0 \)

\[
2. \Rightarrow C_1 = \frac{C_o}{\int_0^\infty \exp \left( -\frac{4}{9} z^3 \right) \, dz} = \frac{C_o}{\left( \frac{9}{4} \right)^{1/3} \Gamma \left( \frac{1}{3} \right)} = \frac{C_o}{1.15} \]

(BC. 3 ? \( \Rightarrow \theta = 0 \) or \( \theta \sim 0 \) \( a_1 = 0 \); it is not clear how Levich has done it)

Hence, \( z = \frac{3}{4} \sqrt{\frac{3v_o}{4} \, y \sin \theta \sqrt{DR^2 \sqrt{\frac{3v_o}{4}} \left( \theta - \frac{\sin 2\theta}{2} \right) + a_1}^{1/3}} \)

\[
C = \frac{C_o}{1.15} \int_0^\infty \exp \left( -\frac{4}{9} z^3 \right) \, dz \quad C(y, \theta) \quad \text{or} \quad C(r, \theta)
\]

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Flux, \( J = D \frac{\partial C}{\partial y} \bigg|_{y=0} = \frac{DC_o}{1.15} \frac{3}{4DR^2} \frac{3v_o}{\sin \theta} \left( \frac{\theta - \sin 2 \theta}{2} \right)^{\frac{1}{3}} \)

It is clear that \( J \propto v_o^{\frac{1}{3}}, D^{\frac{2}{3}}, R^{-\frac{2}{3}}, \) and \( f(\theta) \)

At \( \theta = 0 \) (incident point) flux is maximum. At \( \theta = \pi \) (separation point) flux is zero.

\[ \text{BL } \delta_c \text{ from } J \sim \frac{DC_o}{\delta_c} \Rightarrow \delta_c = \frac{1.15 \left( \frac{\theta - \sin 2 \theta}{2} \right)^{\frac{1}{3}}}{\sin \theta} \frac{3}{4DR^2} \]

**Diffusion BL:**

\[ \delta_c = 0 \text{ at } \theta = 0 \text{ and } \delta_c \sim R \text{ at } \theta = 180^\circ \]

**Total molar flowrate** = \( \int \int J \, dA = 2\pi R^2 \int_0^{\pi} J \sin \theta \, d\theta \)

\[ = \frac{DC_o R^3}{1.15} \frac{3}{4DR^2} \frac{3v_o}{\sin \theta} \cdot 2\pi \int_0^{\pi} \frac{\sin^2 \theta \, d\theta}{\left( \theta - \sin 2 \theta \right)^{\frac{1}{3}}} \]

\[ = 7.98D^{2/3}v_o^{\frac{1}{3}}R^{4/3}C_o \]

\[ = 4\pi DC_o R \left( 0.64Pe^{\frac{1}{3}} \right) \text{ for } Pe \gg 1 \text{ (From Levich)} \]

For \( Pe \rightarrow 0 \) (stagnant liquid), start from \( \nabla^2 C = 0 \) to calculate \( W \) as:

\[ W = 4\pi DC_o R \]

\[ (Sh = \frac{k_m \delta p}{D} = 2) \]

See BSL. Simply integrate using

\[ BCs \quad C(0) = 0, \text{ and } C(\infty) = C_o \]

\[ \text{to solve } C(r) = C_o \left( 1 - \frac{R}{r} \right) \text{ and then calculate } J = -D \nabla C \text{ at } r = R \]

**For \( Pe \sim 1 \) (a mathematical number for gas – flow?)**

\[ W = 4\pi DC_o R \left( 1 + 0.64Pe^{\frac{1}{3}} \right) : \text{Amazing! Compare it to the previous case } Pe \gg 1 \]

Analogous to mass transfer (diffusion) for \( Sc \gg 1 \) (liquid) from/to spherical particle in creeping flow, the heat transfer rate (\( Pr \gg 1 \)) from a heated sphere of radius \( R \), with a viscous fluid in creeping flow past the sphere has been calculated in BSL. Therein, the velocity profiles were calculated as before. However, the solution was sought differently, viz. using Taylor-series expansion for the velocity fields expressed in terms of interfacial velocity gradient, and then using the Von Karman boundary layer integral expression. The final expressions for \( \delta_T(\text{thermal boundary layer}) \) and the total heat flow rate are as follows:
\[
\delta_T = 0.91(2R)(RePr)^{-1/3} \left( \frac{\pi - \theta + \frac{1}{2} \sin \theta}{\sin \theta} \right)^{1/3}
\]
\[
\theta = 0.991 (\pi D^2) (T_o - T_\infty) \left( \frac{k}{D} \right) (RePr)^{1/3}
\]

(Here, \( D = 2R, \& \theta \) has been taken from the rear end of the sphere, which is the same as \( \pi - \theta \) of the Levich’s solution). Interestingly, but for small differences in the coefficients, and the assumption \( Re \sim 1 \), these solutions are similar to those of the previous solutions for mass transfer derived by Levich:

\[
\delta_c = 1.15 \left( \frac{\theta - \frac{1}{2} \sin 2\theta}{\sin \theta} \right)^{1/3} \sqrt[3]{\frac{4DR^2}{3v_o}} \quad (here, D \equiv D_m)
\]

\[
W = 4\pi DC_o R \left( 0.64 (ReSc)^{1/3} \right)
\]

(Note: \( Pe = ReSc = \frac{v_o(2R)}{\nu}, \nu = \frac{2(v_oR)}{D} \); most of the heat transfer occurs in the incident region where \( \delta_T \) is small.)
Prototype example 16: Mass transfer to a slowly falling (liquid) drop in a vapor or gas. Alternatively, consider mass transfer to a slowly rising (gas) bubble in a liquid (Levich).

This example is analogous to the previous example of mass transfer to a falling spherical solid particle. The difference lies in convective/diffusion at the liquid-vapor/gas interface vs. that at the fluid-solid interface. The velocity of fluid motion at the stationary solid surface is zero (no-slip condition with the relative velocity being zero). On the other hand, the liquid within the drop (or gas within a bubble) is, however, circulating. Therefore, at such vapour-liquid drop interface, although the normal velocity component is zero, the common tangential velocity in two phases is non-zero. All it implies is that hydrodynamics must be resolved afresh before solving the species balance equation in the boundary layer:

\[ v_r \frac{\partial C}{\partial r} + v_\theta \frac{1}{r} \frac{\partial C}{\partial \theta} = D \frac{\partial^2 C}{\partial r^2} \]  \hspace{1cm} (1) \hspace{1cm} (same as example 15; one radial term is dropped)

where, \( C \) is the concentration of species diffusing from the surface of the drop into the liquid inside. The BCs are

- \( r \to \infty \), \( C = C_o \)
- \( r = a \), \( C = C_1 \)
- \( \theta = 0 \) and \( r = a \) (stagnation point), \( C = C_o \)

What about \( v_r \) and \( v_\theta \)? For spherical coordinate system,

\[ v_\theta = -\frac{1}{r \sin \theta} \frac{\partial \psi}{\partial r}, \hspace{0.5cm} v_r = \frac{1}{r^2 \sin \theta} \frac{\partial \psi}{\partial \theta} \]  \hspace{1cm} (\( \nabla \cdot \vec{V} = 0 \))

We have to substitute \( \psi \) from hydrodynamic solution, in which case NS equation must be solved for both phases (outside and inside the drop) and the interfacial velocity and shear stress should be matched (recall the example of the flow of two immiscible liquids having different viscosities in a horizontal tube (BSL)). For the present case, see Levich for detailed hydrodynamic or velocity calculations. Here, we skip the calculations and directly write down the solutions:
\[
\psi \approx -v_0 ay \sin^2 \theta \\
v = \frac{2(\rho' - \rho)ga^2}{3\mu} \left( \mu + \mu' \right)
\]

(2) (terminal or settling velocity of the drop, or its COM)

In this present case, the drop may also be considered motionless, with the coordinate system moving along with the center of gravity of the falling drop, while the outer liquid moves in the opposite direction at velocity, \(-U\); \(U\) being the velocity of the drop's motion in the inertial frame. The above expression passes into the Stoke's equation for flow past a solid, with \(\mu \ll \mu'\):

\[
v_t = \frac{2}{9} \frac{(\rho' - \rho)ga^2}{\mu}; \quad \text{(note } v > v_t)\]

\(\Rightarrow\) The liquid at the surface of the drop moves at the tangential velocity \(v_0 \theta = v_o \sin \theta\), where, \(v_o\) is the magnitude of the velocity at the drop's equator:

\[
v_o = \frac{\mu}{2 \mu + \mu'} \frac{v}{\sin^3 \theta}
\]

(Here, \(v\) is the same as in eq. 2)

Let us revert and work on \(\theta \) & \(\psi\) as the variables instead of \(r\) and \(\theta\) (same as before):

\[
\frac{\partial C}{\partial r} = \frac{\partial C}{\partial \psi} \frac{\partial \psi}{\partial r} = -r \sin \theta v_\theta \left( \frac{\partial C}{\partial \psi} \right)_\theta
\]

\[
\left( \frac{\partial C}{\partial \theta} \right)_r = \left( \frac{\partial C}{\partial \psi} \right)_\psi + \frac{\partial C}{\partial \psi} \frac{\partial \psi}{\partial \theta} = \left( \frac{\partial C}{\partial \theta} \right)_\psi + r^2 \sin \theta v_r \left( \frac{\partial C}{\partial \psi} \right)_\theta
\]

Considering that we are solving \(C(\theta, r)\) or \(C(\psi, \theta)\) near the surface of the drop:

\(y = r - a\), where \(y \ll a\)

The species balance equation is transformed to

\[
\frac{\partial C}{\partial \theta} = Da^3 (v_\theta)_{y=0} \sin^2 \theta \left( \frac{\partial^2 C}{\partial \psi^2} \right) - (3) \quad \text{(same as before)}
\]

Substituting \(v_\theta\) in eq. (3), \(\frac{\partial C}{\partial \theta} = Da^3 v_o \sin^3 \theta \left( \frac{\partial^2 C}{\partial \psi^2} \right)\)

Again, similar to the previous case/prototype example, introduce a new variable

\[
t = Da^3 v_o \int \sin^3 \theta d\theta = Da^3 v_o \left( \frac{\cos^3 \theta}{3} - \cos \theta \right) + a_1 \quad -(4) \quad \text{(what is } a_1?)
\]

Or, \(\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial \psi^2}\)

BC 1. \(C = C_o \psi \rightarrow -\infty;\)
2. \( C = C_1 \) \( \psi \to 0; \)
3. \( C = C_o \) at forward stagnation point, \( r = a \) & \( \theta = 0 \)
(The last condition implies \( C = C_o \) @ \( t = t_o = a_1 - \frac{2}{3} D a^2 v_o \))

The solution is
\[
C(\psi, t) = \frac{2(C_o-C_1)}{\sqrt{\pi}} \int_0^{2/\sqrt{\pi}} \exp(-z^2) \, dz + C_1 \quad (a_1 disappears mysteriously!)
\]

Substitute the value of \( \psi \) as \( (-v_o a y \sin^2 \theta) \) and \( t \) from (4)
\[
C = \frac{2(C_o-C_1)}{\sqrt{\pi}} \int_0^N \exp(-z^2) \, dz + C_1 \quad \text{where, } N = \frac{av_o \sin^2 \theta y}{2 \sqrt{D v_o a^3 \left( \frac{2}{3} \cos \theta + \frac{1}{3} \cos^3 \theta \right)}}
\]

Calculate flux,
\[
J_m = D \left( \frac{\partial C}{\partial y} \right)_{y=0} = -\frac{D v_o a \sin^2 \theta (C_o-C_1)}{2 \sqrt{\pi D v_o a^3 \left( \frac{2}{3} \cos \theta + \frac{1}{3} \cos^3 \theta \right)}} = \left( \frac{D v_o}{a} \right)^{1/2} \frac{3}{\sqrt{\pi}} \sqrt{\frac{(1+\cos \theta)^2}{2+\cos \theta}} (C_o-C_1) = \frac{D(C_o-C_1)}{\delta_c}
\]
where, \( \delta_c \) is the mass BL thickness = \( \frac{\pi}{3} \left( \frac{a D}{v_o} \right)^{1/2} \sqrt{\frac{2+\cos \theta}{(1+\cos \theta)^2}} \)

Thus, \( J_m \)
\[
\begin{align*}
\propto & \frac{1}{2} v_o^2 \\
\propto & a^{-1/2}
\end{align*}
\]
\( \propto f(\theta) \quad @ \theta = \pi, \text{ } J \text{ is smallest } (0)(\text{also, mathematically there is a singularity at } \delta_c \to \infty) \)

**Note:** The above-solution is valid when \( y \ll a \). As an approximation, \( J |_{r=a} = \frac{D(C_o-C_1)}{a} \)

Total \( W \) (mass flow rate) = \( 2\pi a^2 \int_0^\pi \int_0^{2/\sqrt{\pi}} \sin \theta \, d\theta \) (integrated over the surface)
\[
= 2\sqrt{3} \pi a^2 \left( \frac{D v_o}{a} \right)^{1/2} \int_0^{\pi/2} \sin \theta (C_o-C_1) \int_0^{\pi/2} \frac{D v_o}{a} \frac{1}{2} a^2 \]

Introducing \( Re = \frac{v_o a}{\nu}, Sc = \frac{v}{D}, Sh \) (Sherwood #) = \( \frac{Wa}{4\pi a^2 D(C_o-C_1)} \) (how?),
\[
Sh = \frac{2}{\sqrt{\pi a}} \left( Pe \right)^{1/2} \left( \frac{\mu}{\mu + \mu'} \right)^{1/2} \quad ; \quad Pe = Re Sc
\]

Also, compare \( W \) with that for the diffusion to a solid spherical particle (previous example) under similar condition (same \( Re \)): \( W \propto Pe^{1/2} \text{ or } Re^{1/2} \). \( \text{The diffusional flow to the drop is greater than the solid particle.} \text{ Why? Because there is a sink in drop?? No.} \)

\( \Rightarrow \text{At high } Re, \text{ complexities in determining the dependence of } W \text{ or } Sh \text{ on } Pe \text{ arise because of wake formation downstream of the drop, or the deformation of drop to a non-spherical shape. By dimensionless analysis, it can, however, be shown that } W \approx \frac{D(C_o-C_1) 4\pi a^2}{\sqrt{Pe}} \text{ at high } Re. \)
Prototype example 17: Convection/diffusion to the surface of a circular rotating disk (Levich)

Note: If there is no rotation, then we would have been discussing potential flow of an axisymmetric cylindrical jet striking a horizontal surface. Thus, boundary layer (momentum and/or mass) over the disk surface arises in this case because of rotation of the disk. Also, fluid acquires radial velocity under the influence of the centrifugal force, which in turn induces negative Y-direction flow towards the disk, as a replenishment.

\[ V_r = V_\theta = 0 \] \[ V_y = -v_0 \] \( y \rightarrow \infty \) implies replenishment of fluid towards surface

No edge effect (infinitely wide disk)

Exact solution of the hydrodynamic equations has been obtained by Von Korman and Cochran.

Solution: NS equation for BL over disk surface (assume axial symmetry, \( \frac{\partial}{\partial \theta} = 0 \) (no \( \theta \) dependence)

\[ V_r \frac{\partial v_r}{\partial r} - \frac{v_r^2}{r} + V_y \frac{\partial v_r}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial r} + \nu \left( \frac{\partial^2 v_r}{\partial y^2} + \frac{\partial^2 v_r}{\partial r^2} + \frac{1}{r} \frac{\partial v_r}{\partial r} - \frac{v_r}{r^2} \right) \] : \( r \) - momentum

\[ V_r \frac{\partial v_\theta}{\partial r} - \frac{v_r v_\theta}{r} + V_y \frac{\partial v_\theta}{\partial y} = \nu \left( \frac{\partial^2 v_\theta}{\partial y^2} + \frac{\partial^2 v_\theta}{\partial r^2} + \frac{1}{r} \frac{\partial v_\theta}{\partial r} - \frac{v_\theta}{r^2} \right) \] : \( \theta \) - momentum

\[ V_r \frac{\partial v_y}{\partial r} + V_y \frac{\partial v_y}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial y} + \nu \left( \frac{\partial^2 v_y}{\partial y^2} + \frac{\partial^2 v_y}{\partial r^2} + \frac{1}{r} \frac{\partial v_y}{\partial r} \right) \] : \( y \) - momentum

\[ \frac{\partial p}{\partial r} \approx 0 \text{ (no } \nabla p \text{ along } r) \] (As noted above, fluid acquires \( V_r \) because of the centrifugal force)

Assume a similarity solution:

\[ V_r = r \omega F(\xi) \] \[ \xi = \frac{\omega r}{\sqrt{v}} y \] (dimensionless)

\[ V_\theta = r \omega G(\xi) \]

\[ V_y = \sqrt{\nu \omega} H(\xi) \]

\[ p = -\rho v \omega P(\xi) \] \( (p \sim \rho V_y^2) \)

Plug into NS equations, and Continuity:
\[
\begin{align*}
F^2 - G^2 + F'H &= F'' : r \\
2FG + G'H &= G'' : \theta \\
HH' &= P' + H'' : y \\
2F + H &= 0 \quad : \text{Continuity}
\end{align*}
\]

BCs: \[\begin{align*}
\xi &= 0 & F &= 0, \quad G &= 1, \quad H &= 0 \\
\xi \to \infty & F &= 0, \quad G &= 0, \quad H &= -\alpha
\end{align*}\]

Here, \(\alpha = \frac{v_o}{\sqrt{\nu \omega}}\) (to be determined; \(v_o\) is unknown)

In this case, series solutions are sought. Apparently, \(F\) & \(G\) become small and \(H \to -\alpha\), as \(\xi \to \infty\). Therefore, the quadratic terms can be neglected. Use linearize equations for large values of \(\xi\):

1) \(F'' \approx -F'\alpha \Rightarrow F = e^{-\alpha \xi}\)
2) \(G'' \approx -G'\alpha \Rightarrow G = e^{-\alpha \xi}\)

All it implies is that the asymptotic expansion of \(F, G,\) and \(H\) must be exponentials of the form \(e^{-\alpha \xi}\):

\[
\begin{align*}
A, B & \text{ are unknown} \\
F &= Ae^{-\alpha \xi} - \frac{A^2 + B^2}{2a^2} e^{-2\alpha \xi} + A(\frac{A^2 + B^2}{4a^4}) e^{-3\alpha \xi} + \ldots \\
G &= Be^{-\alpha \xi} - \frac{B(\frac{A^2 + B^2}{12a^4})}{e^{-3\alpha \xi} + \ldots} \\
H &= -\alpha + \frac{2A}{\alpha} e^{-\alpha \xi} + \ldots
\end{align*}
\]

Similarly, for small values of \(\xi\) (at the surface)

\[
\begin{align*}
F &= a\xi - \frac{\xi^2}{2} + \frac{1}{3} b\xi^3 + \ldots \\
G &= 1 + b\xi + \frac{1}{3} a\xi^3 + \ldots \\
H &= -\alpha \xi^2 + \frac{1}{3} \xi^3 + \ldots
\end{align*}
\]

See Frobenius method. \(F\) and \(H\) are 0 at the surface and \(G\) is 1.

The constants \(A, B, a, b\) and \(\alpha\) should be chosen so that \(F, G, H, F', G', H'\) remain continuous, when one matches the two series. However, numerical integration yields \(a = 0.51023, \quad b = -0.616, \quad A = 0.934, \quad B = 1.208, \quad \alpha = 0.88447\).

Thus, \(V_y \approx -0.89\sqrt{\nu \omega}\) as \(y \to \infty\) (\(\alpha = \frac{v_o}{\sqrt{\nu \omega}} = -v_o\) (suction velocity or replenishment velocity of fluid towards disk))

\[V_y \approx -0.51\sqrt{\frac{\omega^3}{\nu}} y^2 \quad \text{for} \quad y \ll \sqrt{\frac{\nu}{\omega}} \quad \text{(close to the surface)}\] (check the dimensionless variable, \(H\))

Similar calculations for \(F\) and \(G\). \(F, G, H\) are shown below (check the solutions at the boundary):

\[
\begin{align*}
\delta_o &= 3.6 \sqrt{\frac{\nu}{\omega}} \\
\text{Levich assumes} \\
V_y &\sim -0.8v_o \text{ at } \delta_o
\end{align*}
\]
From (non-dimensionalized) velocity distribution trends shown in the plot,

1. @ξ = 3.6, or δ₀ = 3.6 \sqrt{\frac{V}{\omega}}; \ V_y \sim 0.8 of the limiting value, \ ν_o.

   @ the disk surface, \ V_y = 0

2. @ξ = 3.6, G \approx 0.05 \Rightarrow V_θ \to 0.05 \ V_θ_{max}

   @ the disk surface, \ G(ξ) = 1 \ and \ V_θ = R\omega \ (from \ V_θ = r\omega \ G(ξ)).

Thus, δ₀ defines boundary layer thickness on the disk surface, within which the radial and tangential velocity components are not zero; only axial component exists beyond that layer.

**Streamlines:**

![Streamlines Diagram]

Let us revert to the concentration boundary layer, δ_c

\[ V_r \frac{\partial c}{\partial r} + V_\theta \frac{\partial c}{\partial \theta} + V_y \frac{\partial c}{\partial y} = D \left( \frac{\partial^2 c}{\partial y^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{1}{r^2} \frac{\partial^2 c}{\partial \theta^2} \right) : \text{species balance in the BL} \]

⇒ \[ V_y \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2} : \left( V_y(y) \right) \] It is important to note that \ V_r \neq 0 in BL.

**BCs** 1. \ C = 0 \ at \ y = 0 \ (disk surface) \ (Levich writes that this condition holds good for maximum diffusional flux to the surface. However, such condition should hold good for the fast kinetics)

2. \ C = C_o \ \ y \to \infty

Integrating the equation twice,

\[ C = a_1 \int_0^y \exp \left\{ \frac{1}{D} \int_0^t V_y(z)dz \right\} dt + a_2 \]

\[ a_2 = 0 \ from \ BC \ 1 \]

BC 2: \[ C_o = a_1 \int_0^\infty \exp \left\{ \frac{1}{D} \int_0^t V_y(z)dz \right\} dt \]
In principle the integral should be evaluated from 0 to \( \delta_o \) with \( V_y \approx 0.51 \frac{\omega^3}{v} y^2 \) and \( \delta_o \) to \( \infty \) with \( V_y \approx -0.89 \frac{\sqrt{\omega}}{\nu} \). Neglecting (turns out to be negligible) the diffusion or concentration within the 2nd integral,

\[
C = C_o \int_0^{\infty} e^{-v^3 dv} \int_0^{\infty} e^{-v^3 dv}
\]

(See Levich for details; heavy maths), where \( Y = \frac{y}{\delta_o} \approx 2y/\delta_o \left( \frac{v}{D} \right)^{\frac{1}{3}} \)

\[
\text{Diffusion flux to disk:}
\]

\[
J = D \frac{\partial C}{\partial y} \bigg|_{y=0} = 0.62 D^{\frac{3}{3}} v^{\frac{1}{6}} \omega^{1/2} C_o \rightarrow C_o \text{ is the free stream concentration}
\]

\( \rightarrow C = 0 @ y = 0 \) represents fast kinetics.

\[
\delta_c = \frac{DC_o}{J} = 1.61 \left( \frac{D}{v} \right)^{\frac{1}{3}} \sqrt{\nu} \approx 0.5 \left( \frac{D}{v} \right)^{\frac{1}{3}} \delta_o
\]

Thus \( \delta_c \ll \delta_o \) for \( Sc \gg 1 \) (liquid) \( (\delta_o = 3.6 \sqrt{\nu} / \omega) \).

Note that \( \delta_c \) is not a function of \( r \) \( \Rightarrow \) the thickness of the boundary layer is constant over the entire disk surface. Compare this situation with the boundary layer flow with suction. Also, the expression matches well with \( \delta_c \) for flow over a flat plate \( \delta_c \sim D^{\frac{1}{3}} \nu^{\frac{1}{6}} \sqrt{\nu} / \sqrt{\omega} \), except for the numerical coefficient.

Total mass flow rate of the species

\[
W = \frac{\pi D^2 C_o R^2}{1.61(D/v)^{\frac{1}{3}} \sqrt{\nu}} \approx 1.9D^{\frac{3}{3}} v^{\frac{1}{6}} \sqrt{\omega} R^2 C_o
\]

With finite kinetics, say 1st order and surface concentration, \( C_o, J = \frac{DC_o}{1.61(D/v)^{\frac{1}{3}} \sqrt{\nu} + \frac{D}{k}} = \frac{D}{\delta_c} (C_o - C_s) \)

(1) There are two rates in series:

- \( k \to \infty \): diffusion controlled (fast kinetics) (same as the previous case)
- \( k \to 0 \) \( J \approx k C_o \) (reaction controlled) \( C_s \to C_o \)

(2) \( J \propto \omega^{1/2} \)

\[
J_o \propto 10^{\omega^{1/2}} \Rightarrow \text{can be experimentally verified also, assume a uniformly accessible surface}
\]

\[
Re = \frac{\omega R^2}{v} \sim 10^4 - 10^5 \text{ laminar flow}
\]
Lecture #27

Example 19: CFD-based transport modelling of a CVD reactor (gas and surface phase reaction (or adsorption-desorption) in a vertical thermal reactor)

Preamble: At the outset you should have noticed that this example is titled “example”, and not “prototype example” as titled for the previous 17 examples discussed in this lecture series.

CFD has significantly grown over the past twenty five years to the extent that traditional course on transport phenomena is gradually giving way to engineering software like Fluent where the focus is more on application using model simulation results, rather on understanding the fundamental steps of transport phenomena. You can see a similar situation in the present use of Aspin vis a vis Treybal’s book on mass transfer at the undergraduate level in chemical engineering! Or, in the use of NAG or MATLAB libraries and a graduate level course on numerical methods for solving ODEs or PDEs. While the emphasis on understanding the basics of transport phenomena can never be undermined, it is good to discuss at least one example on the applications of CFD, as a software, in chemical engineering. In this last lecture series, we solve concentration profiles in a vertical thermal reactor stacked with silicon wafers, commonly used in semiconductor industries, during a common purge cycle. To make the example simple, we discuss here the purge schedule of a CVD reactor before the reaction is started. The problem statement goes like this.

Problem statement: Consider a vertical CVD reactor stacked with silicon wafers. Before chemical processing on the wafers is started, the reactor with the wafers must be purged using a high purity inert gas (nitrogen or argon) to drive off moisture or any gaseous species left behind in the reactor from the previous step, or atmospheric gaseous impurities, for example moisture, intruded into the reactor. Purging is done from the top of the reactor, with the bottom end closed. The purge gas flows through the annular space between the stack and reactor walls, sweeping the impurities downwards along with it. From the perspective of chemical engineering, or mass transfer, the purging step or process may be diffusion-controlled, as the purge gas will not penetrate the gas space between the wafers because of symmetricity in flow conditions and a relatively smaller wafer spacing or pitch. Thus, the impurities must diffuse radially outward to be carried out of the reactor by the downward flowing purge gas in the annular space. We are interested in developing a practical purge schedule or a mathematical model to predict gas concentration levels everywhere in the reactor, including annular space and between the wafers, and both in the gas phase and on the surface of the wafer. While doing so (i.e., developing model), we should remain focussed on Transport Phenomena as far as possible. To this end, typical dimensions and conditions in such a CVD reactor are: wafer size: 2 – 20” diameter, reactor diameter: 6 – 30”, wafer spacing: ¼ - 1”, number of wafers: 25 – 200, gas
flowrate: 1 – 5 slpm, reactor wall temperature: 25 - 1000 °C. Some conditions are shown in the figure below, as an example.

Stage 1: Tube needs to be cleaned (purged) before the stack of substrate (wafers) is brought into the furnace. Therefore, the furnace is continuously purged, with the bottom-end of the reactor open to the atmosphere. We need to know the status of moisture level in stage 1 before we get into stage 2 (wafer stack brought in and the bottom door closed).

Wish \( C_g(z, r) =? \)

Species (moisture or impurity) balance in the reactor:

\[
V_x \frac{\partial C_g}{\partial z} = D_g \left( \frac{\partial^2 C_g}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_g}{\partial r} \right) \right)
\]

or, \( V \cdot \nabla C_A = D_g \nabla^2 C_A + R_A \)

What is \( V_x \equiv \) ?

Let us assume \( V_x = \frac{2Q}{\pi R^2} \left( 1 - \frac{r^2}{R^2} \right) \) (Re < 2100)

Now, \( C_g^* = \frac{c_g - c_{go}}{c_{go} - c_{gi}}, \ r^* = \frac{r}{R} \)

\( z^* \neq \frac{z}{R P_e} \frac{\partial^2 C_g}{\partial z^2} \ll 1 \)

\( C_g = c_{go} = 1.5\% \) (atmospheric moisture)

This is due to the reverse BC, \( c_{go} \gg c_{gi} \). You cannot drop axial diffusion term, considering that this is the step which is responsible for bringing in moisture from atmosphere into the reactor. Such phenomenon is termed “back-diffusion” in the literature. Here, \( R P_e \) is not a correct characteristics convective length. Once you are sure you cannot drop any term, you can non-dimensionalize with any characteristics dimensions you prefer. It should also be clear to you that there is nothing extra-ordinary significance of
such a situation (back-diffusion). Be it Fick’s 1st law of diffusion or Fourier’s 1st law of heat conduction, the mass or heat flux is always considered in the inertial frame. Therefore, a species can diffuse in the opposite direction of a fluid flow, because of concentration gradients, as much as heat can flow by conduction against convection in a fluid-flow, because of the temperature gradients.

\[
V_z^* = \frac{V_z}{V_{z_{max}}}; \quad z^* \text{ or } r^* = \frac{z \text{ or } r}{R \text{ or } L}
\]

\[
\frac{\partial C_g}{\partial z^*} = \frac{1}{P_e(R, L)} \nabla^2 C_g^* + \left( \frac{\partial^2 C_g}{\partial z^*^2} + \frac{1}{r^*} \frac{\partial}{\partial r^*} \left( r^* \frac{\partial C_g}{\partial r^*} \right) \right)
\]

But \( P_e \gg 1 \)?

Not a valid statement; this \( P_e \) number is just a mathematical dimensionless number.

**Conclusion:** You must bring BC (and physics of the problem) into picture before you non-dimensionalize the equation and decide to drop or retain a term, as an approximation.

**BCs:**
- \( z = 0, \quad C_g = C_{gi} \approx 0 \)
- \( z = L, \quad C_g = C_{go} \)
- \( r = 0, \quad \frac{\partial C_g}{\partial r} = 0 \)
- \( r = R, -D \frac{\partial C_g}{\partial r} = 0 \) \( \text{(non-reactive wall)} \)

**How do you solve?** It is an elliptic PDE.

- Method of lines will easily work. \( C_g = C_g(r, z) \) can be solved numerically.

However, if you consider non-isothermal condition (cold incoming gas and hot reactor walls), think of natural convection and swirling effects in the furnace, especially at the outlet of the reactor, with some fluid streams reversing at the exit. These situations will require simultaneously solving the momentum and energy balance equations along with species conservation equation. This is where commercial engineering software like Fluent becomes useful. Either way, the solution for \( C_g = C_g(r, z) \) for stage 1 becomes the initial condition for stage 2.

**Stage 2:**

For how long you should purge?

\( C_g(t, r, z) =? \)

Velocity profile is nearly parabolic
First solve for velocity (and temperature fields, if required) in the annular spacing and between wafers.

**Intuition:** Since wafer spacing is small & gas flow in the reactor is symmetric in \( r \)-direction, there is a **dead space** or volume of gas in the spacing. Thus, the stack is like a solid rod. Gaseous impurities diffuse radially outward to the annular space. There could be some edge effects, with gas streamlines penetrating the wafer space sideways from the annular space:

\[
\text{small spacing} \quad [\quad] \quad \text{large spacing} \quad [\quad]
\]

**Annular space:** \( 0 < z < L \) and \( R_w \leq r \leq R \)

\[
(1) \quad \frac{\partial C_g}{\partial t} + V_z \nabla C_g = D_g \nabla^2 C_g + \frac{R}{V_o} \\
\frac{\partial C_g}{\partial t} + V_z \frac{\partial C_g}{\partial z} = D_g \left( \frac{\partial^2 C_g}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_g}{\partial r} \right) \right)
\]

— Now the axial (diffusion) term can be dropped, as Pe >> 1.

\( V_z \equiv \text{velocity in the annular space} = \text{steady state solution is known} \& \text{can be superimposed on species balance equation.} \)

\( t = 0, \quad C_g = C_g(r,z) = C_g^o \quad (\text{solved from the previous stage 1}) \)

\( z = 0, \quad C_g = C_{gi} \)

\( r = R, -D \frac{\partial C_g}{\partial r} = 0 \quad (\text{no reaction at the reactor walls}) \)

\( r = R_w, -D \frac{\partial C_g}{\partial r} = \text{flux (z)? or } C^+ = C^- \quad \text{and/or } -D\nabla C^+ = -D\nabla C^- \quad (\text{concentration and concentration gradients at the interface of wafer-spacing and annular space should be matched}) \)

There is no \( \frac{\partial^2 C_g}{\partial z^2} \) term in the conservation equation. If you prefer to retain it, you need 2\text{nd} BC:

\( -D \frac{\partial C_g}{\partial z} = 0; \quad (\text{and not } C_g = C_{go} \text{ as the bottom door of the reactor is closed}) \)

**Between each wafer spacing:**
Each gas-spacing between two wafers is disconnected from the other. The impurity leaks from the wafer space into the annular space, and is washed out or convected downward with the purge gas.

\[
(2) \quad \frac{\partial C_g}{\partial t} + V_z^{\scriptstyle z} \frac{\partial C_g}{\partial z} = D_g \left( \frac{\partial^2 C_g}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_g}{\partial r} \right) \right); \quad 0 \leq r \leq R_w; \quad -\frac{ts}{2} \leq z \leq \frac{ts}{2} \text{ (for each wafer-space)}
\]

(As noted earlier, there is no flow between wafers. In other words, there is a dead volume of the gas)
\[
t = 0, \quad C_g = C^o_g
\]
\[
r = 0, \quad \frac{\partial C_g}{\partial r} = 0
\]
\[
r = R_w, \quad -D \frac{\partial C_g}{\partial r} = \text{Flux}(z) \quad \text{or} \quad C^+ = C^- \quad \text{and/or} \quad -D \nabla C^+ = -D \nabla C^-
\]
\[
z = 0, \quad -D \frac{\partial C_g}{\partial z} = 0
\]
\[
z = \pm \frac{ts}{2}, \quad -D \frac{\partial C_g}{\partial z} = 0
\]

How about \( \frac{\partial^2 C_g}{\partial z^2} \ll \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_g}{\partial r} \right) ? \) This is also a good approximation considering that wafer spacing is usually small. Compare this approximation with \( \frac{\partial C_g}{\partial r} \ll V_z^{\scriptstyle z} \frac{\partial C_g}{\partial z} \) for the annular space. The modified equation is as follows:

\[
\frac{\partial C_g}{\partial t} = D_g \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_g}{\partial r} \right) \quad - (2)
\]

IC and BCs. \( t = 0, \quad C_g = C^o_g \)
\[
r = 0, \quad \frac{\partial C_g}{\partial r} = 0
\]
\[
r = R_w, \quad \text{flux}(z) = -D \frac{\partial C_g}{\partial r} \quad \text{or} \quad C^+ = C^- \quad \text{and/or} \quad -D \nabla C^+ = -D \nabla C^-
\]

It is clear that both conservation equations, one for the annular space and the other for spacing between each pair of wafers should be solved simultaneously. Also, note that the flux term, \( \text{flux}(z) \) is common to the conservation equations. In other words, flux and/or concentrations at \( r = R_w \) must be matched between two domains of computations (Fluent can easily handle such case!). Another approximation may be considered: Quasi steady-state for the first equation (annular space). Actually, this simplification, i.e., \( \frac{\partial C_g}{\partial t} = 0 \) for annular space is valid considering the fact that the characteristic time of diffusion for the species in the wafer space \( (R_w^2/D) \) is much longer than that of convection (residence time \( L/V_z^{\scriptstyle z} \)) in the annular space.
Summarize (from Transport Phenomena perspectives)

(1) In stage 1, axial diffusion term for the annular space cannot be neglected (it is a rare case)

(2) Pseudo-steady state may be assumed for the gas phase in the annular space.

(3) Two eqs 1 and 2 are related through BC (Flux) ⇒ Two different domains.

(4) concentration profiles in the entire reactor can be solved going back and forth between the independent numerical solutions to equations 1 & 2. At every time of computation for the wafer space, the gas-phase concentration profiles are established in the annular phase, and then the flux and concentration at the edge of the wafers are calculated.

Special Case: Adsorption-desorption of moisture on wafer surface; equation 2 needs to be modified. The heterogeneous adsorption-desorption rate on the wafer surface is included in the conservation equation as the homogenous source of reaction:

$$\frac{\partial c_g}{\partial t} = D_g \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c_g}{\partial r} \right) - s(k_1 c_g - k_2 c_s) \quad (2)$$

where, $c_s$ is the surface phase moisture concentration (moles/cm$^2$) and $k_1$ and $k_2$ are the first order adsorption and desorption reaction constants of moisture on silicon surface, respectively. You should be able to recognize $s$ (2/ts) as the surface area per unit volume of the wafer space. Bringing on $c_s$, a new variable in the equation implies also writing down the surface phase moisture concentration balance equation:

$$\frac{\partial c_s}{\partial t} = k_1 c_g - k_2 c_s$$

ICs and BCs: $t = 0$, $c_g = c_g^0$, and $c_s^0 = c_g^0 k_1/k_2$

$r = 0$, $-D \frac{\partial c_g}{\partial r} = 0$

$r = R_w$, flux$(z) = -D \frac{\partial c_g}{\partial r}$

Qualitative model simulation results:

1) Within each wafer space:
In the annular space:

\[ C_g(t) \]

\[ C_{gi} \]

\[ t = 0 \]

\[ z \rightarrow L \]

→ **We close** this lecture series with the above-example on a CFD application in chemical engineering, and with the following remark. It is extremely difficult for an instructor to create a balance among the three aspects of Transport Phenomena: momentum (fluid dynamics), heat, and mass transport. The focus of this course is largely on heat and mass transport, with three prototype examples discussed for momentum transport, and a limited discussion of boundary layer theory and turbulence. However, a takeaway message for the students should be that they must explore complementary examples or situations by taking a cue from the analogy between mass and heat transport. For examples, the Nusselt–Graetz, Nusselt, and Brinkman problems discussed in heat transport can have an equivalent situation in mass transport, in particular, reactive mass transfer with chemical reactions at the tube walls (recall one of the problems in Mid Sem exam). Also, three prototype examples 24 - 26 discussed in mass transport have an analogous situation in heat transport, as discussed in Levich’s book itself, and also, in the other books (BSL and Deen). Such exercise will clearly improve your grip on transport phenomena.

→ **At the end** of this lecture series, students should also have noted that nearly all prototype examples were solved using two mathematical methods: Combination of variables (Similarity Transform) and Separation of variables. Personally, it remains intriguing to me why the other disciplines, namely, Mechanical Engineering and Aerospace Engineering, have steadily migrated to numerical methods in solving fluid dynamics-based problems by making full use of the presently available high speed computers and computational platform including supercomputers, while chemical engineering continues to largely rely on analytical solutions or mathematical methods. Deen’s book published as late as in 1998 is a good example of what I am referring to.

→ **In a regular semester**, these course materials are covered in 27-28 lectures of 1 h 15 min duration each, or 42 lectures of 50 min duration each. For record and due acknowledgement, most of these materials were part of my graduate level lectures delivered by Prof. Jose Wendt way back in 1995 at the University of Arizona, Tucson, USA. At Kanpur, I offer this course to graduate students only. The final year UG students are selectively admitted depending on the subjects they have cleared. To this end, you are welcome to send me any comments, or mistakes or errors you notice in the lectures, to my email id: vermanishith@gmail.com or nishith@iitk.ac.in.
Finite Difference-based Numerical Methods in Chemical Engineering
Lecture #01

Finite Difference-based Numerical Methods in Chemical Engineering

Recommended Books:

1) *Linear Algebra* by Gilbert Strang, Cengage, 4th ed.

**Objective:** Learn a few basic numerical techniques (Finite Difference) to solve simple ODEs/PDEs/algebraic equations derived from a variety of heat and mass transfer related conservation equations.

- Analytical methods yield exact solutions, often in infinite series; use mathematical functions.
- Numerical methods yield approximate solutions; use numbers, computations; results are dependent on the method accuracies and limited by computers machine errors.

**Course focuses on**

- Algebra (Matrix Operation)
- Methods (Finite Difference)

**Requires knowledge of**

- Computer Programming (because large # of iterations)
  (there are engineering software, e.g., Matlab, NAG, IMSL, Polymath)
- No numerical analysis in this course!

**Examples:** (Applications in chemical engineering)

1. **Distillation:**

![Distillation Diagram]

**Assume:** Constant molar flowrates of vapor & liquid.

Binary components: A, B

(more volatile)

**Species balance on \( i^{th} \) plate:**
\[ L_i = x_i L \]
\[ V_i = y_i V \]
\[ y_i = k_i x_i \quad \text{(equilibrium)} \]

Therefore,
\[ V_i = \left( \frac{y_i}{x_i} \right) \left( \frac{V}{L} \right) L_i \]

or \[ V_i = A_i L_i \]

And,
\[ V_i + L_i = V_{i+1} + L_{i-1} \quad \text{(in = out)} \]

\[ \begin{array}{c}
V_i \\
V_{i+1}
\end{array} \]
\[ \begin{array}{c}
l_{i-1} \\
l_i \\
\vdots
\end{array} \]
\[ \cdots \quad i^{th} \text{ plate} \]

\[ V_i + V_i/A_i - \frac{V_{i-1}}{A_{i-1}} - V_{i+1} = 0 \]

Re-arrange
\[ A_{i-1} V_{i-1} + (1 - A_i) V_i - V_{i+1} = 0 \]

\[ i = 1, N \]

Thus, there are ‘N’ equations and (N+2) variables \( (V_0 \cdots V_{N+1}) \)

However, \( V_{N+1} \) and \( L_o \) are known (inlet or boundary conditions)

Re-arrange for all trays \( i = 1, N \)

\[ (1 - A_1) V_1 - V_2 = -A_0 V_o (= L_o) \quad \text{(known)} \]
\[ A_1 V_1 + (1 - A_2) V_2 - V_3 = 0 \]
\[ \vdots \]
\[ A_{N-1} V_{N-1} + (1 - A_N) V_N = V_{N+1} \quad \text{(known)} \]

\[ (N) \]

We have a set of algebraic equations (linear/non-linear) represented as

\[ AX = \bar{b} \]

\[ \begin{array}{cccccccc}
(1 - A_1) & -1 & 0 & 0 & 0 & 0 \\
A_1 & (1 - A_2) & -1 & 0 & 0 & 0 \\
0 & A_2 & (1 - A_3) & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & A_{N-1} & (1 - A_N)_{N \times N}
\end{array} \]

\[ \begin{array}{c}
\text{coefficient matrix} \\
\text{column vectors or} \\
\text{(N x 1) matrix}
\end{array} \]

\[ \begin{array}{c}
\text{rows} \\
\text{column}
\end{array} \]
\[
\bar{X} = \begin{bmatrix}
V_1 \\
V_2 \\
\vdots \\
V_N
\end{bmatrix}, \quad \bar{b} = \begin{bmatrix}
L_0 \\
\vdots \\
V_{N+1}
\end{bmatrix} \quad \text{(Known)}
\]

Alternatively, 
\[
\begin{bmatrix}
(1 - A_1) & -1 & 0 & 0 & 0 & 0 \\
(1 - A_1) & -1 & 0 & 0 & 0 & 0 \\
A_1 & (1 - A_2) & -1 & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & 0 & 0 & A_{N-1} & (1 - A_{N+1})
\end{bmatrix}_{N \times N} \begin{bmatrix}
V_1 \\
V_2 \\
\vdots \\
V_{N+1}
\end{bmatrix}_{N \times 1} = \begin{bmatrix}
L_0 \\
\vdots \\
V_{N+1}
\end{bmatrix}_{N \times 1}
\]

* represented as matrix multiplication

**Note:**

Most of the finite difference methods lead to the discretization of ODEs/PDEs and a set of algebraic equations.

You have to solve a set of algebraic equations using Gauss Elimination, G-Jordan, etc, methods.

**Example 2:**

**Particle settling**

\[
\frac{dv}{dt} = g - \frac{\rho_f}{\rho_p} g - \frac{1}{2} \rho_f v^2 \left( \pi \frac{d_p^2}{4} \right)
\]

\[
\frac{d\rho}{dt} = g - \frac{\rho_f}{\rho_p} g - C_D \left( \frac{1}{2} \rho_f v^2 \right) A_p
\]

**Force balance on the particle:**
\[
\frac{dv}{dt} = A - BC_D(v)v^2
\]
\[= A - B\Phi(v)\]
\[t = 0, \quad v = 0\]

Therefore, you have to solve an initial value problem (ODE).

**Solution:**

- Linear or non-linear
- Homogeneous or non-homogeneous
- Or a set of ODEs.

**Methods:** RK-4, Euler Forward, etc.

**Example 3:** Heating or cooling of a moving particle \((\nabla T(r) = 0)\)

\[t = 0, \quad v_p = 0\]

\[T = T_o > T_f (\text{constant})\]

\[h_f\]

\[T(t) = ? \quad \text{(convective heat transfer coefficient)}\]

**Assume/ Apply lump-body approach \((B_i \to 0)\)**

1. Energy balance over entire particle \(\frac{hd_p}{k_p} \to 0, \quad k_p \gg hd_p\)

\[mC_p \frac{dT}{dt} = -hA_s(T - T_f)\]

\[(A_s = \pi d_p^2)\]

(No temperature gradient inside the particle)

\[h = h(Nu) \Rightarrow \frac{hd_p}{k_f} = f(Re, p, Pr)\]

or \(h = h(v_p); \quad Re = \frac{v_1d_p\rho_f}{\mu_f}, Pr = \left(\frac{C_p\mu}{k}\right)_f\)

2. Time-dependence of velocity (see previous example) and energy balance equation can be written as
\[ \frac{dv_p}{dt} = A - B\Phi(v_p) \]
\[ \frac{dT}{dt} = C D(v_p) - E \]

\( t = 0 \quad v_p = 0, \quad T = T_o \)

Type equation here.

In this example, two ODEs are to be solved; first \( y_1 \) and then \( y_2 \):

\[ \begin{align*}
\frac{dy_1}{dt} &= f(y_1) \\
\frac{dy_2}{dt} &= \Phi(y_1, y_2)
\end{align*} \]

Two ODEs

**Example 4:** Heating or cooling of a stationary solid \((\nabla T \neq 0)\) in a moving fluid

\[ t = 0 \quad T = T_o > T_f (\text{constant}) \]

\[ \text{fluid temperature} \]

Energy balance within the particle:

\[ \rho C_p \frac{dT}{dt} = \frac{k}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T}{\partial r} \right) \]

Assume \( \nabla T(r) = 0, \text{i.e., there is temperature gradient inside the particle} \)

Now, we have to solve a PDE equation (unsteady – state 1D on space)

Under the steady-state condition with/without a source term, the equation will be reduced to a 2nd order ODE or a boundary value problem.

**Example 5:** Mass transfer in a tubular liquid flow (steady- state)
\[ C_A = C_{in} \]

\[ t = 0 \]

\[ \begin{array}{c}
\uparrow r \\
\rightarrow \ldots \textbf{water flow} \rightarrow \downarrow v_z(r)
\end{array} \]

tube length = L

For \( R_e < 2100 \)

\[ v_z(r) = 2
v_o \left( 1 - \frac{r^2}{R^2} \right) \]

\[ (water - flow) \]

\[ c(t, z, r) = ? \]

Species (A) balance in the CV \((2\pi r \Delta z \Delta r)\)

\[ \begin{array}{c}
\downarrow \text{CV}
\end{array} \]

\[ \frac{\partial C_A}{\partial t} + v_z \nabla C_A = D \nabla^2 C_A + r (= 0) \]

(no reaction)

\[ \frac{\partial C_A}{\partial t} + 2v_o \left( 1 - \frac{r^2}{R^2} \right) \frac{\partial C_A}{\partial z} + v_r \frac{\partial C_A}{\partial r} = D \left( \frac{\partial^2 C_A}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_A}{\partial r} \right) \right) \]

\[ t = 0, \quad C_A = 0 \quad \text{everywhere} \]

\[ 0^+ \quad z = 0 \quad C_A = C_{in} \]

\[ z = L \quad \frac{\partial C_A}{\partial z} = 0 \quad \text{(long tube approximation)} \]

\[ r = 0, \quad \frac{\partial C_A}{\partial r} = 0 \quad \text{(symmetric)} \]

\[ = R \quad - \frac{\partial C_A}{\partial r} = 0 \quad \text{(non - reactive wall)} \]

In this example, we have a transient/unsteady-state 2D (space) problem or a PDE to solve.

Under the steady-state condition with/without a source term, the equation will be reduced to an elliptic PDE or 2nd order (in both z and r) PDE.
Lecture #02

Linear Algebraic Equations

\[
\begin{align*}
    f_1(X_1, X_2, \ldots, X_n) &= 0 \\
    f_2(X_1, X_2, \ldots, X_n) &= 0 \\
    \vdots \quad & \quad \vdots \\
    f_n(X_1, X_2, \ldots, X_n) &= 0
\end{align*}
\]

system of \( n \) linear algebraic equations

or

\[
\begin{align*}
    a_{11}X_1 + a_{12}X_2 + \cdots + a_{1n}X_n &= b_1 \\
    a_{21}X_1 + a_{22}X_2 + \cdots + a_{2n}X_n &= b_2 \\
    \vdots \quad & \quad \vdots \\
    a_{n1}X_1 + a_{n2}X_2 + \cdots + a_{nn}X_n &= b_n
\end{align*}
\]

\( n \) # of independent equations to solve \( n \) # of variables

or

\[
AX = \bar{b} \quad \quad \quad A\bar{X} = \bar{b}
\]

where \( A = \text{coefficient matrix} \)

\[
A = \begin{bmatrix}
    a_{11} & a_{12} & \cdots & a_{1n} \\
    a_{21} & a_{22} & \cdots & a_{2n} \\
    \vdots & \vdots & \ddots & \vdots \\
    a_{n1} & a_{n2} & \cdots & a_{nn}
\end{bmatrix}
\]

\( (a_{ij} \text{ is a general element; } i, j = 1 \text{ to } n) \)

\[
X = \text{matrix} = \begin{bmatrix}
    X_1 \\
    X_2 \\
    \vdots \\
    X_n
\end{bmatrix}_{n \times 1}
\]

\[
b = \text{matrix} = \begin{bmatrix}
    b_1 \\
    b_2 \\
    \vdots \\
    b_n
\end{bmatrix}_{n \times 1}
\]

\[
\bar{X} = \text{column vector} = \begin{bmatrix}
    X_1 \\
    X_2 \\
    \vdots \\
    X_n
\end{bmatrix}, \quad \bar{b} = \text{column vector} = \begin{bmatrix}
    b_1 \\
    b_2 \\
    \vdots \\
    b_n
\end{bmatrix}
\]
Note: In general, a matrix has \( n \times m \) elements

Therefore, \( a_{ij} \):  
- \( i = 1 \) to \( n \)
- \( j = 1 \) to \( m \)

If \( n = m \), there may be unique solution and the rank of the matrix = \( m \)

In general, rank \( >, =, < m \) (3 cases)

(For more, refer a book on matrix operation)

In this course, we will be solving a number of equations with as many variables:

\[
\begin{align*}
3x + 2y &= 5 \\
x - y &= 6
\end{align*}
\]

or

\[
\begin{align*}
3x + 2y + z &= 5 \\
x + y - z &= 2 \\
2x + 2y - 2z &= 4
\end{align*}
\]

etc.

Some properties of a matrix and operation

Symmetric matrix, \( a_{ij} = a_{ji} \)
Square matrix, \( n = m \)
Diagonal matrix, \[
\begin{bmatrix}
\vdots & \cdots & \cdots & \cdots & \cdots \\
0 & \ddots & 0 & \cdots & 0 \\
0 & 0 & \ddots & \ddots & \vdots \\
\vdots & \vdots & \ddots & \ddots & \vdots \\
0 & 0 & 0 & \cdots & a_{nn}
\end{bmatrix}_{n \times n}
\]
(only diagonal elements)

Banded matrix (tridiagonal)
\[
\begin{bmatrix}
a_{11} & a_{12} & 0 & 0 & \cdots & 0 \\
a_{21} & a_{22} & a_{23} & 0 & \cdots & 0 \\
0 & a_{32} & a_{33} & a_{34} & \cdots & 0 \\
\vdots & \vdots & \vdots & \ddots & \ddots & \vdots \\
0 & 0 & 0 & 0 & a_{nn-1} & a_{nn}
\end{bmatrix}_{n \times n}
\]

(The first and last rows have only two non-zero elements and all other rows have 3 elements, one on the diagonal and the other two on each side of the diagonal element)

Upper/Lower triangular matrix:
(All elements below and above the diagonal are zero, respectively)

UTM:
\[
\begin{bmatrix}
a_{11} & a_{12} & a_{13} & \cdots & a_{1n} \\
a_{22} & a_{23} & \cdots & a_{2n} \\
\vdots & \vdots & \ddots & \vdots \\
0 & \cdots & \cdots & a_{nn-1} \\
0 & \cdots & \cdots & a_{nn}
\end{bmatrix}_{n \times n}
\]

LTM:
\[
\begin{bmatrix}
a_{11} & a_{21} & a_{31} & \cdots & 0 \\
a_{21} & a_{22} & a_{32} & \cdots & \vdots \\
a_{31} & a_{32} & a_{33} & \cdots & \vdots \\
\vdots & \vdots & \ddots & \ddots & \vdots \\
a_{n1} & a_{n2} & \cdots & a_{nn-1} & a_{nn}
\end{bmatrix}_{n \times n}
\]

Operation:
Summation: \( [A]_{m \times n} = [B]_{m \times n} + [C]_{m \times n} \)
Multiplication (rules):

\[ A_{m\times n} \times B_{n\times l} = C_{m\times l} \]

Therefore, multiplication is not permissible for \( B \times A \) \( n \times l \quad m \times n \) \( \text{different} \quad l \neq m \)

Also, these multiplications are permissible:

\[
\begin{bmatrix}
5 & 1 \\
3 & 2 \\
0 & 3
\end{bmatrix}_{3\times2}
\times
\begin{bmatrix}
-3 & 0 \\
1 & 0
\end{bmatrix}_{2\times2}
; \\
\begin{bmatrix}
5 & 1 \\
3 & 2 \\
0 & 3
\end{bmatrix}_{3\times2}
\times
\begin{bmatrix}
-4 & -3 & 2 \\
2 & 7 & -3
\end{bmatrix}_{2\times3}
; \\
\begin{bmatrix}1 & 3 & 2\end{bmatrix}_{1\times3}
\times
\begin{bmatrix}0 \\
5 \\
-8\end{bmatrix}_{3\times1}
\]

Rule: \( C_{ij} = \sum_{k=1}^{k} a_{ik} \times b_{kj} \)

examples:

\[
\begin{bmatrix}
3 & 1 \\
8 & 6 \\
0 & 4
\end{bmatrix}_{3\times2}
\times
\begin{bmatrix}
5 & 6 \\
7 & 2
\end{bmatrix}_{2\times2}
= \\
\begin{bmatrix}
(3 \times 5 + 1 \times 7) & 3 \times 6 + 1 \times 2 \\
(8 \times 5 + 6 \times 7) & (8 \times 6 + 6 \times 2) \\
0 \times 5 + 4 \times 7 & (0 \times 6 + 4 \times 2)
\end{bmatrix}_{3\times2}
\]

Inverse of a matrix:

\[ [A]^{-1} \Rightarrow [A]_{m\times n} \times [A]_{n\times m}^{-1} = [I] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \]

Identity matrix

For 2 \times 2 matrix

\[ [A]^{-1} = \frac{1}{|A|} \begin{bmatrix} a_{22} & -a_{12} \\ -a_{21} & a_{11} \end{bmatrix} \quad \text{where} \quad A = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \]

Note: \(|A| = (a_{11} \times a_{22} - a_{12} \times a_{21}) \neq 0 \]

else, matrix A is considered to be singular.

For bigger size matrices, there are special methods to determine \([A]^{-1}\), discussed later.

Transpose of a matrix \([A]^T\):

\[ [A] = \begin{bmatrix} a_{11} & a_{12} & \ldots & a_{1n} \\ a_{m1} & a_{m2} & \ldots & a_{mn} \end{bmatrix}, \quad [A]^T = \begin{bmatrix} a_{11} & a_{21} & \ldots & a_{m1} \\ a_{1n} & \ldots & \ldots & a_{mn} \end{bmatrix}_{n\times m} \]

(rows have been interchanged with columns)
example: \[
[A] = \begin{bmatrix}
 a_1 \\
 a_2 \\
 \vdots \\
 a_n \\
\end{bmatrix}_{n \times 1} \Rightarrow [A]^T = [a_1 \ a_2 \ \cdots \ a_n]_{1 \times n}
\]

Let us get back to solving a set of algebraic equations:

\[
[A][X] = \{b\} \quad \text{or} \quad [A][X] = [b] \\
\text{or} \quad A \vec{X} = \vec{b}
\]

\[
X = A^{-1}b
\]

Finding solution to the set of linear algebraic equation is nothing but finding inverse of the coefficient matrix, followed by multiplication with \(b\).

Generally, Cremer’s rule works nicely for small matrix:

\[
X_j = \frac{|A_j|}{|A|}
\]

\(A_j\) is determined by replacing \(j^{th}\) column of \(A\) by \(b\).

Therefore, if \(A = \begin{bmatrix} 3 & 5 & 7 \\ 2 & 0 & 8 \\ -1 & 2 & 5 \end{bmatrix} \); \(b = \begin{bmatrix} 7 \\ 3 \\ 2 \end{bmatrix}\)

\[
X_2 = \begin{bmatrix} 3 & 7 & 7 \\ 2 & 3 & 8 \\ -1 & 2 & 5 \end{bmatrix} \bigg/ |A|; \ |A| \neq 0
\]

\[
X_3 = \begin{bmatrix} 3 & 5 & 7 \\ 2 & 0 & 3 \\ -1 & 2 & 2 \end{bmatrix} \bigg/ |A|, etc.
\]

Let us briefly discuss unique solution, singularity, and rank \((r)\) of a \((m \times n)\) matrix. (Read the textbook for details)

Consider the following set of equations:

\[
2x_1 + 3x_2 = 11 \\
4x_1 + 6x_2 = 22
\]

Note: Two equations are not independent.

and \(|A| = \begin{bmatrix} 2 & 3 \\ 4 & 6 \end{bmatrix}_{2 \times 2} = 0\)
Therefore, there is no unique solution, coefficient matrix is singular and $r$ of such matrix $= 1 < 2$ or $m(\# \text{ of equations}) < n(\# \text{ of variables})$

$$2x_1 + 3x_2 = 11$$
$$x_1 + x_2 = 4$$

**Note:** Two equations are independent.

$$|A| = \begin{bmatrix} 2 & 3 \\ 1 & 1 \end{bmatrix}_{2 \times 2} \neq 0; \text{ and } m = n, \ r = 2(n)$$

There is a unique solution.

Geometrically, two equations represent two straight lines intersecting at a unique point.

Similarly, 3 independent equations for 3 variables will represent 3 planes on a geometrical space; two planes intersecting will yield a straight line, and two straight lines intersecting will yield a point $(X_1, X_2, X_3)$, or the unique solution to the equations.

$$2x_1 + 3x_2 - x_3 = 11$$
$$x_1 + x_2 + x_3 = 4$$
$$x_1 + 2x_2 + 2x_3 = 7$$

**Note:** There are three linearly independent equations representing three non-parallel equations. In this case, $m = n, \ r = 3(n)$. 

---

Note: Two equations are independent.
Lecture #03

Gauss Elimination

It is the most widely used method to solve a set of linear algebraic equations. The method reduces the original matrix to an upper triangular matrix which can also be used to determine the determinant of the matrix. Interestingly, one can also inspect the intermediate steps/solutions to determine singularity, rank, and number of independent equations.

General steps: \[ A\vec{x} = \vec{b} \quad \text{where } A \text{ is a } 3 \times 3 \text{ matrix} \]

\[
\begin{align*}
    a_{11}x_1 + a_{12}x_2 + a_{13}x_3 &= b_1 \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots R_1 \\
    a_{21}x_1 + a_{22}x_2 + a_{23}x_3 &= b_2 \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots R_2 \\
    a_{31}x_1 + a_{32}x_2 + a_{33}x_3 &= b_3 \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots R_3
\end{align*}
\]

or

\[
\begin{bmatrix}
    a_{11} & a_{12} & a_{13} \\
    a_{21} & a_{22} & a_{23} \\
    a_{31} & a_{32} & a_{33}
\end{bmatrix}
\begin{bmatrix}
    x_1 \\
    x_2 \\
    x_3
\end{bmatrix} =
\begin{bmatrix}
    b_1 \\
    b_2 \\
    b_3
\end{bmatrix}
\]

\( R_1 \), first row is called pivot row and first non-zero element \((a_{11})\) is called pivotal element. Subsequent operations are performed around pivot row and pivotal element.

Step 1:

\[
\begin{bmatrix}
    a_{11} & a_{12} & a_{13} \\
    0 & a_{22}' & a_{23}' \\
    0 & a_{32}' & a_{33}'
\end{bmatrix}
\begin{bmatrix}
    x_1 \\
    x_2 \\
    x_3
\end{bmatrix} =
\begin{bmatrix}
    b_1' \\
    b_2' \\
    b_3'
\end{bmatrix}
\]

Briefly, the first equation is divided by \(a_{11}\), multiplied by \(a_{21}\), and subtracted from the second equation to yield the modified equation (2)

\[
\begin{align*}
    a_{22}' &= a_{22} - \left(\frac{a_{21}}{a_{11}}\right) \times a_{12} \\
    a_{23}' &= a_{23} - \left(\frac{a_{21}}{a_{11}}\right) \times a_{13} \\
    b_2' &= b_2 - \left(\frac{a_{21}}{a_{11}}\right) \times b_1
\end{align*}
\]

Similarly,

\[
\begin{align*}
    a_{32}' &= a_{32} - \left(\frac{a_{31}}{a_{11}}\right) \times a_{12} \\
    a_{33}' &= a_{33} - \left(\frac{a_{31}}{a_{11}}\right) \times a_{13} \\
    b_3' &= b_3 - \left(\frac{a_{31}}{a_{11}}\right) \times b_1
\end{align*}
\]

or, in the simplest form \( R_2' = R_2 - R_1 \left(\frac{a_{21}}{a_{11}}\right) \)
\[ R'_3 = R_3 - R_1 \left( \frac{a_{31}}{a_{11}} \right) \]

**Note:** Multiplication or division of an equation, or subtraction or addition of one independent equation from/to another independent equation does not yield a new independent equation. Therefore, at the end of step 1 we still have three linearly independent equations, although modified, to solve.

**Geometrically,** two planes (non-parallel) will intersect to yield a straight line. Therefore, step 1 has yielded two straight lines by the intersections of plane (eq 1) with plane 2 (eq 2) and with plane 3 (eq 3).

**Step 2:** Follow the similar procedure. Now \( R'_2 \) (2\textsuperscript{nd} row) becomes pivotal equation and \( a_{22}' \) becomes pivotal element.

\[
\begin{bmatrix}
a_{11} & a_{12} & a_{13} \\
0 & a_{22}' & a_{23}' \\
0 & 0 & a_{33}''
\end{bmatrix}
\begin{bmatrix}
\mathbf{x}_1 \\
\mathbf{x}_2 \\
\mathbf{x}_3
\end{bmatrix} =
\begin{bmatrix}
b_1' \\
b_2' \\
b_3''
\end{bmatrix}
\]

where,

\[
a_{33}'' = a_{33}' - \left( \frac{a_{32}'}{a_{22}'} \right) \times a_{23}'
\]

\[
b_3'' = b_3' - \left( \frac{a_{32}'}{a_{22}'} \right) \times b_2'
\]

or in the simplest form, \( R''_3 = R'_3 - R'_2 \left( \frac{a_{32}'}{a_{22}'} \right) \)

**Geometrically,** two straight lines (\( R'_2 \) and \( R'_3 \)) intersect at a point.

**Note:** At the end of step 2 an upper triangular matrix is obtained. The three modified algebraic equations are as follows:

\[
\begin{align*}
a_{11}x_1 + a_{12}x_2 + a_{13}x_3 &= b_1' \\
a_{22}'x_2 + a_{23}'x_3 &= b_2' \\
a_{33}''x_3 &= b_{33}''
\end{align*}
\]

This is a new set of three linearly independent algebraic equations to solve! Here ‘new’ means ‘modified’.
Reverse (back) substitution (to determine $\bar{x}$):

\[ x_3 = b_3'' / a_{33}'' \text{ (from the last row)} \]

\[ x_2 = \frac{b_2' - a_{23}' x_3}{a_{22}'} \text{ (from the 2\textsuperscript{nd} last row)} \]

\[ x_1 = \frac{b_1 - a_{12} x_2 - a_{13} x_3}{a_{11}} \text{ (from the 1\textsuperscript{st} row)} \]

In general, for the i\textsuperscript{th} variable of ‘n’ equations

\[ x_i = \frac{b_i^{(i-1)} - \sum_{j=i+1}^{n} a_{i j}^{(i-1)} x_j^{(i-1)}}{a_{ii}^{(i-1)}} \]

A large number of equations ($n > 3$) requires a programming code to solve.

**Evaluation of determinant:**

Consider a simple $2 \times 2$ matrix

\[ A = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \]

\[ \Rightarrow \det A = (a_{11} \times a_{22} - a_{21} \times a_{12}) \]

Apply GE method

\[ A' = \begin{bmatrix} a_{11} & a_{12} \\ 0 & a_{22}' \end{bmatrix} \]

\[ a_{22}' = (a_{22} - \left( \frac{a_{21}}{a_{11}} \right) \times a_{12}) \]

The determinant of the modified matrix $A' = (a_{11} \times a_{22} - a_{21} \times a_{12}) = \text{same as } \det(A)$

“Value of determinant is not changed by the forward elimination step of GE”. This must be true because forward step only modifies the equations.

Take $3 \times 3$ matrix:

\[ \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \]

\[ \Rightarrow \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ 0 & a_{22}' & a_{23}' \\ 0 & 0 & a_{33}'' \end{bmatrix} \]

\[ [A] \]

\[ [A'] \]

\[ \det [A] = \det [A'] = a_{11} a_{22}' a_{33}'' \text{ (can be checked)} \]

Therefore,

\[ \det [A] \Rightarrow \text{product of the diagonal elements of its upper triangular matrix} \]
Note that the swapping of rows of a matrix does not alter values of determinant. However, sign changes: \((-1)^k\), where \(k\) is the number of times rows are swapped.

Re-visit

\[ \text{det}[A]_{3\times3} = a_{11}a_{22}'a_{33}'' \quad (\text{product of the diagonal elements of UTN of } A) \]

**Note:** 1. For a matrix to be non-singular \( \text{det}[A] \neq 0 \)

\[ \text{or} \quad a_{11}a_{22}'a_{33}'' \neq 0 \]

Alternatively, the corresponding three equations are linearly independent; rank of

\[ [A] = \# \text{of variables} = \# \text{of eqns} = 3. \]

Geometrically, three planes intersect at a unique point in space, or none of them is \( \parallel \) to the other.

Alternatively,

If \( a_{33}'' = 0 \), \( \text{det}[A] = 0 \) \( \Rightarrow \) the matrix is singular; rank of the matrix = 2\((< 3)\); only first two equations are linearly independent; the problem is under-determined and one more equation is required to solve\((x_1, x_2, x_3)\). Algebraically, 3\(^{rd}\) plane is \( \parallel \) to one of the other two planes.

**Pivoting and ill-conditioning:**

\[ A\tilde{X} = \tilde{b} \Rightarrow \tilde{X} = A^{-1}\tilde{b} \quad ; \quad A^{-1} = \frac{Ad[A]}{|A|} \]

Therefore, for \( \tilde{X} \) to be solved or \( A \) to be invertible, \( |A| \neq 0 \). Yet if \( |A| \to 0 \) (or it is a small number), a small change in \( |A| \) will lead to a large change in \( A^{-1} \).

\( \square \) **Note:** \( Y = \frac{1}{X} \), \( \frac{dy}{dx} = -\frac{1}{x^2} \)

In other words, a small change in \( X \) will lead to large change in \( Y \).

In such case, the problem is said to be ill-conditioned. To invert such a matrix, large machine precision may be required, and one has to be careful with round-off errors.

Recall, determinant of a matrix is the product of the diagonal elements of UTN. Therefore, pivotal elements should not only be zero, but also large, or the matrix should be “diagonally strong”.

---

16
Example:  \[ 0.0001x_1 + x_2 = 1 \]  \[ x_1 + x_2 = 2 \]

Working with 4\(^{th}\) decimal, apply GE with 0.0001 as the pivotal element to obtain 
\[ x^T = [0.0000 \quad 1.0000] \] which is wrong. Now, swap the equations as 
\[ x_1 + x_2 = 2 \]
\[ 0.0001x_1 + x_2 = 1 \]

Apply GE to obtain 
\[ x^T = [1.0000 \quad 1.0000] \] which is 4\(^{th}\) decimal accurate.

This is called pivoting. Swap the row, so that the pivotal element is relatively larger. Also, 
scaling (or multiplying equation (A) by 10000) can be done before applying GE.

Example: Solve by GE:

\[
\begin{bmatrix}
1 & -1 & 2 \\
2 & -2 & 3 \\
1 & 1 & 1
\end{bmatrix}
\begin{bmatrix}
x_1 \\
x_2 \\
x_3
\end{bmatrix}
=
\begin{bmatrix}
-8 \\
-20 \\
-2
\end{bmatrix}
\]

Step 1:
\[
\begin{bmatrix}
1 & -1 & 2 \\
0 & 0 & -1 \\
0 & 2 & -1
\end{bmatrix}
\begin{bmatrix}
x_1 \\
x_2 \\
x_3
\end{bmatrix}
=
\begin{bmatrix}
-8 \\
-4 \\
+6
\end{bmatrix}
\]

Row pivoting is required (or swap 2\(^{nd}\) equation with 3\(^{rd}\) so that pivotal elemental is non – zero).

\[
\begin{bmatrix}
1 & -1 & 2 \\
0 & 2 & -1 \\
0 & 0 & -1
\end{bmatrix}
\begin{bmatrix}
x_1 \\
x_2 \\
x_3
\end{bmatrix}
=
\begin{bmatrix}
-8 \\
+6 \\
-4
\end{bmatrix}
\]

We have now UTM. Reverse substitution will yield
\[ x^T = [-11 \quad 5 \quad 4] \]

\[ \text{det}(A) = 1 \times 2 \times -1 = -2 \neq 0 \] (matrix is singular, rank = 3, all 3 equations are linearly independent ). Also, note that we swapped one time. So, there is the multiplication with -1.

Column pivoting (generally it should be avoided)

\[
\sqrt{\begin{bmatrix}
1 & 2 & -1 \\
0 & -1 & 0 \\
0 & -1 & 2
\end{bmatrix}}
\begin{bmatrix}
x_1 \\
x_2 \\
x_3
\end{bmatrix}
=
\begin{bmatrix}
-8 \\
-4 \\
+6
\end{bmatrix}
\]

Column 2 is replaced with column 3 to make the pivotal element \( \neq 0 \). However, note that the variables \( x_2, \text{ and } x_3 \) are also swapped in the column vector \( \vec{x} \), else you would be solving a different set of equations!
\[ \begin{align*}
  x_1 + 2x_2 - x_3 &= -8 \\
  -x_2 &= -4 \\
  -x_2 + 2x_3 &= +6
\end{align*} \] (left) original equation
\[ \begin{align*}
  x_1 + 2x_3 - x_2 &= -8 \\
  -x_3 &= -4 \\
  2x_2 - x_3 &= +6
\end{align*} \] (right) swapped equation

Proceed as follows:

\[ \begin{pmatrix}
  1 & -2 & -1 \\
  0 & -1 & 0 \\
  0 & 0 & 2
\end{pmatrix} \begin{bmatrix}
  x_1 \\
  x_3 \\
  x_2
\end{bmatrix} = \begin{bmatrix}
  -8 \\
  -4 \\
  10
\end{bmatrix} \]

Reverse substitution will yield \( x^T = [-11, 5, 4] \)
Lecture #04

Gauss-Jordan

1. Procedure is similar to that of GE

2. Normalize the pivotal element

3. Eliminate the unknown from all rows, below and above the pivot row

4. No back substitution is required as required in GE.

\[
A\vec{X} = \vec{b}
\]

\[
\begin{bmatrix}
 a_{11} & a_{12} & a_{13} \\
 a_{21} & a_{22} & a_{23} \\
 a_{31} & a_{32} & a_{33}
\end{bmatrix}
\begin{bmatrix}
 x_1 \\
 x_2 \\
 x_3
\end{bmatrix}
= \begin{bmatrix}
 b_1 \\
 b_2 \\
 b_3
\end{bmatrix}
\]

Step 1:

\[
a_{1j}' = \frac{a_{1j}}{a_{11}} \quad j = 1,3 \text{ (normalize } a_{11} \text{ pivotal element) to 1.0)}
\]

\[
b_1' = \frac{b_1}{a_{11}}
\]

\[
\begin{align*}
a_{2j}' &= a_{2j} - a_{1j}' \times a_{21} \\
a_{3j}' &= a_{3j} - a_{1j}' \times a_{31}
\end{align*}
\]

\[
\begin{align*}
b_2' &= b_2 - b_1' \times a_{21} \\
b_3' &= b_3 - b_1' \times a_{31}
\end{align*}
\]

\[
\begin{bmatrix}
 1 & a_{12}' & a_{13}' \\
 0 & a_{22}' & a_{23}' \\
 0 & a_{32}' & a_{33}'
\end{bmatrix}
\begin{bmatrix}
 \vec{x}
\end{bmatrix}
= \begin{bmatrix}
 b_1' \\
 b_2' \\
 b_3'
\end{bmatrix}
\]

Step 2:

\[
a_{2j}'' = \frac{a_{2j}'}{a_{22}'} \quad j = 2,3 \text{ (normalize pivotal element of } 2^{nd} \text{ row to 1.0)}
\]

\[
b_2'' = \frac{b_2'}{a_{22}'}
\]

\[
\begin{align*}
a_{1j}'' &= a_{1j}' - a_{2j}' \times a_{12}' \\
b_1'' &= b_1' - b_2' \times a_{12}'
\end{align*}
\]

Note this is the extra step in GE.

\[
\begin{align*}
a_{3j}'' &= a_{3j}' - a_{2j}' \times a_{32}' \\
b_3'' &= b_3' - b_2' \times a_{32}'
\end{align*}
\]

This is the same step as in GE.
Step 3: \( b_3''' = b_3'' / a_{33}'' \) (normalize pivotal element to 1)

\[
\begin{bmatrix}
1 & 0 & a_{13}'' \\
0 & 1 & a_{23}'' \\
0 & 0 & a_{33}''
\end{bmatrix}
\begin{bmatrix}
x_1 \\
x_2 \\
x_3
\end{bmatrix} = \begin{bmatrix} b_1'' \\ b_2'' \\ b_3'' \end{bmatrix}
\]

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
x_1 \\
x_2 \\
x_3
\end{bmatrix} = \begin{bmatrix} b_1''' \\ b_2''' \\ b_3''' \end{bmatrix}
\]

Therefore, \( X^T = b'''^T : solution \).

No back substitution is required for a unit matrix!

Make a note that G-J method can also be used to determine inverse of the matrix, if working on the augmented matrix. **Check text books for more details.**

**example:**

\[
\begin{bmatrix}
1 & -1 & 2 \\
1 & 1 & 1 \\
2 & -2 & 3
\end{bmatrix}
\begin{bmatrix}
x_1 \\
x_2 \\
x_3
\end{bmatrix} = \begin{bmatrix} -8 \\ -2 \\ -20 \end{bmatrix}
\]

\[
\begin{bmatrix}
1 & -1 & 2 \\
0 & 2 & -1 \\
0 & 0 & -1
\end{bmatrix}
\begin{bmatrix}
x_1 \\
x_2 \\
x_3
\end{bmatrix} = \begin{bmatrix} -8 \\ 6 \\ -4 \end{bmatrix} \quad \text{(pivotal element already had ‘1’ ⇒ no need to normalize!)}
\]

\[
\begin{bmatrix}
1 & -1 & 2 \\
0 & 1 & -0.5 \\
0 & 0 & -1
\end{bmatrix}
\begin{bmatrix}
x_1 \\
x_2 \\
x_3
\end{bmatrix} = \begin{bmatrix} -8 \\ 3 \\ -4 \end{bmatrix} \quad \text{(pivotal row was divided by 2 to make pivotal element to be 1)}
\]

\[
\begin{bmatrix}
1 & 0 & 1.5 \\
0 & 1 & -0.5 \\
0 & 0 & -1
\end{bmatrix}
\begin{bmatrix}
x_1 \\
x_2 \\
x_3
\end{bmatrix} = \begin{bmatrix} -5 \\ 3 \\ -4 \end{bmatrix} \quad \text{(rows were subtracted above and below from the pivotal row)}
\]

\[
\begin{bmatrix}
1 & 0 & 1.5 \\
0 & 1 & -0.5 \\
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
x_1 \\
x_2 \\
x_3
\end{bmatrix} = \begin{bmatrix} -5 \\ 3 \\ 4 \end{bmatrix} \quad \text{(pivotal element was made to be 1)}
\]

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
x_1 \\
x_2 \\
x_3
\end{bmatrix} = \begin{bmatrix} -11 \\ 5 \\ 4 \end{bmatrix} \quad \text{(rows 1 & 2 subtracted from the pivotal row)}
\]

\[
X^T = [-11 \ 5 \ 4]^T
\]

You should ensure that the programming code for G-J is written by modifying the code for GE, instead of writing afresh, by changing the indices for i and j.
**LU Decomposition**: Two similar/identical methods

Dolittle               Crout’s

\[ A \vec{X} = \vec{b} \]

(This method is considered to be the best if only right hand side \( \vec{b} \) changes from problem/case to problem/case)

\[ A = LU \]

decompositions into \( L \) and \( U \)

\[
\begin{bmatrix}
1 & 0 & 0 \\
l_{21} & 1 & 0 \\
l_{31} & l_{32} & 1
\end{bmatrix}
\begin{bmatrix}
U_{11} & U_{12} & U_{13} \\
0 & U_{22} & U_{23} \\
0 & 0 & U_{33}
\end{bmatrix}
\]

\[
\begin{bmatrix}
l_{11} & 0 & 0 \\
l_{21} & l_{22} & 0 \\
l_{31} & l_{32} & l_{33}
\end{bmatrix}
\begin{bmatrix}
1 & U_{12} & U_{13} \\
0 & 1 & U_{23} \\
0 & 0 & 1
\end{bmatrix}
\]

In either case, steps are as follows:

\[ A = LU \quad \text{(decompose)} \]

\[ LU \vec{X} = \vec{b} \quad \Rightarrow L\vec{d} = \vec{b}, \quad \text{solve for } \vec{d} \text{ first} \]

\[ U\vec{X} = \vec{d} \quad \Rightarrow \text{solve for } \vec{X} \]

Example: \[
\begin{bmatrix}
1 & -1 & 2 \\
1 & 1 & 1 \\
2 & -2 & 3
\end{bmatrix}
\begin{bmatrix}
\vec{X}
\end{bmatrix}
= \begin{bmatrix}
-8 \\
-2 \\
-20
\end{bmatrix}
\]

\[ A = \begin{bmatrix}
l_{11} & 0 & 0 \\
l_{21} & 1 & 0 \\
l_{31} & l_{32} & 1
\end{bmatrix}_{3 \times 3}
\begin{bmatrix}
U_{11} & U_{12} & U_{13} \\
0 & U_{22} & U_{23} \\
0 & 0 & U_{33}
\end{bmatrix}_{3 \times 3}\]

\[
\begin{bmatrix}
U_{11} & U_{12} & U_{13} \\
l_{21}U_{11} & (l_{21}U_{12}) & (l_{21}U_{13}) \\
l_{31}U_{11} & (l_{31}U_{12}) & (l_{31}U_{13}) \\
\end{bmatrix}
\begin{bmatrix}
l_{21U_{22}} & + & U_{23} \\
l_{31U_{22}} & + & U_{33}
\end{bmatrix}_{3 \times 3}
\]

Match,

\[ U_{11} = 1, \quad U_{12} = -1, \quad U_{13} = 2 \]
\[ l_{21}U_{11} = 1, \quad l_{21}U_{12} + U_{12} = 1, \quad l_{21}U_{13} + U_{23} = 1 \]
\[ l_{31}U_{11} = 2, \quad l_{31}U_{12} + l_{32}U_{23} = -2, \quad l_{31}U_{13} + l_{32}U_{23} + U_{33} = 3 \]

Therefore, there are 9 unknown & 9 equations to solve and the problem is well defined.

**How do we obtain LU?**

Well, use GE to reduce \( A \) to an upper triangular matrix \( U \).

However, in addition, store multiplication coefficients of GE as the coefficients \( l_{21}, l_{31}, \text{and} l_{32} \) of lower triangular matrix

\[ l_{ik} = \frac{a_{ik}}{a_{kk}}; \quad k = 1 \text{ to } n - 1 \]
\[ i = k + 1 \text{ to } n \]

It is clear that the programming code used for GE to reduce the matrix \( A \) to UTM (U) is the same as that for determining U of LU decomposition method. In addition, the coefficients of \( L \) are also determined automatically by defining an extra coefficient \( l_{ik} \) (see above) in the same programming code.

Example:

\[ A = \begin{bmatrix} 1 & -1 & 2 \\ 1 & 1 & 1 \\ 2 & -2 & 3 \end{bmatrix} \]

**Step 1:**

\[
\begin{bmatrix}
1 & 0 & 0 \\
l_{21} & 1 & 0 \\
l_{31} & l_{32} & 1
\end{bmatrix}
\begin{bmatrix}
U_{11} & U_{12} & U_{13} \\
0 & U_{22} & U_{23} \\
0 & 0 & U_{33}
\end{bmatrix}
\]

\[ L \quad U \]

\[
\begin{bmatrix}
l_{21} = 1 & 0 & 0 \\
l_{31} = 1 & 1 & 0 \\
l_{32} = 0 & 1
\end{bmatrix}
\begin{bmatrix}
1 & -1 & 2 \\
0 & 2 & -1 \\
0 & 0 & -1
\end{bmatrix}
\]

\[ L \quad U \]

\[ \begin{bmatrix}
1 & -1 & 2 \\
1 & 1 & 1 \\
2 & -2 & 3
\end{bmatrix}
= \begin{bmatrix}
1 & 0 & 0 \\
1 & 1 & 0 \\
2 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
1 & -1 & 2 \\
0 & 2 & -1 \\
0 & 0 & -1
\end{bmatrix}
\]

\[ A \quad L \quad U \]
Step 2: \[ L\tilde{d} = \tilde{b} \]

\[
\begin{bmatrix}
1 & 0 & 0 \\
1 & 1 & 0 \\
2 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
d_1 \\
d_2 \\
d_3
\end{bmatrix}
=
\begin{bmatrix}
-8 \\
-2 \\
-20
\end{bmatrix}
\]

\[ d_1 = -8 ; \quad d_2 = -2 + 8 = 6; \quad d_3 = -20 + 16 = -4 \]

\[ d^T = [-8 \quad 6 \quad -4] \]

(Note: you have done forward substitution or solved a LTM, which is just opposite to solving an UTM or reverse/backward substitution step of GE)

Step 3: \[ U\bar{X} = \tilde{d} \]

\[
\begin{bmatrix}
1 & -1 & 2 \\
0 & 2 & -1 \\
0 & 0 & -1
\end{bmatrix}
\begin{bmatrix}
X_1 \\
X_2 \\
X_3
\end{bmatrix}
=
\begin{bmatrix}
-8 \\
6 \\
-4
\end{bmatrix}
\]

(Note this is the reverse/backward substitution of GE)

\[ X_3 = 4, \quad X_2 = (6 + 4)/2 = 5, \quad X_1 = -8 + 5 - 8 = -11 \]

\[ X^T = [-11 \quad 5 \quad 4]^T \quad \text{Ans.} \]

You should ensure that you are not writing a fresh code for the LU decomposition method. Rather, you simply modify the code you wrote earlier for the 1st part (forward substitution) of GE, or the code to reduce A to UTM. Then, write a code for inverting LTM and use the previously written code for the back-substitution or the reverse substitution of GE. In other words, the code of LU decomposition has three sub-parts.
Lecture #05

Matrix Inverse $A^{-1} = I$ (definition for $A^{-1}$)

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\]

If $A = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}$, then

\[
\begin{bmatrix}
a_{11} & a_{12} & a_{13} \\
a_{21} & a_{22} & a_{23} \\
a_{31} & a_{32} & a_{33}
\end{bmatrix}
\begin{bmatrix}
b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33}
\end{bmatrix}
= 
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\]

Making use of the rule of matrix multiplication (row×column), it is clear that

\[
\begin{bmatrix}
a_{11} & a_{12} & a_{13} \\
a_{21} & a_{22} & a_{23} \\
a_{31} & a_{32} & a_{33}
\end{bmatrix}
\begin{bmatrix}
b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33}
\end{bmatrix}
= 
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\]

Therefore, $b_{ij}$ can be calculated from as many equations.

However, LU decomposition can be used to determine $A^{-1}$ as well:

\[
A\bar{b}_1 = LU \bar{b}_1 = [1 \ 0 \ 0]^T
\]

\[
\Rightarrow \quad \bar{d}_1
\]

or

\[
L \bar{d}_1 = [1 \ 0 \ 0]^T \quad \Rightarrow \quad \text{determine } \bar{d}_1
\]

So,

\[
U\bar{b}_1 = \bar{d}_1 \quad \Rightarrow \quad \text{determine } \bar{b}_1
\]

Similarly,

\[
A\bar{b}_2 = LU \bar{b}_2 = [0 \ 1 \ 0]^T
\]

or

\[
L \bar{d}_2 = [0 \ 1 \ 0]^T \Rightarrow \text{determine } \bar{d}_2
\]
So, \( Ub_2 = d_2 \Rightarrow \text{determine } b_2, \text{ so forth,} \)

Example: \( [A] = \begin{bmatrix} 25 & 5 & 1 \\ 64 & 8 & 1 \\ 144 & 12 & 1 \end{bmatrix} = LU \)

Apply GE (Forward step)

\[
\begin{bmatrix} 25 & 5 & 1 \\ 0 & -4.8 & 0.56 \\ 0 & -16.8 & -4.36 \end{bmatrix} \Rightarrow \]

\(25 \quad 5 \quad 1\)
\(0 \quad -4.8 \quad 0.56\)
\(0 \quad -16.8 \quad -4.36\)

coefficients used to make 1\(\text{st}\) elements of the rows, bottom of the pivotal row to be zero

\( = \frac{64}{25} \text{ and } \frac{144}{25}\)

or \(2.56 \text{ and } 5.76\)

This is an UTM .

coefficient used to make the 1\(\text{st}\) element of the last row to be zero

\( = \frac{16.8}{4.8} = 3.5\)

Therefore,

\[ L = \begin{bmatrix} 1 & 0 & 0 \\ 2.56 & 1 & 0 \\ 5.76 & 3.5 & 1 \end{bmatrix} \]

or,

\[
\begin{bmatrix} 25 & 5 & 1 \\ 64 & 8 & 1 \\ 144 & 1 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 2.56 & 1 & 0 \\ 5.76 & 3.5 & 1 \end{bmatrix} \begin{bmatrix} 25 & 5 & 1 \\ 0 & -4.8 & -1.56 \\ 0 & 0 & 0.7 \end{bmatrix} \]

\[ \begin{bmatrix} 25 & 5 & 1 \\ 64 & 8 & 1 \\ 144 & 1 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 2.56 & 1 & 0 \\ 5.76 & 3.5 & 1 \end{bmatrix} \begin{bmatrix} 25 & 5 & 1 \\ 0 & -4.8 & -1.56 \\ 0 & 0 & 0.7 \end{bmatrix} \]

Now, determine \( A^{-1} \)

Step 1: \( LU \bar{b}_1 = [1 \ 0 \ 0]^T \)
\[
\begin{bmatrix}
1 & 0 & 0 \\
2.56 & 1 & 0 \\
5.76 & 3.5 & 1
\end{bmatrix}
\begin{bmatrix}
d_1 \\
d_2 \\
d_3
\end{bmatrix}
= 
\begin{bmatrix}
1 \\
0 \\
0
\end{bmatrix}
\]
\[L \vec{d_1}\]
\[d_1 = 1, \quad d_2 = 0 - 2.56 = -2.56, \quad d_3 = 0 - 5.76 + 3.50 \times 2.56 = 3.2\]

2. \[
\begin{bmatrix}
25 & 5 & 1 \\
0 & -4.8 & -1.56 \\
0 & 0 & 0.7
\end{bmatrix}
\begin{bmatrix}
b_{11} \\
b_{21} \\
b_{31}
\end{bmatrix}
= 
\begin{bmatrix}
d_1 \\
d_2 \\
d_3
\end{bmatrix}
\]
\[U \vec{b_1}\]
\[b_{31} = 3.2/0.7 = 4.571, \quad b_{21} = (-2.56 - 4.571 \times (-1.56))/−4.8 = −0.9524\]
\[b_{11} = (1 - 4.571 - 5 \times (-0.9524))/25.0 = 0.04762\]
or, \[\vec{b_1}^T = [0.04762 \quad −0.9524 \quad 4.571]^T\]

3. \[
\begin{bmatrix}
1 & 0 & 0 \\
2.56 & 1 & 0 \\
5.76 & 3.5 & 1
\end{bmatrix}
\begin{bmatrix}
d_1 \\
d_2 \\
d_3
\end{bmatrix}
= 
\begin{bmatrix}
0 \\
1 \\
0
\end{bmatrix}
\]
\[L \vec{d_1}\]
\[\begin{bmatrix}
25 & 5 & 1 \\
0 & -4.8 & -1.56 \\
0 & 0 & 0.7
\end{bmatrix}
\begin{bmatrix}
b_{12} \\
b_{22} \\
b_{32}
\end{bmatrix}
= 
\begin{bmatrix}
0 \\
1 \\
-3.5
\end{bmatrix}
\]
\[U \vec{b_2}\]
\[\vec{b_2}^T = [-0.0833 \quad 1.417 \quad -5.0]^T\]

Similarly,
\[\vec{b_3}^T = [0.03571 \quad -0.4643 \quad 1.429]^T\]

\[A^{-1} = \begin{bmatrix}
0.04762 & -0.0833 & 0.03571 \\
-0.9524 & 1.417 & -0.4643 \\
4.571 & -0.5 & 1.429
\end{bmatrix}\]

⇒ Methods so far to solve \(AX = \vec{b}\) and programming codes:

(a) GE: To solve a large number of algebraic equations, a programming code is required. As earlier shown, GE contains two distinct steps: (1) forward elimination to convert \(\vec{A}\) to an upper triangular matrix (UTM), (2)
Backward/reverse substitution to solve UTM. Therefore, while writing the code; it is recommended that one clearly distinguishes the two steps as “subroutines” (# 1 and 2). You will later see that the other methods also often require one or both of the steps/codes.

(b) GJ: The programming code for GJ is similar to that (code 1) of the forward elimination of GE, with some modification. The second part (code) of GE, ie. reverse substitution is not required. The modification or extra step is simple. First, pivotal elements should be normalized to 1; in addition to subtracting the modified pivotal row from the rows below the ‘ith’ row of GE, the pivotal row is also subtracted from the rows above. Therefore, one extra line is included in the code for GJ.

(c) The code to determine the determinant of the matrix A is the same as that (code 1) for converting A to UTM, ie. the first or forward elimination step of GE. Further, add a line to determine the \( \prod_{i=1}^{n} a_{ii} \) product of the diagonal elements of the UTM ie. one can put the flag to check if any of the \( a_{ii} \) is zero, the matrix is singular and cannot be inverted. One can also write a simple code to check the number # of zeros on the diagonal elements and therefore, determine the rank of the matrix as \( n - \# \).

(d) LU method: The programming code (# 3) is similar to that (code 1) of the forward step of GE, to determine UTM. An extra line in the programming loop is required to store the coefficients \( l_{ik} = \frac{a_{ik}}{a_{kk}} \), used to make the elements of the first column of the UTM to be zero, as the elements of the empty columns of the LTM.

\[
A = \begin{bmatrix} l_{11} & \circ \circ \\
                 l_{21} & l_{22} \end{bmatrix} \times \begin{bmatrix} - & - \\
                                       \end{bmatrix}
\]

\[
\text{LTM} \quad \quad \text{UTM}
\]

(e) Inverse of the matrix: First, the programming code (# 3) of LU is to be used. The forward substitution on LTM will yield/give \( \bar{d} \) (column matrix) and the backward substitution on UTM will yield \( \bar{b} \) (column matrix) (already available; # 2). Therefore, one new code/subroutine (# 4) is required for the forward substitution on LTM, which is not different from that (# 2) for the reverse substitution on UTM:

- \( A = LU \) (code # 3)
- Forward substitution \( \rightarrow \bar{d} \) (code #4)
- Backward substitution \( \rightarrow \bar{b} \) (code # 2)
Lecture #06

Thomas Algorithm (Tridiagonal matrix)

\[ A\bar{X} = \bar{b} \]

\[
\begin{bmatrix}
a_{11} & a_{12} & 0 & \cdots & 0 & 0 & 0 & 0 \\
a_{21} & a_{22} & a_{23} & \cdots & 0 & 0 & 0 & 0 \\
0 & a_{32} & a_{33} & a_{34} & \cdots & 0 & 0 & 0 \\
0 & 0 & a_{43} & a_{44} & a_{45} & \cdots & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & a_{nn-1} & a_{nn}
\end{bmatrix}
\begin{bmatrix}
X_1 \\
X_2 \\
X_3 \\
\vdots \\
X_n
\end{bmatrix}
= 
\begin{bmatrix}
b_1 \\
b_2 \\
b_3 \\
\vdots \\
b_n
\end{bmatrix}
\]

Tridiagonal matrix has 3 non-zero elements in all of its rows, except in the 1\textsuperscript{st} and last row, with one element each on the left and right of the diagonal element. The 1\textsuperscript{st} and last rows have one element on the right and left of the diagonal elements, respectively. It is a banded matrix around its diagonal:

\[
\begin{bmatrix}
\ldots & & & & \cdot & & & \\
\cdot & & & & \vdots & & & \\
\cdot & & & & \vdots & & & \\
\cdot & & & & \vdots & & & \\
\cdot & & & & \cdot & & & \\
\cdot & & & & \cdot & & & \\
\cdot & & & & \cdot & & & \\
\end{bmatrix}
\begin{bmatrix}
X_1 \\
X_2 \\
X_3 \\
\vdots \\
X_n
\end{bmatrix}
= 
\begin{bmatrix}
b_1 \\
b_2 \\
b_3 \\
\vdots \\
b_n
\end{bmatrix}
\]

Therefore, a tridiagonal matrix can be represented using single subscripted indices for its elements:

\[
\begin{bmatrix}
b_1 & c_1 & 0 & 0 & \cdots & 0 \\
a_2 & b_2 & c_2 & 0 & \cdots & 0 \\
0 & a_3 & b_3 & c_3 & \cdots & 0 \\
0 & 0 & 0 & 0 & \cdots & 0 \\
0 & 0 & 0 & 0 & \cdots & 0 \\
\end{bmatrix}
\]

Note that the element in the \(i\textsuperscript{th}\) row is represented as \((a_i, b_i, c_i)\). All \(b\) are on the diagonal.

Therefore, \(A\bar{X} = \bar{d}\), where \(A\) is a tridiagonal matrix and it represents the following set of linear algebraic equations:
\[
\begin{align*}
  b_1x_1 + c_1x_2 &= d_1 \\
  a_2x_1 + b_2x_2 + c_2x_3 &= d_2 \\
  a_3x_2 + b_3x_3 + c_3x_4 &= d_3 \\
  a_4x_3 + b_4x_4 + c_4x_5 &= d_4 \\
  \vdots & \quad \vdots \\
  a_nx_{n-1} + b_nx_n &= d_n
\end{align*}
\]

⇒ You must have noted that for the \(i^{th}\) row, \(b_i\) is the diagonal element multiplied with the variable \(x_i\) in the same row, whereas \(a_i\) is multiplied with \(x_{i-1}\)(the variable above \(i^{th}\) row) and \(c_i\) is multiplied with \(x_{i+1}\)(the variable below \(i^{th}\) row). Naturally, the first and last rows have only two variables.

⇒ (Tridiagonal system is quite common when using Finite Difference 2\textsuperscript{nd} order method to solve boundary value problems or partial differential eq\textsuperscript{ns}.)

**Thomas algorithm to solve such system:**

Step 1:

\(x_1\) is eliminated: \( \left( b_2 - \frac{c_1}{b_1}a_2 \right) x_2 + c_2x_3 = \left( d_2 - \frac{d_1}{b_1}a_2 \right) \)

(by dividing 1\textsuperscript{st} row with \(b_1\), multiplying with \(c_1\) and subtracting from row 2)

\(x_2\) is eliminated: \( \left( b_3 - \frac{c_2}{b_2}a_3 \right) x_3 + c_3x_4 = \left( d_3 - \frac{d_2}{b_2}a_3 \right) \)

\(\vdots\)

\(\vdots\)

\(x_{k-1}\) is eliminated: \( \left( b_k - \frac{c_{k-1}}{b_{k-1}}a_k \right) x_k + c_kx_{k+1} = \left( d_k - \frac{d_{k-1}}{b_{k-1}}a_k \right) \)

It is clear that,

\[
\begin{align*}
  \text{All } a_i \text{ are eliminated} \\
  \text{All } b_i \text{ are modified} \\
  \text{All } c_i \text{ are unaltered} \\
  \text{All } d_i \text{ are modified}
\end{align*}
\]

Last row: \( b_n = b_n - \frac{c_{n-1}}{b_{n-1}}a_n \); \( d_n = d_n - \frac{d_{n-1}}{b_{n-1}}a_n \)

(Note that \(a_n\) has moved to RHS, leaving behind \(b_nx_n\) only on the LHS)
It is important to note that $k^{th}$ row uses the latest modified values of $b_k$ and $d_k$ from the previous $(k-1)$ step. Therefore, there is no need to store the previous values of $(a, b, d)$ while writing the code.

**Back-substitution:**

$$X_n = \frac{d_n}{b_n} \quad (n^{th} \text{ row has only } b_n \text{ and } d_n)$$

$$X_{n-1} = \frac{d_{n-1} - c_{n-1}X_n}{b_{n-1}} \quad (n - 1 \text{ row has } b_{n-1}, c_{n-1}, \text{ and } d_{n-1})$$

⇒ A pseudo programming code can be written as follows:

**Tridiagonal (N, a, b, c, d, X)**

```plaintext
do   i = 1, N
    a(i) =
    b(i) =
    c(i) =
    d(i) =
end do

do   i = 2, N
    \[
    \begin{align*}
    b(i) &= b(i) - a(i) \frac{c(i - 1)}{b(i - 1)} \\
    d(i) &= d(i) - a(i) \frac{d(i - 1)}{b(i - 1)}
    \end{align*}
\]
\quad \text{forward substitution}
end do

$$X_n = \frac{d(n)}{b(n)}$$

do   (i) = N - 1, 1, -1
    \[
    X_i = \frac{d(i) - c(i)X_{i+1}}{b(i)}
    \]
\quad \text{reverse substitution}
end do
Indirect Methods

GE, GJ, LU decomposition are the direct methods to solve $A\vec{X} = \vec{b}$. Simple iterations can also be done to solve a set of algebraic equations, Jacobi and Gauss-Seidel being the two commonly used indirect methods.

**Ex.**

\[
\begin{bmatrix}
2 & 1 & 0 \\
1 & 2 & 1 \\
0 & 1 & 1 \\
\end{bmatrix}
\begin{bmatrix}
X_1 \\
X_2 \\
X_3 \\
\end{bmatrix}
= 
\begin{bmatrix}
1 \\
2 \\
4 \\
\end{bmatrix}
\]

Make a guess $X_1^{(1)}, X_2^{(1)}, X_3^{(1)}$

**Jacobi**

\[X_1^{(2)} = \frac{1 - X_2^{(1)}}{2}\]
\[X_2^{(2)} = \frac{2 - X_1^{(1)} - X_3^{(1)}}{2}\]
\[X_3^{(2)} = \frac{4 - X_2^{(1)}}{1}\]

Takes all $X_s^{(k-1)}$ of the previous iteration

**Gauss-Seidel**

\[X_1^{(2)} = \frac{1 - X_2^{(1)}}{2}\]
\[X_2^{(2)} = \frac{2 - X_1^{(2)} - X_3^{(1)}}{2}\]
\[X_3^{(2)} = \frac{4 - X_2^{(2)}}{1}\]

Uses the most latest iterated values of $X_s$.

In general: $A\vec{X} = \vec{b}$

**Jacobi**

$X_i^{(k+1)} = \frac{b_i - \sum_{j=1}^{n} a_{ij} X_j^{(k)}}{a_{ii}(\neq 0)}$ \hspace{1cm} \text{(}j \neq i\text{)}$

\[
\text{diagonal elements}
\]

**G-S**

\[
X_i^{(k+1)} = \begin{cases}
\frac{b_i - \sum_{j=1}^{i-1} a_{ij} X_j^{(k+1)} - \sum_{j=i+1}^{n} a_{ij} X_j^{(k)}}{a_{ii}(\neq 0)}
\end{cases}
\]

updated \hspace{1cm} \text{updated values}

latest \hspace{1cm} \text{latest values}

old \hspace{1cm} \text{old values}
At any $i^{th}$ row:

\[
\begin{array}{cccc}
1 & \cdots & i-1 & i & i+1 & \cdots & N \\
\hline
\text{updated} & \text{values} & \text{old} & \text{values} \\
(k+1) & (k)
\end{array}
\]

Schematically,

- Elements: multiply with the variables 1 to $x_{i-1}$
- $G$-S (modified)
  \[ X_i = \lambda X_i^{(new)} + (1 - \lambda) X_i^{(old)} \]
  \[ \lambda = 1 \text{ (unmodified)} \]
  \[ 0 < \lambda < 1 \Rightarrow \text{under} - \text{relaxation factor} \]
  \[ 1 < \lambda < 2 \Rightarrow \text{over} - \text{relaxation factor} \]
  \[ ('\lambda' \text{is often assumed depending upon guesses, etc}) \]

Look differently! : LDU method
\[
\begin{bmatrix}
  a_{11} & a_{12} & \ldots & a_{1n} \\
  \vdots & \vdots & & \vdots \\
  a_{n1} & \ldots & \ldots & a_{nn}
\end{bmatrix}_{n \times n} =
\begin{bmatrix}
  0 & 0 & \ldots & 0 \\
  a_{21} & 0 & \ldots & 0 \\
  \vdots & \vdots & \ddots & \vdots \\
  a_{n1} & \ldots & \ldots & a_{nn}
\end{bmatrix} +
\begin{bmatrix}
  \begin{bmatrix} 0 \\
  a_{21} \\
  \vdots \\
  a_{n1}
\end{bmatrix} & \begin{bmatrix} \vdots \\
  \vdots \\
  \vdots \\
  a_{nn}
\end{bmatrix}
\end{bmatrix} +
\begin{bmatrix}
  0 & 0 & \ldots & 0 \\
  0 & 0 & \ldots & 0 \\
  \begin{bmatrix} a_{n1} \\
  a_{n1} \\
  \vdots \\
  a_{nn}
\end{bmatrix} & \begin{bmatrix} \vdots \\
  \vdots \\
  \vdots \\
  a_{nn}
\end{bmatrix}
\end{bmatrix}
\]

\[
\text{strictly lower triangular matrix (} L \text{)} + D \text{ (diagonal elements only)} + \text{strictly upper triangular matrix (} U \text{)}
\]

\[
A = L + D + U
\]

\[
A\bar{X} = \bar{b}
\]

\[
(L + D + U)\bar{X} = \bar{b} \Rightarrow D\bar{X} = \bar{b} - L\bar{X} - U\bar{X}
\]

or

\[
\bar{X} = \frac{\bar{b} - L\bar{X} - U\bar{X}}{D}
\]

Jacobi:

\[
\bar{X}^{(k+1)} = \frac{\bar{b} - (L + U)\bar{X}^{(k)}}{D}
\]

or

\[
X_i^{(k+1)} = \frac{b_i - \sum_{j=1}^{n} X_j^{(k)} a_{ij}}{a_{ii}} \quad ; \quad j \neq i \ (j = i \text{ will represent diagonal element})
\]

\[
\text{G - S : } (L + D)\bar{X} = \bar{b} - U\bar{X}
\]

\[
(L + D)\bar{X}^{(k+1)} = \bar{b} - U\bar{X}^{(k)}
\]

\[
D\bar{X}^{(k+1)} = \bar{b} - U\bar{X}^{(k)} - L\bar{X}^{(k+1)}
\]

\[
X_i^{(k+1)} = \frac{b_i - \sum_{j=1}^{i-1} X_j^{(k+1)} a_{ij} - \sum_{j=i+1}^{n} X_i^{(k+1)} a_{ij}}{a_{ii}}
\]

(same as before) \quad (a_{ii} \neq 0)

Both methods will lead to the same solutions, with different # of iterations.
Lecture #07

Homogeneous linear algebraic equations

- Represents a special class of problems, also known as the Eigenvalue or Characteristic type of problems

Mathematically represented as \( A\vec{x} = 0 \) or \( \vec{b} = 0 \) (null vector)

\[
\begin{pmatrix}
  a_{11}x_1 + a_{12}x_2 + \cdots + a_{1n}x_n = 0 \\
  \vdots \\
  a_{n1}x_1 + a_{n2}x_2 + \cdots + a_{nn}x_n = 0
\end{pmatrix}
\]

Naturally, a trivial solution is \( \vec{x} = 0 \). In the simplest geometrical term, two straight lines or three planes intersect at the origin:

\[
\begin{align*}
x_1 - x_2 &= 0 \\
x_1 - 0.3x_2 &= 0
\end{align*}
\]

⇒ A more interesting problem to solve is in seeking a non-trivial solution when \( \det(A) = 0 \) or \( r < m \). Such simultaneous set of homogeneous linear equations when \( \det(A) = 0 \) is common in several engineering and mechanics applications, and also in the initial and boundary value problems. Such situation is better known as the eigenvalue problem and is represented by eigenvalues and the corresponding eigenvectors.

Compare this situation to the earlier discussed set of non-homogeneous linear algebraic equation \( A\vec{x} = \vec{b} \), where we sought a unique solution, when \( \det|A| \neq 0 \). Comparatively,

<table>
<thead>
<tr>
<th>Non-homogeneous equations</th>
<th>Homogeneous equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A\vec{x} = \vec{b} )</td>
<td>( A\vec{x} = 0 )</td>
</tr>
<tr>
<td>( \det(A) \neq 0 )</td>
<td>( \det(A) = 0 )</td>
</tr>
<tr>
<td>( r = m )</td>
<td>( r &lt; m )</td>
</tr>
<tr>
<td>Unique solution</td>
<td>Non-trivial solution</td>
</tr>
</tbody>
</table>

Eigenvalue problem
Let us look at

\[ A \bar{X} = \lambda \bar{X} \]  \hspace{1cm} (1) \]

where \( A \) is the coefficient matrix and \( \lambda \) is a non-zero number.

Matrix scalar quantity

or \[ (A - \lambda I)\bar{X} = 0 \]  \hspace{1cm} (2) \]

where \( I \) is an identity matrix

\[
I = \begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\]

Equation 1 or 2 represents eigenvalue problem and such equations commonly occur in several dynamic studies of distillation, adsorption and CSTR, viz. in solving \( \frac{d\bar{Y}}{dt} = 0 \). Equation (2) can also be written as

\[
\begin{align*}
(a_{11} - \lambda)X_1 + a_{12}X_2 + \cdots + a_{1n}X_n &= 0 \\
a_{21}X_1 + (a_{22} - \lambda)X_2 + \cdots + a_{2n}X_n &= 0 \\
\vdots & \vdots \\
a_{n1}X_1 + a_{n2}X_2 + \cdots + (a_{nn} - \lambda)X_n &= 0
\end{align*}
\]

or

\[
\begin{bmatrix}
a_{11} & a_{12} & \cdots & a_{1n} \\
\vdots & \vdots & & \vdots \\
a_{n1} & a_{n2} & \cdots & a_{nn}
\end{bmatrix}
\begin{bmatrix}
X_1 \\
X_2 \\
\vdots \\
X_n
\end{bmatrix}
= \lambda
\begin{bmatrix}
X_1 \\
X_2 \\
\vdots \\
X_n
\end{bmatrix}
\]

or

\[
A(\text{coefficient matrix}) \begin{bmatrix}
X_1 \\
X_2 \\
\vdots \\
X_n
\end{bmatrix}
= \lambda
\begin{bmatrix}
X_1 \\
X_2 \\
\vdots \\
X_n
\end{bmatrix}
\]

Re-visit \[ A\bar{X} = \lambda \bar{X} \] - eigenvalue problem

Most vectors \( \bar{X} \) will not satisfy such an equation. A common vector \( (iX_1 + jX_2) \) will change direction and magnitude to \( (ib_1 + jb_2) \) on the transformation by \( A \). Only certain special vectors \( \bar{X} \), called eigenvectors, corresponding to only special numbers, \( \lambda \) (\textit{either} + \textit{ve} \textit{or} - \textit{ve}) , called eigenvalues, will satisfy the above equation. In such case, the eigenvector \( \bar{X} \) does not change its direction or does not rotate when transformed by the coefficient matrix \( A \), but is only scaled by the eigenvalue \( \lambda \). See the geometrical representation below:
It turns out that \((n \times n)\) matrix \(A\) will give 'n' \(\lambda_s\) (eigenvalues), and each eigenvalue will give 'n' eigenvectors that will also be linearly independent. As an example,

\[
\begin{bmatrix}
a_{11} & a_{12} \\
a_{21} & a_{22}
\end{bmatrix}_{2 \times 2} \text{ will have } 2 \lambda_s \quad (\lambda_1 \text{ & } \lambda_2) \Rightarrow \begin{cases} 
\lambda_1 \rightarrow \{X\}_1 \\
\lambda_2 \rightarrow \{X\}_2
\end{cases}
\]

Both vectors \(\{X\}_1, \& \{X\}_2\) will satisfy \(A\vec{X} = \lambda\vec{X}\). They will also be linearly independent so that they can be used as a basis for the space-description. They may be orthogonal or non-orthogonal.

Similarly, \((3 \times 3)\) \(A\) matrix will give \(3\lambda_3(\lambda_1, \lambda_2, \lambda_3)\). Each \(\lambda\) will give three independent vectors \(\{X\}_1, \{X\}_2, \{X\}_3\) satisfying \(A\vec{X} = \lambda\vec{X}\).
or \((A - \lambda I)\vec{X} = 0\)

Linear algebra tells us that for \(\vec{X}\) to have a non-trivial solution \(\det|(A - \lambda I)| = 0\).

**Example:** \[ A = \begin{bmatrix} 2 & 1 \\ 1 & 2 \end{bmatrix} \]

\[ A\vec{X} = \lambda\vec{X} \]

\[ (A - \lambda I)\vec{X} = 0 \]

\[ \det \begin{bmatrix} 2 - \lambda & 1 \\ 1 & 2 - \lambda \end{bmatrix} = 0 \Rightarrow (2 - \lambda)^2 - 1 = 0 \]

\[ \lambda_1 = 1, \quad \lambda_2 = 3 \]

\[ \lambda_1 = 1: \quad \begin{bmatrix} 2 & 1 \\ 1 & 2 \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \end{bmatrix} = \begin{bmatrix} X_1 \\ X_2 \end{bmatrix} \]

Both equations yield \(X_1 = -X_2\) or \(X_1 + X_2 = 0\) \((r = 1)\)

So, \(\vec{X}\) \((\lambda_1 = 1)\): \((i - j) \equiv \{1\} \quad \{-1\}\)

\[ \lambda_2 = 3: \quad \begin{bmatrix} 2 & 1 \\ 1 & 2 \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \end{bmatrix} = 3 \begin{bmatrix} X_1 \\ X_2 \end{bmatrix} \]

Both equations yield \(X_1 = X_2\) or \(X_1 - X_2 = 0\) \((r = 1)\)

\[ \vec{X}\) \((\lambda_2 = 3)\): \((i + j) \equiv \{1\} \quad \{1\}\)

Note two vectors \((i - j)\) and \((i + j)\) are linearly independent and can be used as a basis for defining 2D space. They need not be orthogonal! They can be used as a linear combination of any other vector \(\vec{B}\) in 2D space:

\[ \vec{B} = c_1(i + j) + c_2(i - j) \]
System of ODEs

It may represent dynamics, i.e. how a system behaves due to a perturbation around steady state value. Such situation is common in kinetics and the heat and mass transfer related problems in chemical engineering.

\[
\begin{align*}
\frac{dx_1}{dt} &= f_1(X_1 \ldots X_n) \\
\frac{dx_2}{dt} &= f_2(X_1 \ldots X_n) \\
\vdots
\frac{dx_n}{dt} &= f_n(X_1 \ldots X_n)
\end{align*}
\]

\[\Rightarrow \quad \text{dynamics} \]

\[
\frac{d\bar{X}}{dt} = \bar{f}(\bar{X}) \quad [\bar{X}]^T \equiv [X_1, \ldots, X_n]
\]

Under SS, \(\bar{f}(\bar{X}) = 0\) \(\Rightarrow\) \(\bar{X} = \bar{X}_s\)

or

\[
\begin{align*}
f_1(X_1 \ldots X_n) &= 0 \\
f_2(X_1 \ldots X_n) &= 0 \\
\vdots
f_n(X_1 \ldots X_n) &= 0
\end{align*}
\]

These sets of algebraic equations may represent energy or species balance under SS.

Define, \(\bar{X}(t) = ?\)

\(\xi(t) = \bar{X}(t) - \bar{X}_s\) (deviation/departure/error variables)

\(\text{Element-wise}\) \(\xi_1(t) = X_1(t) - X_{1s}\)

or \(\xi_i(t) = X_i(t) - X_{is}\) \((i = 1 \ldots n)\)

or, \(\frac{d\xi}{dt} = \frac{d\bar{X}(t)}{dt} = \bar{f}(\bar{X})\)

or, \(\frac{d\xi_i}{dt} = f_i(X_1 \ldots X_n)\) \((i = 1 \ldots n)\)

\[
= f_1(X_{1s} + \xi_1, X_{2s} + \xi_2, \ldots X_{ns} + \xi_n) \\
= f_1(X_{1s}, X_{2s}, X_{3s}, \ldots X_{ns}) + \frac{\partial f_i}{\partial x_1} \bigg|_{X_{1s}} \xi_1 + \frac{\partial f_i}{\partial x_2} \bigg|_{X_{2s}} \xi_2 + \ldots + \frac{\partial f_i}{\partial x_n} \bigg|_{X_{ns}} \xi_n
\]

\[(SS)^0\]
\[ \xi_1 = (X_1 - X_{1s}), \quad \xi_2 = (X_2 - X_{2s}) \ldots \ldots, \xi_n = (X_n - X_{ns}) \]

(Taylor series expansion for multivariables: retain 1st order terms only, i.e. small departure from SS)

\[
\begin{align*}
\frac{d\xi_1}{dt} &= \begin{bmatrix} \frac{\partial f_1}{\partial X_1} & \frac{\partial f_1}{\partial X_2} & \ldots & \frac{\partial f_1}{\partial X_n} \end{bmatrix} \begin{bmatrix} \xi_1 \\ \xi_2 \\ \vdots \\ \xi_n \end{bmatrix} \\
\frac{d\xi_2}{dt} &= \begin{bmatrix} \frac{\partial f_2}{\partial X_1} & \frac{\partial f_2}{\partial X_2} & \ldots & \frac{\partial f_2}{\partial X_n} \end{bmatrix} \begin{bmatrix} \xi_1 \\ \xi_2 \\ \vdots \\ \xi_n \end{bmatrix} \\
\vdots \\
\frac{d\xi_n}{dt} &= \begin{bmatrix} \frac{\partial f_n}{\partial X_1} & \frac{\partial f_n}{\partial X_2} & \ldots & \frac{\partial f_n}{\partial X_n} \end{bmatrix} \begin{bmatrix} \xi_1 \\ \xi_2 \\ \vdots \\ \xi_n \end{bmatrix}
\end{align*}
\]

(row \times column multiplication rule)

Note: For two variables \( X_1 \) and \( X_2 \)

\[
\frac{d\xi_1}{dt} = \left. \frac{\partial f_1}{\partial X_1} \right|_{X_{1s}} (X_1 - X_{1s}) + \left. \frac{\partial f_1}{\partial X_2} \right|_{X_{2s}} (X_2 - X_{2s})
\]

\[
\frac{d\xi_2}{dt} = \left. \frac{\partial f_2}{\partial X_1} \right|_{X_{1s}} (X_1 - X_{1s}) + \left. \frac{\partial f_2}{\partial X_2} \right|_{X_{2s}} (X_2 - X_{2s})
\]

or,

\[
\begin{align*}
\frac{d\xi_1}{dt} &= \begin{bmatrix} \frac{\partial f_1}{\partial X_1} \\ \frac{\partial f_1}{\partial X_2} \\ \vdots \\ \frac{\partial f_1}{\partial X_n} \end{bmatrix} (X_1 - X_{1s}) \\
\frac{d\xi_2}{dt} &= \begin{bmatrix} \frac{\partial f_2}{\partial X_1} \\ \frac{\partial f_2}{\partial X_2} \\ \vdots \\ \frac{\partial f_2}{\partial X_n} \end{bmatrix} (X_2 - X_{2s})
\end{align*}
\]

or,

\[
\frac{d\xi}{dt} = A\xi \quad \text{or} \quad \xi' = A\xi
\]

where \( A = \begin{bmatrix} \frac{\partial f_1}{\partial X_1} & \ldots & \frac{\partial f_1}{\partial X_n} \\ \vdots & \ddots & \vdots \\ \frac{\partial f_n}{\partial X_1} & \ldots & \frac{\partial f_n}{\partial X_n} \end{bmatrix} \); \( A \) is called the Jacobian matrix of \( \bar{f} \).

Thus, we started from

\[
\frac{d\bar{X}}{dt} = \bar{f}(\bar{X})
\]

And derived:

\[
\frac{d\bar{\xi}}{dt} = A\bar{\xi}
\]

where \( \bar{\xi} = (\bar{X} - \bar{X}_s) \), and \( A \) is the Jacobian matrix of \( \bar{f} \) as

\[
\begin{bmatrix} \frac{\partial f_1}{\partial X_1} & \ldots & \frac{\partial f_1}{\partial X_n} \\ \vdots & \ddots & \vdots \\ \frac{\partial f_n}{\partial X_1} & \ldots & \frac{\partial f_n}{\partial X_n} \end{bmatrix}
\]
Lecture #08 (continue..)

Seeking solution to \( \frac{d\bar{\xi}}{dt} = A\bar{\xi} \quad \text{or} \quad \xi' = A\bar{\xi} \)

Let us assume, \( \xi_i = z_i e^{\lambda t}, \quad i = 1 \ldots n \quad (\text{solution}) \)

(This is the most plausible solution to a simple ODE)

or, \( \bar{\xi} = \bar{z} e^{\lambda t} \quad (\lambda = \text{scalar}, \quad \bar{z} = \text{constant vector}) \)

Substitute,

\[
z_i \lambda e^{\lambda t} = a_{i1} z_1 e^{\lambda t} + a_{i2} z_2 e^{\lambda t} + \cdots + a_{in} z_n e^{\lambda t} \quad (i = 1 \ldots n)
\]

or,

\[
\begin{align*}
a_{11}z_1 + a_{12}z_2 + \cdots + a_{1n}z_n &= \lambda z_1 \\
\vdots & \\
a_{n1}z_1 + a_{n2}z_2 + \cdots + a_{nn}z_n &= \lambda z_n
\end{align*}
\]

\( (\sum_{j=1}^{n} a_{ij}z_j = \lambda z_i; \quad i = 1, \ldots n) \)

or, \( A\bar{z} = \lambda \bar{z} \quad \bar{z}^T = [z_1 \ldots z_n] \)

or, \( (A - \lambda I)\bar{z} = 0 \quad \text{where} \quad A = \begin{bmatrix} a_{11} & \cdots & a_{1n} \\ \vdots & \ddots & \vdots \\ a_{n1} & \cdots & a_{nn} \end{bmatrix} \)

Thus, we have got a set of homogeneous equations which describes the characteristics of the system dynamics AND this equation can represent an eigenvalue problem. In summary, we started from

\[
\frac{d\bar{X}}{dt} = \bar{f}(\bar{X})
\]

and got

\[
\frac{d\bar{\xi}}{dt} = A\bar{\xi}
\]

where, \( A = \text{Jacobian matrix of } \bar{f} \) and \( \bar{\xi} = \bar{z} e^{\lambda t} \)

Now, we have \( (A - \lambda I)\bar{z} = 0 \)

Therefore, for a non-trivial solution (eigenvalue problem)

\[
\det|A - \lambda I| = 0 \quad (r < m)
\]
Solve for \( \lambda_i \) (eigenvalues) from the \( n^{th} \) degree polynomial on \( \lambda' \) after you have expanded the \((n \times n)\) \( |A - \lambda I| \) matrix to determine its determinant. Recall, every \( \lambda_i(i = 1 \ldots n) \) will give one \( \vec{z}^{(i)} \) eigenvector so that \( A\vec{z}^{(i)} = \lambda_i\vec{z}^{(i)} \). In other words,

\[
egin{align*}
\lambda_1 &\rightarrow \vec{z}^{(1)} e^{\lambda_1 t} \\
\lambda_2 &\rightarrow \vec{z}^{(2)} e^{\lambda_2 t} \\
\vdots &\quad \\
\lambda_n &\rightarrow \vec{z}^{(n)} e^{\lambda_n t}
\end{align*}
\]

And all these eigenvectors are linearly independent

Therefore, we have a general solution:

\[
\vec{\xi} = c_1 \vec{z}^{(1)} e^{\lambda_1 t} + c_2 \vec{z}^{(2)} e^{\lambda_2 t} + \cdots + c_n \vec{z}^{(n)} e^{\lambda_n t}
\]

where, \( c_1, c_2, \ldots c_n \) are arbitrary constants to be determined from initial conditions.

Numerical values of \( \lambda' \) decides how solution will behave i.e. error \( \xi \) or perturbation or deviation from SS will grow or decay. If the real part of \( \lambda \) is \( -\nu e' \), \( y \rightarrow y_s \) or solution will decay; if \( \nu e' \) solution will grow ⇒ (unstable)

**Example:** Study the dynamics

\[
\begin{align*}
X_1' &= -3X_1 + 2X_2 \\
X_2' &= X_1 - 2X_2
\end{align*}
\]

**Note:** If there is a non-homogeneous part in the equations, ignore it because only homogenous parts contribute to the growth or decay of the solution.

or \[ \frac{d\vec{x}}{dt} = A\vec{x}, \quad A = \begin{bmatrix} -3 & 2 \\ 1 & -2 \end{bmatrix} \]

Determine \( \lambda \): \det \begin{bmatrix} -3 - \lambda & 2 \\ 1 & -2 - \lambda \end{bmatrix} \Rightarrow \lambda^2 + 5\lambda + 4 = 0 \quad (\text{characteristic polynomial})

\[ \lambda_1 = -1, \quad \lambda_2 = -4 \quad \text{(two unique solutions or eigenvalues)} \]
Determine corresponding eigenvectors:

\[ \lambda_1 = -1: \quad \begin{bmatrix} -3 & 2 \\ 1 & -2 \end{bmatrix} \begin{Bmatrix} X_1 \\ X_2 \end{Bmatrix} = -1 \begin{Bmatrix} X_1 \\ X_2 \end{Bmatrix} \]

or \(-3X_1 + 2X_2 = -X_1\) and \(X_1 - 2X_2 = -X_2\) \(\Rightarrow X_1 = X_2 \Rightarrow \vec{X}^{(1)} = \begin{Bmatrix} 1 \\ 1 \end{Bmatrix}\) 

\(r = 1 < m\)

\[ \lambda_2 = -4 \quad X_1 = -2X_2 \quad \Rightarrow \vec{X}^{(2)} = \begin{Bmatrix} -2 \\ 1 \end{Bmatrix} \]

Check \(\vec{X}^{(1)}\) and \(\vec{X}^{(2)}\) are linearly independent.

\(\Rightarrow\) Note: both \(\lambda_s\) are \(-ve\). Therefore, the solutions will decay to the SS values or perturbation will die/decay, or solutions will not grow, or the systems will be stable.

General solution:

\[ \vec{X} = C_1 \vec{X}^{(1)} e^{\lambda_1 t} + C_2 \vec{X}^{(2)} e^{\lambda_2 t} \]

or \[ \begin{Bmatrix} X_1 \\ X_2 \end{Bmatrix} = C_1 e^{-t} \begin{Bmatrix} 1 \\ 1 \end{Bmatrix} + C_2 e^{-4t} \begin{Bmatrix} -2 \\ 1 \end{Bmatrix} \]

or \[ \begin{Bmatrix} X_1 \\ X_2 \end{Bmatrix} = C_1 e^{-t} - 2C_2 e^{-4t} \]

\[ X_2 = C_1 e^{-t} + C_2 e^{-4t} \]

(Note: For repeat or complex \(\lambda\), check the books for the methods to determine \(\vec{X}\))

Ex. \([A] = \begin{bmatrix} 0 & 2 & 3 \\ -10 & -1 & 2 \\ -2 & 4 & 7 \end{bmatrix}\) determine all \(\lambda_s\) and \(\vec{X}_s\).

From \(\text{det}[A - \lambda I] = 0 \Rightarrow \lambda_1 = 1, \lambda_2 = 2, \lambda_3 = 3\)

\(\text{A 3} \times \text{3 matrix will give 3}\lambda_s\)

\[ \lambda_1 = 1 \quad [A - \lambda I] \vec{X} = 0 \Rightarrow \begin{bmatrix} -1 & 2 & 3 \\ -10 & -2 & 2 \\ -2 & 4 & 6 \end{bmatrix} \begin{Bmatrix} X_1 \\ X_2 \\ X_3 \end{Bmatrix} = 0 \]

Apply Gauss Elimination:

\[ \begin{bmatrix} -1 & 2 & 3 \\ 0 & -22 & -28 \\ 0 & 0 & 0 \end{bmatrix} \begin{Bmatrix} X_1 \\ X_2 \\ X_3 \end{Bmatrix} = 0 \]
You will get only 2 independent eqns: \((\text{rank } r = 2 < m, \det(\cdot) = 0)\)

\[
\begin{align*}
X_1 &= 2X_2 + 3X_3 \quad \Rightarrow \\
-22X_2 - 28X_3 &= 0
\end{align*}
\]

choose \(X_3 = 1\)

\[
\begin{align*}
X_1 &= \frac{5}{11} \\
X_2 &= -\frac{14}{11}
\end{align*}
\]

Therefore,

\[
\bar{X}^{(1)} = \begin{bmatrix} \frac{5}{11} \\ -\frac{14}{11} \\ 1 \end{bmatrix}
\]

Similarly for

\[
\begin{align*}
\lambda_2 &= 2: & \left[\bar{X}^{(2)}\right]^T &= \begin{bmatrix} 1/2 & -1 & 1 \end{bmatrix} \\
\lambda_3 &= 3: & \left[\bar{X}^{(3)}\right]^T &= \begin{bmatrix} 1/2 & -3/4 & 1 \end{bmatrix}
\end{align*}
\]

Note: These are all linearly independent vectors \((\bar{X}^{(1)}_0 \neq C_1\bar{X}^{(2)} + C_2\bar{X}^{(3)})\). They may not be orthogonal.

Spring-problem (2nd order ODEs can also describe/represent an eigenvalue problem)

Force balance or mass \(m_1\) and \(m_2\), when the two blocks are displaced by \(X_1\) & \(X_2\) in the right direction from its original position:
\[ m_1 \frac{d^2 X_1}{dt^2} = -K X_1 + K (X_2 - X_1) \]
\[ m_2 \frac{d^2 X_2}{dt^2} = -K (X_2 - X_1) - K X_2 \]

\[ X_i = A_i \sin(\omega t) \text{ (assume a solution)} \]

(\text{or} \ \bar{X} = \bar{A} \sin(\omega t))

Therefore,

\[ X_i'' = -A_i \omega^2 \sin \omega t \]

Substitute,

\[ \begin{cases} 
\left( \frac{2K}{m_1} - \omega^2 \right) A_1 - \frac{K}{m_1} A_2 = 0 \\
- \frac{K}{m_2} A_1 + \left( \frac{2K}{m_2} - \omega^2 \right) A_2 = 0 
\end{cases} \]

\[ \text{or} \]

\[ \begin{vmatrix} 
\left( \frac{2K}{m_1} - \omega^2 \right) & - \frac{K}{m_1} \\
- \frac{K}{m_2} & \left( \frac{2K}{m_2} - \omega^2 \right) 
\end{vmatrix} \begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = 0 \]

Therefore, the characteristic equation describes an eigenvalue problem (or spring dynamics is an eigenvalue problem). It has assumed the form of

\[ (A - \omega^2 I) \bar{X} = 0 \]

where \( \omega^2 = \lambda \), \( A = \begin{bmatrix} \frac{2K}{m_1} & - \frac{K}{m_1} \\ - \frac{K}{m_2} & \frac{2K}{m_2} \end{bmatrix} \) and \( \bar{X} = \begin{bmatrix} X_1 \\ X_2 \end{bmatrix} \)

\text{Example (From Kreysig’s Math book)}

\[ m_1 = m_2 = 40 \text{ kg} \; ; \; K = 200 \text{ N/m} \]

For a non-trivial solution \( \det(A - \omega^2 I) \bar{X} = 0 \)

\[ \text{eq}^{ns}: \quad (10 - \omega^2) A_1 - 5 A_2 = 0 \]
\[ -5 A_1 + (10 - \omega^2) A_2 = 0 \]
\[ \det() : (10 - \omega^2)^2 - 25 = 0 \]

\[ \lambda_1 = 15, \quad \lambda_2 = 5 \quad \text{or} \quad \omega_1 = \sqrt{\lambda_1}, \quad \omega_2 = \sqrt{\lambda_2} \]

\[ \lambda_1 = 15 \quad A_1 = -A_2 \quad \text{or} \quad A^{(1)} = \begin{bmatrix} 1 \\ -1 \end{bmatrix} \]

\[ \lambda_2 = 5 \quad A_1 = A_2 \quad \text{or} \quad A^{(2)} = \begin{bmatrix} 1 \\ 1 \end{bmatrix} \]

General solution:

\[ \vec{X} = C_1 \vec{A}^{(1)} \sin \omega_1 t + C_2 \vec{A}^{(2)} \sin \omega_2 t \]

or \[ \begin{bmatrix} X_1 \\ X_2 \end{bmatrix} = C_1 \begin{bmatrix} 1 \\ -1 \end{bmatrix} \sin \omega_1 t + C_2 \begin{bmatrix} 1 \\ 1 \end{bmatrix} \sin \omega_2 t \]

\[ \begin{array}{c}
\text{or} \quad X_1 = C_1 \sin \omega_1 t + C_2 \sin \omega_2 t \\
\text{and} \quad X_2 = -C_1 \sin \omega_1 t + C_2 \sin \omega_2 t
\end{array} \]

Graphical representation of block oscillations:
Lecture #09

One more example of eigenvalue or characteristic type of problem:

Let us revisit Jacobi iteration to invert a matrix.

\[ A\vec{X} = \vec{b} \]
\[ \Rightarrow (L + D + U)\vec{X} = \vec{b} \]
\[ \Rightarrow D\vec{X} = \vec{b} - (L + U)\vec{X} \]

or \( \vec{X} = D^{-1}\vec{b} - D^{-1}(L + U)\vec{X} \)

or \( \vec{X} = S\vec{X} + \vec{C} \)

or \( \vec{X}^{(k+1)} = S\vec{X}^{(k)} + \vec{C} \) : Jacobi Iteration formula

S is called stationary matrix because very often, matrix \( A \) or \( (L, D, U) \) do not change and are fixed. It is \( \vec{b} \) (right hand side) that varies from one problem to the other, as a forcing function.

Define, error vector \( \vec{e}^{(k)} = \vec{X}^{(k)} - \vec{X} \)

Approximate value at iteration \# \( k \)

True value

Similarly,

\[ \vec{e}^{(k+1)} = \vec{X}^{(k+1)} - \vec{X} \]
\[ = S(\vec{X}^{(k)} - \vec{X}) = S\vec{e}^{(k)} \]

or \( \vec{e}^{(k+1)} = S\vec{e}^{(k)} \)

or \( \vec{e}^{(k)} = S^k \vec{e}^{(0)} \) (you should realize that it is an eigenvalue problem/equation
\[ A\vec{X} = \lambda\vec{X} \] with \( \lambda = 1 \))

For \( k \to \infty \) \( S^k \to 0 \) for convergence because \( \vec{e}^{(k)} \to 0 \) as \( \vec{e}^{(0)} \neq 0 \)

Therefore, criteria for the convergence: \( S^k \to 0 \) as \( k \to \infty \)

Let \( \{y_j\}_{j=1}^n \) be the eigenvectors corresponding to the \( \lambda_j \) eigenvalue of the stationary matrix
$S(n \times n)$. Recall eigenvectors are linearly independent. So, they can form the basis of $n$ dimensional space. Alternatively, any vector can be represented as the linear combination of the eigenvectors.

Therefore,

$$e^{(0)} = \sum_{j=1}^{n} c_j \nu_j$$

where $S \nu_j = \lambda_j \nu_j$

or $S \nu_1 = \lambda_1 \nu_1$, etc.

$$e^{(1)} = S e^{(0)} = \sum_{j=1}^{n} c_j \nu_j \lambda_j$$

$$e^{(2)} = S^2 e^{(0)} = \sum_{j=1}^{n} c_j \nu_j \lambda_j^2$$

(use $S \nu_j = \lambda_j \nu_j$)

$$e^{(k)} = \sum_{j=1}^{n} c_j \nu_j \lambda_j^k$$

For convergence, $k \to \infty$  $e^{(k)} \to 0$  or $|\lambda_j| < 1$  $(j = 1 \cdots n)$

For a $n \times n$ $S$ matrix, there will be $\lambda_1 \cdots \lambda_n$ eigenvalues.

If $|\lambda_{\text{max}}| < 1$  then all  $\lambda_j < 1$

Therefore, for Jacobi Iteration to converge: $|\lambda_{\text{max}}| < 1$

$$\text{(Max } \lambda_j \text{) } \equiv \text{spectral radius } \rho(S) < 1$$

There is the Gershgorin Theorem (Check the book by Strang) which states that in such case

$$\sum |a_{ij}| < |a_{ii}|$$

non – diagonal elements  \hspace{0.5cm} diagonal elements

Such matrix is said to be diagonally strong. It is a desirable characteristic of a matrix to be inverted. Compare two extreme situations:

Note that zero or no iterations are required to solve an identity matrix! Also, a diagonally strong matrix will require relatively fewer number of iterations. On the other hand, the above right hand matrix is a singular matrix and cannot be inverted. Similarly, a matrix with smaller
value-numbers on its diagonal relative to the other elements in the same row will require a relatively larger number of iterations to converge.

**Power Method**

The previous examples have shown that the 'dynamics' of a 1st order system can be inspected or characterized by determining $\lambda_{\text{max}}$ and $\lambda_{\text{min}}$, instead of all $\lambda$s. Therefore, a $n \times n$ matrix will have $n\lambda$s, and the overall response of the system will be the least sensitive to $\lambda_{\text{min}}$ and most sensitive to $\lambda_{\text{max}}$. The response corresponding to the other $\lambda$s will be intermediate. **Power method** is commonly used to determine $\lambda_{\text{max}}$ and also, $\lambda_{\text{min}}$.

If $[A]_{n \times n}$ matrix has $n\lambda$s (eigenvalues), then one can write $|\lambda_1| > |\lambda_2| > \cdots > |\lambda_n|$

And $AX = \lambda_{\text{max}}X$ and $AX = \lambda_{\text{min}}X$

**Method:** Make a guess of $X^T = [1 \ 0 \ 1]$ or $[1 \ 1 \ 0]$ (say, for a $3 \times 3$ matrix)

Then $AX^{(0)} \Rightarrow X^{(1)}$

Use $X^{(1)} = \frac{X^{(1)}}{\|X^{(1)}\|} = \frac{AX^{(0)}}{\|AX^{(0)}\|}$

\[
\left(\text{magnitude (you are scaling or normalizing the vector, i.e. } \tilde{a}/|a| \text{ or } \tilde{a}/\sqrt{a_1^2 + a_2^2 + a_3^2})\right)
\]

$X^{(k)} = \frac{AX^{(k-1)}}{\|AX^{(k-1)}\|}, \quad k = 1, 2, 3 (\# \ of \ iterations)$

Can be shown that when $k \to \infty$, $\|AX^{(k-1)}\| \to |\lambda_{\text{max}}|$

In other words, after sufficient # of iterations, one obtains maximum eigenvalue and the vector $X^{(k-1)}$ when transformed by ‘A’ matrix does not rotate and is just scaled by $\lambda_{\text{max}}$, i.e.

$AX^{(k-1)} = \lambda_{\text{max}}X^{(k)}$

In other words, $X^{(k-1)}$ and $X^{(k)}$ have the same directions.
Example: Determine $\lambda_{\text{max}}$ of $A = \begin{bmatrix} 0 & 2 & 3 \\ -10 & -1 & 2 \\ -2 & 4 & 7 \end{bmatrix}$

$v^{(1)} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \equiv [1 \ 0 \ 0]^T$ \hspace{1cm} (1st guess)

$v^{(2)} = \begin{bmatrix} 0 & 2 & 3 \\ -10 & -1 & 2 \\ -2 & 4 & 7 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ -2 \\ -2 \end{bmatrix} = \begin{pmatrix} 0.0000 \\ -0.9806 \\ -0.1961 \end{pmatrix}$

$|\lambda| = \sqrt{104} = 10.198$

$v^{(3)} = \begin{bmatrix} 0.0000 \\ -0.9806 \\ -0.1961 \end{bmatrix} \bigg/ \sqrt{2.5495^2 + 0.5884^2 + 5.2951^2} = \begin{pmatrix} -0.3714 \\ 0.55698 \\ 0.7428 \end{pmatrix}$

After 20 iterations,

$X^{(20)} = \begin{pmatrix} -0.3714 \\ 0.55698 \\ 0.7428 \end{pmatrix}$ with $\lambda^{(20)} = 3.0014$

You will see a gradual convergence from 10.198 to 3.0014.

The basics remains the same:

$AX^{(19)} = \lambda_{\text{max}}X^{(20)}$ and $X^{(19)}$ and $X^{(20)}$ will have approximately the same direction.

$\Rightarrow$ It can be shown that $\lambda_{\text{min}}$ of $A = \frac{1}{\lambda_{\text{max}}}$ where $\lambda_{\text{max}}$ is the highest eigenvalue of the inverse of matrix $A$ or $A^{-1}$:

$A\bar{X} = \lambda_{\text{max}}\bar{X}$

or $\bar{X} = A^{-1}(\lambda_{\text{max}}\bar{X}) = \lambda_{\text{max}}(A^{-1}\bar{X})$

or $A^{-1}\bar{X} = (\frac{1}{\lambda_{\text{max}}})\bar{X}$

or $B\bar{X} \equiv \lambda'_{\text{max}}\bar{X}$

where $B$ is $A^{-1}$ and $\lambda_{\text{min}}$ of $A$ is $\frac{1}{\lambda'_{\text{max}}}$ of $B$ where $\lambda'_{\text{max}}$ is the highest $\lambda$ of $B$. 
The $\lambda_{\text{max}}$ to $\lambda_{\text{min}}$ ratio is known as stiffness ratio and indicates the stiffness (maximum rate of change in the functional value corresponding to $\lambda_{\text{max}}$ relative to minimum rate corresponding to $\lambda_{\text{min}}$) of the system. A ratio $> 10$ indicates the system to be stiff requiring a fine step size for calculations (to be discussed later).

**Notes (From Strang's book):**

If $X$ is an eigenvector of $A$ corresponding to $\lambda_{\text{max}}$ and $A$ is invertible, then $X$ is also an eigenvector of $A^{-1}$ corresponding to the inverse of its $\lambda_{\text{max}}$.

Eigenvectors corresponding to different $\lambda_s$ are linearly independent.

A matrix and its transpose have the same eigenvalues.

A matrix is singular if and only if it has zero $\lambda$. A non-singular matrix has all non-zero $\lambda_s$.

$$\sum \lambda_i = \text{trace of } A = \sum_{i=1}^{n} a_{ii}$$

$$\prod \lambda_i = \det(A)$$

The $\lambda_s$ of an upper or lower triangular matrix are the elements on its main diagonal.

[It also follows that $\det A = \det(\text{UTM of } A) = \prod(a_{ii})_{\text{UTM}}$]

**Quiz 1**
Lecture #10

Nonlinear Algebraic Equations

Solving \[
F_1(X_1 \ldots X_n) = 0 \\
F_2(X_1 \ldots X_n) = 0 \\
\vdots \\
F_n(X_1 \ldots X_n) = 0
\]

or \( \bar{F}(\bar{X}) = 0 \)

or \[
\bar{F}(\bar{X}) = \left\{ \frac{F_1(\bar{X})}{\vdots} \frac{F_n(\bar{X})}{=} 0
\]

where, \( F_1(\bar{X}) \) takes the form such as \( (X_1 - \sin X_1) = 0 \)

or \( X_1 - \sin X_2 = 0 \)

and \( X_1 = e^{x_2} \)

Solving a set of nonlinear algebraic equations is naturally difficult.

Let us begin with solving one nonlinear equation:

\[
f(\alpha) = 0 \quad \text{(Root finding)} \quad \alpha = ?
\]

Closed Methods

1. Bracketing method (for a monotonically increasing or decreasing function)

Step 1: Corner the root. Find \( X_l \) and \( X_U \) such that

\[
f(X_l)f(X_U) < 0
\]

All it means is that one root is cornered or bracketed. Some functions may have multiple
roots (be careful and corner all three roots separately by plotting the function qualitatively but accurately).

\[ X_m^{(1)} = \frac{X_U + X_l}{2} = X_{old} \]

Check \( f(X_m) = 0 \). If true, you have the root or \( X_m = \alpha \)

If not, check \( \Rightarrow \) if \( f(X_m)f(X_l) < 0 \). If true,

\[ X_U = X_m \] (replace \( X_U \) with \( X_m \))

else \( X_l = X_m \) (replace \( X_l \) with \( X_m \))

(This way, you are cornering the root or coming closer to the root)

(Note: The other check \( f(X)f(X_U) < 0 \) will also work. If \(-ve \) \( X_l = X_m \) else \( X_U = X_m \))

Step 3:

\[ X_m^{(2)} = \frac{X_U + X_l}{2} = X_{new} \] \((X_U \& X_l \text{ are new values})\)

\{ you can begin error checks after 2nd iterations only \}

\[ |\xi_a| = \left| \frac{x_m^{\text{new}} - x_m^{\text{old}}}{x_m^{\text{old}}} \right| \times 100 < \varepsilon \] (specified by user)

else go to step 2 (keep iterating)

\mbox{till} \left| \frac{x^{(i+1)} - x^{(i)}}{x^{(i)}} \right| \times 100 < \varepsilon

Example: Van der Waals gas law/equation:

\[ (P + \frac{a}{V^2})(V - b) = \text{constant} \]
It is clear that this equation is polynomial in $V$ with $n = 3$.

Let us assume that the other variables and constants are known and the simplified equation takes the following form:

$$f(V) = 0$$

$$V^3 - 0.165V - 3.993 \times 10^{-4} = 0$$

Calculate $V$ or find the roots

Step 0: Bracket the root: $V\{0, 0.11\}$

$$X_l = 0, \quad X_U = 0.11$$

1. Check $f(X_l)f(X_U) < 0$

So that the root is bracketed (cornered)

2. $X_m^{(1)} = \frac{0 + 0.11}{2} = 0.055$ (3 digits accurate after decimal)

$$f(0.055)f(0) = 3.993 \times 10^{-4} \times 6.655 \times 10^{-5} > 0$$

(You would have checked whether $f(0.055) \times f(0.11) < 0$ or not as well!)

$$X_l = 0.055, \quad X_U = 0.11$$ (remains the same)

3. $X_m^{(2)} = \frac{X_l + X_u}{2} = \frac{0.055 + 0.011}{2} = 0.0825 = X_{\text{new}}$

$$f(X_m^{(2)}) = -1.622 \times 10^{-4}$$

Check $f(X_l)f(X_m) < 0$

$$X_U = 0.0825, \quad X_l = 0.055$$

4. Check $\varepsilon_a = \left| \frac{0.0825 - 0.055}{0.055} \right| \times 100 = 50.00\% > 0.2\%$ ($\varepsilon_s$)

Therefore, $X_m = \frac{0.055 + 0.0825}{2} = 0.06875$

Do 10 iterations to obtain $X_m = 0.0625$ with $\varepsilon_a = 0.1721\% < 0.2\%$
Ans. V (root) = 0.0625.

You should also prepare a table while solving:

<table>
<thead>
<tr>
<th>X_l</th>
<th>X_U</th>
<th>X_m</th>
<th>( f(X_m)f(X_l) &lt; 0 )</th>
<th>or</th>
<th>( f(X_m)f(X_U) &gt; 0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \checkmark )</td>
<td>( \checkmark )</td>
<td>( \checkmark )</td>
<td>Yes</td>
<td>|</td>
<td></td>
</tr>
<tr>
<td>( \checkmark )</td>
<td></td>
<td>( X_m )</td>
<td>No</td>
<td></td>
<td></td>
</tr>
<tr>
<td>:</td>
<td></td>
<td></td>
<td>10.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2. False – Position method (Regular-Falsi)

(This method is similar to the previous one, except draw a straight line connecting \( X_U \) and \( X_m \) to determine the intersection on X axis as the approximate value for the root)

Step 1: Bracket root

\[
f(X_U)f(X_l) < 0
\]

2. \( X_r^{(1)} = X_U - \frac{f(X_U)}{f(X_l) - f(X_U)} \times (X_l - X_U) \)

\[
\left( \frac{f(X_U)}{X_U - X_r} = \frac{0 - f(X_l)}{X_r - X_l} \right)
\]

\[
= \frac{X_U f(X_l) - X_l f(X_U)}{f(X_l) - f(X_U)} = X_{old}
\]

3. Check: \( f(X_r)f(X_l) < 0 \) or \( f(X_r)f(X_U) < 0 \)

\[
X_U = X_r \quad \text{or} \quad X_l = X_r
\]

\[
X_r^{(2)} = \frac{X_U f(X_l) - X_l f(X_U)}{f(X_l) - f(X_U)} = X_{new}
\]

Check \( \varepsilon_a < \varepsilon_e \) else go to 2; iterate till convergence. Note that it is difficult to choose between two methods. In general, this method is faster. There are always exceptions. Try \( f(X) = X^{10} - 1! \)
Open Methods

1. Fixed Point Iteration.

Step 1. \( f(X) = 0 \) ⇒ Modify/transform it to

\[
f(X) = X - g(X) = 0
\]

eg. \( f(X) = X - \cos X \)

or \( X - e^X \)

(Try for \( x^2 - 1 \) as \( X - g(X) = 0 \) or \( X = g(X) \))

Sometimes it is not straightforward & there may be more than one combination.

The working formula is

\[
Y = X = g(X)
\]

(2 equations and find its interaction)

\[
X_3 X_2 X_1 X_0
\]

Therefore, a sequence is generated.

\[
X_{n+1} = g(X_n)
\]

Sometimes, one has to start from left to the root; sometimes there is a divergence or spiral convergence, depending on type of functions.

\[
|g'(X)| < |Y'(X)| = 1 \quad \text{at } X = X_n
\]
**Note:** Closed methods often generate at least one root. Open methods may sometimes result in divergence depending upon type of function and starting guess, $X_0$. However, if they converge, they will do more quickly than the closed methods.

Step 2: Start with $X_0$

$$X_1 = g(X_0)$$

Step 3: Check $\varepsilon_a = \left| \frac{X_1 - X_0}{X_1} \right| < \varepsilon_s$

If not, $X_{old} = X_r$ (iterated value)

$$X_r = g(X_{old})$$

Check $\varepsilon_a = \left| \frac{X_r - X_{old}}{X_{old}} \right| < \varepsilon_s$

Else keep on iterating, keeping in mind the sequence $X_{n+1} = g(X_n)$.

### 2. Newton-Raphson Method

(Most popular method to solve a non-linear algebraic equation)

- **Step 1:** Choose

  $$X_r = X_0 \text{ (guess)}$$

  2. $f'(X_r) = \text{tangent at } X_r = \frac{f(X_r)}{X_0 - X_1}$

  $$X_1 = X_r - \frac{f(X_r)}{f'(X_r)}$$

- **Step 2:**

  (Note: $f'(X_r) \neq 0$)

  3. If $\varepsilon_a = \left| \frac{X_1 - X_r}{X_r} \right| \times 100 \leq \varepsilon_s$ stop

    $\alpha = X_1$ (root)

    else $X_r = X_1$ (repeat the steps)

- Sequence: $X_{i+1} = X_i - \frac{f(X_i)}{f'(X_i)}$; $f'(X_i) \neq 0$

  and $\varepsilon_{i+1} = \left| \frac{X_{i+1} - X_i}{X_i} \right| \times 100$
Notes: ⇒
- \( f'(X) \neq 0 \) is the major drawback of the method. There is a price for computing \( f'(X) \)
- Simple to code and convergence is fast (see later)
- There are cases of divergence and ‘missing’ roots, depending on function and initial guess

In all such cases, the best strategy is to plot and locate all roots graphically (qualitatively but accurately), and also, start close to the root.

The **NR method** can be derived from the Taylor series expansion showing the order of error in the method.

\[
f(X_{i+1}) = f(X_i) + f'(X_i)(X_{i+1} - X_i) + \frac{f''(X_i)}{2!} (X_{i+1} - X_i)^2 + \ldots
\]

\[
\approx f(X_i) + f'(X_i)(X_{i+1} - X_i) + O(h^2) \quad \text{(error)}
\]

If \( f(X_{i+1}) = 0 \), root is located

\[
X_{i+1} = X_i - \frac{f(X_i)}{f'(X_i)}
\]

**Example (NR):** \( f(X) = X^3 - 0.165X^2 + 3.993 \times 10^{-4}; f'(X) = 3X^2 - 0.33X \)

Step 1. \( X_0 = 0.05 \): Plot \( f(X) \) and choose \( X_0 \) close to the intersection of \( f(X) \) with \( X \) – axis

2. \( f'(X_0) = 3X_0^2 - 0.33X_0 \Rightarrow X_1 = X_0 - \frac{f(X_0)}{f'(X_0)} = 0.06242 \)

3. \( \varepsilon = \left| \frac{0.06242 - 0.0500}{0.0500} \right| \times 100 = 24.84\% \)

4. \( X_2 = X_1 - \frac{f(X_1)}{f'(X_1)} = 0.06238 \)

\( \varepsilon = 0.06411 \Rightarrow \alpha = 0.06238 \text{ (root)} \) (accurate to the 1st significant digit after decimal)
Lecture #11

Newton-Raphson (Multi-variables)

\[ F_1(X_1, X_2 \ldots X_n) = 0 \]
\[ F_2(X_1, X_2 \ldots X_n) = 0 \]
\[ \vdots \]
\[ F_n(X_1, X_2 \ldots X_n) = 0 \]

\[ \Rightarrow F(\bar{X}) = 0 \]

or \[ F_i(\bar{X}) = 0, \quad i = 1 \ldots n \]

Taylor-expansion of multi-variables:

\[ F_1(\bar{X}^{(k+1)}) \approx F_1(\bar{X}^{(k)}) + \frac{\partial F_1}{\partial X_1} \bigg|_{\bar{X}^{(k)} \neq X_1} (X_1^{(k+1)} - X_1^{(k)}) + \frac{\partial F_1}{\partial X_2} \bigg|_{\bar{X}^{(k)} \neq X_2} (X_2^{(k+1)} - X_2^{(k)}) + \ldots \]

\[ \frac{\partial F_1}{\partial X_n} \bigg|_{\bar{X}^{(k)} \neq X_n} (X_n^{(k+1)} - X_n^{(k)}) \quad (1^{st} \text{order accurate}) \]

\[ F_2(\bar{X}^{(k+1)}) \approx F_2(\bar{X}^{(k)}) + \frac{\partial F_2}{\partial X_1} \bigg|_{\bar{X}^{(k)} \neq X_1} (X_1^{(k+1)} - X_1^{(k)}) + \frac{\partial F_2}{\partial X_2} \bigg|_{\bar{X}^{(k)} \neq X_2} (X_2^{(k+1)} - X_2^{(k)}) + \ldots \]

\[ \frac{\partial F_2}{\partial X_n} \bigg|_{\bar{X}^{(k)} \neq X_n} (X_n^{(k+1)} - X_n^{(k)}) \]

\[ \vdots \]

\[ F_n(\bar{X}^{(k+1)}) \approx F_n(\bar{X}^{(k)}) + \frac{\partial F_n}{\partial X_1} \bigg|_{\bar{X}^{(k)} \neq X_1} (X_1^{(k+1)} - X_1^{(k)}) + \frac{\partial F_n}{\partial X_2} \bigg|_{\bar{X}^{(k)} \neq X_2} (X_2^{(k+1)} - X_2^{(k)}) + \ldots \]

\[ \frac{\partial F_n}{\partial X_n} \bigg|_{\bar{X}^{(k)} \neq X_n} (X_n^{(k+1)} - X_n^{(k)}) \]

If \( \bar{X}^{(k+1)} = \alpha \) (root at \((k + 1)^{th}\) iteration for all variables) \( \Rightarrow F_i(\bar{X}^{(k+1)}) = 0, \)

\( (i = 1 \ldots n) \)
\begin{align*}
\begin{bmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ F_n \end{bmatrix} &= \begin{bmatrix} F_1 \\ F_2 \\ \vdots \\ F_n \end{bmatrix}^{(k)} + \begin{bmatrix} \frac{\partial F_1}{\partial x_1} & \frac{\partial F_2}{\partial x_1} & \cdots & \frac{\partial F_n}{\partial x_1} \\ \frac{\partial F_1}{\partial x_2} & \frac{\partial F_2}{\partial x_2} & \cdots & \frac{\partial F_n}{\partial x_2} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial F_1}{\partial x_n} & \frac{\partial F_2}{\partial x_n} & \cdots & \frac{\partial F_n}{\partial x_n} \end{bmatrix} \begin{bmatrix} \Delta X_1 \\ \Delta X_2 \\ \vdots \\ \Delta X_n \end{bmatrix} \\
\Delta X_1 &= X_1^{(k+1)} - X_1^{(k)}, \text{ etc}
\end{align*}

or
\begin{align*}
\begin{bmatrix} \frac{\partial F_1}{\partial x_1} & \frac{\partial F_2}{\partial x_1} & \cdots & \frac{\partial F_n}{\partial x_1} \\ \frac{\partial F_1}{\partial x_2} & \frac{\partial F_2}{\partial x_2} & \cdots & \frac{\partial F_n}{\partial x_2} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial F_1}{\partial x_n} & \frac{\partial F_2}{\partial x_n} & \cdots & \frac{\partial F_n}{\partial x_n} \end{bmatrix} \begin{bmatrix} \Delta X_1 \\ \Delta X_2 \\ \vdots \\ \Delta X_n \end{bmatrix} &= \begin{bmatrix} F_1 \\ F_2 \\ \vdots \\ F_n \end{bmatrix}^{(k)}
\end{align*}

or
\begin{align*}
\overline{J} \Delta \overline{x}^{(k)} &= -\overline{F}^{(k)}
\end{align*}

or
\begin{align*}
\Delta \overline{x}^{(k)} &= -\overline{J}^{-1} \overline{F}^{(k)}
\end{align*}

or
\begin{align*}
\overline{x}^{(k+1)} &= \overline{x}^{(k)} - \overline{J}^{-1} \overline{F}^{(k)} \Rightarrow \text{ Multi-variable NR method (similar in form to single variable NR method)}
\end{align*}

Example: $F_1(\overline{Y}) = 4 - 8 \overline{Y}_1 + 4 \overline{Y}_2 - 2 \overline{Y}_1^3 = 0$

$F_2(\overline{Y}) = 1 - 4 \overline{Y}_1 + 3 \overline{Y}_2 + \overline{Y}_2^2 = 0$

Starting guess values
\begin{align*}
\overline{Y}^{(1)} &= [\overline{Y}_1 \ \overline{Y}_2]^T \Rightarrow [0.5 \ 0.5]^T
\end{align*}

Apply NR multivariable method formula:
\begin{align*}
\overline{x}^{(k+1)} &= \overline{x}^{(k)} - \overline{J}^{-1} \overline{F}^{(k)}
\end{align*}

or
\begin{align*}
\begin{bmatrix} \overline{Y}_1^{(k+1)} \\ \overline{Y}_2^{(k+1)} \end{bmatrix} &= \begin{bmatrix} \overline{Y}_1^{(k)} \\ \overline{Y}_2^{(k)} \end{bmatrix} - \begin{bmatrix} \frac{\partial F_1}{\partial \overline{Y}_1} & \frac{\partial F_1}{\partial \overline{Y}_2} \\ \frac{\partial F_2}{\partial \overline{Y}_1} & \frac{\partial F_2}{\partial \overline{Y}_2} \end{bmatrix}^{-1} \begin{bmatrix} F_1^{(k)} \\ F_2^{(k)} \end{bmatrix}
\end{align*}
\[
\begin{align*}
\{Y_1\} & = \{0.5\} - \begin{bmatrix} (-8 - 6Y_1^2) & 4 \\ -4 & (3 + 2Y_2) \end{bmatrix}^{-1} \begin{bmatrix} F_1 \\ F_2 \end{bmatrix}_{0.5,0.5} \\
& = \{0.5\} - \begin{bmatrix} -9.5 & 4 \\ -4 & 4 \end{bmatrix}^{-1} \begin{bmatrix} 1.75 \\ 0.75 \end{bmatrix} \\
& = \{0.5\} + \frac{1}{22} \begin{bmatrix} 4 & -4 \\ 4 & -9.5 \end{bmatrix} \begin{bmatrix} 1.75 \\ 0.75 \end{bmatrix}
\end{align*}
\]

(Note: For 2 \times 2 matrix simple Cramer’s rule was applied to determine the inverse of the matrix, else apply \(G - J\) or LU decomposition method can be used for a large size matrix)

\[
Y_1^{(1)} = 0.5 + \frac{1}{22} (4 \times 1.75 - 4 \times 0.75) = 0.6818
\]

\[
Y_2^{(1)} = 0.5 + \frac{1}{22} (4 \times 1.75 - 9.5 \times 0.75) = 0.4943
\]
Continue iteration till there is a convergence. One can prepare a table like this:

<table>
<thead>
<tr>
<th>#</th>
<th>(Y_1)</th>
<th>(Y_2)</th>
<th>(F_1)</th>
<th>(F_2)</th>
<th>(\frac{\partial F_1}{\partial Y_1})</th>
<th>(\frac{\partial F_1}{\partial Y_2})</th>
<th>(\frac{\partial F_2}{\partial Y_1})</th>
<th>(\frac{\partial F_2}{\partial Y_2})</th>
<th>(Y_1)</th>
<th>(Y_2)</th>
<th>(\varepsilon_{a1})</th>
<th>(\varepsilon_{a2})</th>
</tr>
</thead>
<tbody>
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<td>1</td>
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<td></td>
</tr>
</tbody>
</table>

**Secant Method**

(Another common open method; it does not require derivative to compute. Requires two starting adjacent guess values instead)

**Step1:**

**Straight line:** Choose \(X_{i-1}\) and \(X_i\) adjacent guess values near the root ‘\(a\)’.

1. Draw straight line connecting \(f(X_{i-1})\) and \(f(X_i)\). Find intersection on X axis \(\rightarrow X_{i+1}\)

\[
f'(X_{i+1}) = \frac{f(X_i)}{X_i - X_{i+1}} = \frac{f(X_{i-1})}{X_{i-1} - X_{i+1}}
\]

\[
X_{i+1} = X_i - f(X_i) \times \frac{(X_i - X_{i-1})}{f(X_i) - f(X_{i-1})}
\]

or

\[
X_{i+1} = X_i - \frac{f(X_i)}{f(X_i) - f(X_{i-1})} : \text{sequence}
\]
Check if \( f(X_{i+1}) \rightarrow (you\ have\ hit\ the\ root) \), else repeat with \( X_i \) and \( X_{i+1} \) following the above sequence.

- The method converges faster than Bisection method, but slower that NR. It is preferred over NR to avoid \( f' = 0 \).
- If \( X_i \to X_{i-1} \), note \( X_{i+1} = X_i - \frac{f(X_i)}{f'(X_i)} \) (same as NR!)

At this stage, let us look at Taylor’s series. Any function \( f(X) \) can be expanded as:

\[
\begin{align*}
& f(X) = f(X_0) + f'(X_0)(X - X_0) + \frac{f''(X_0)}{2!} (X - X_0)^2 + \cdots \frac{f^n(X_0)(X - X_0)^n}{n!} + \cdots \text{ to } \infty \quad \text{(exact)} \\
& \Rightarrow \quad f(X_{i+1}) = f(X_i) + f'(X_i)(X_i - X_i) + \frac{f''(X_i)}{2!} (X_{i+1} - X_i)^2 + \cdots \frac{f^n(X_i)(X_{i+1} - X_i)^n}{n!} + \cdots \text{ to } \infty \quad \text{(exact)}
\end{align*}
\]

or, \( f(X_{i+1}) \approx f(X_i) + \frac{f'(X_i)(X_{i+1} - X_i)}{1!} + \frac{f''(X_i)(X_{i+1} - X_i)^2}{2!} + \cdots \) \( 0(h^3) \) (accurate to \( 2^{nd} \) order)

or truncation error is \( 0(h^3) \) (accurate to \( 2^{nd} \) order)

\[
\begin{align*}
& \approx f(X_i) + \frac{f'(X_i)(X_{i+1} - X_i)}{1!} + 0(h^2) \quad \text{(approximate)} \\
& \quad \text{(accurate to } 1^{st} \text{ order or truncation error is } 0(h^2))
\end{align*}
\]

(error is one order greater than the accuracy of the method)

\[
= f(X_i) + f'(X_i)(X_{i+1} - X_i) + \cdots \frac{f^n(X_i)(X_{i+1} - X_i)^n}{n!} + R_{n+1} \quad \text{(exact!)}
\]

where, \( R_{n+1} = \frac{f^{n+1}(\xi)(X_{i+1} - X_n)^{n+1}}{(n+1)!} \quad \text{(can be exactly determined)} \)

However, \( \xi \) is ‘some’ number between \( X_{i+1} \) and \( X_i \).

Therefore,

\[
\begin{align*}
& f(X_{i+1}) = f(X_i) + \frac{f'(X_i)(X_{i+1} - X_i)}{1!} + \frac{f^2(\xi)(X_{i+1} - X_i)^2}{2!} \quad \text{(exact)}
\end{align*}
\]
\[ f(X_i) + \frac{f'(\xi)(X_{i+1} - X_i)}{1!} \quad (1^{st} \text{Mean Value Theorem}) \]

In other words, \( f'(\xi) = \frac{f(X_{i+1}) - f(X_i)}{(X_{i+1} - X_i)} \)

All it means there is \( \xi \) somewhere between \( X_i \) and \( X_{i+1} \), where the tangent equals the divided difference between two end points \( X_i - X_{i+1} \).

**Note:** Taylor series is used to determine the error or accuracy of a numerical method, or to determine the convergence of the method.

---

**Convergent Analysis**

**Fixed Point Iteration method**

\[ f(X) = X - g(X) \]

or \( X^{(n+1)} = g(X^{(n)}) \) \( (\text{iteration}) \)

If \( \alpha \) is the root then \( \alpha - g(\alpha) = 0 \)

Error at \( (n + 1)^{th} \) iteration = \( |\text{True Value} - \text{Approximate Value}| \)

\[ e^{n+1} = |\alpha - X^{(n+1)}| \]

\[ = |g(\alpha) - g(X^{(n)})| \]

\[ = |g'(\bar{X})(\alpha - X^{(n)})| \quad : \text{Recall Mean Value Theorem.} \bar{X} \text{ is between} \]

\( \alpha \) and \( X^{(n)} \)

\[ = |g'(\bar{X})e^n| \]

\[ \frac{e^{n+1}}{e^n} = |g'(\bar{X})| < 1 \] for error to decrease as \( n \to \infty \) where \( \bar{X} \) is \{\( \alpha , X^n \} \)

**NR Convergent**

\[ X^{k+1} = X^k - \frac{f_k}{f'_k}; \quad f'_k \neq 0 \]

\[ e^{(k+1)} = |\alpha - X^{k+1}| = \left| \alpha - X^k + \frac{f_k}{f'_k} \right| \]
\[ f(X^{k+1}) = f(X^k) + f_k'(X^{k+1} - X^k) + f''(\bar{X}) \left( \frac{(X_{k+1} - X_k)^2}{2!} \right) \]

\[ (\bar{X} : \{X_k, X_{k+1}\}) \]

If \( X^{k+1} \) is the root \((\alpha)\)

\[ 0 = f(X^k) + f_k'((\alpha - X^k) + \frac{(\alpha - X_k)^2}{2!} f''(\bar{X}) \]

\[ \therefore e^{(k+1)} = \left| \frac{f''(\bar{X})}{2 f_k'} (\alpha - X_k)^2 \right| \]

\[ = \left| \frac{f''(\bar{X})}{2 f_k'} (e^k)^2 \right| \]

\[ \frac{e^{(k+1)}}{(e^k)^2} = \left| \frac{f''(\bar{X})}{2 f_k'(\alpha)} \right| ; \quad f'(\alpha) \neq 0 \]

If \( k \to \infty \) \( e^{(k+1)} \) decreases by the square of the error in the previous step. In other words, the method has \textit{quadratic} convergence (fast convergence), although the method is only 1st order accurate. This is the special feature of NR method.
Lecture #12

Function Approximation: Interpolation

Fit a line passing through the data points to predict the functional value at an intermediate data. The line must pass through the data. The method is used to interpolate, for example, certain properties such as enthalpy and vapour pressure, at an intermediate point where the functional values or properties are not available.

Therefore, the data provided for the interpolation must be reliable/accurate.

Mathematically, interpolating function must be smooth (differential); continuous and pass through all data points. Compare it to ‘regression’ (best fit to the data) when the line need not pass through each data. Regression is used for prediction when data are experimentally measured or approximately calculated. Therefore, the regressed data may have errors.

(No regression topic to be covered in this course; no extrapolation as well!)

The main motivation for developing an interpolating function is not only to predict the functional value at an interpolating/intermediate point, but also to approximate a continuous \( f(x) \) or a discrete data set, \( y(x) \) as the \( n^{th} \) degree polynomial, \( P_n(x) \); thus the name of the current topic: function approximation. You will see in the later lessons that once you have your own approximated simple \( P_n(x) \), you will forgo the complex \( f(x) \) and work on \( P_n(x) \) instead, not only for calculating functional values at the intermediate points but also for computing \( f'(x) \) and \( f''(x) \) as \( P_n'(x) \) and \( P_n''(x) \), respectively. Also, all formulae for integration are also derived from \( P_n(x) \).
Interpolating function for ‘n’ data points

\[ P_{n-1}(X) = a_{n-1}X^{n-1} + a_{n-2}X^{n-2} + \cdots + a_0 \]  

a polynomial of degree \((n - 1)\).

If there are ‘n’ data points, a unique polynomial of degree \((n-1)\) passes through the points:

Ex. 1. \(y = mx + b \) (1\(^{st}\) order polynomial) passing through two data points. Two unknowns & two equations to solve \(m\) and \(b\):

2. Three data points

\[ y = ax^2 + bx + c \]  

(2\(^{nd}\) order polynomial, a quadratic equation)

(3 equations to solve three unknowns \(a, b, c\))

3. Thus, ‘n’ data points will have a unique polynomial of degree \((n - 1)\) passing through the points.

\[ y = a_{n-1}x^{n-1} + a_{n-2}x^{n-2} + \cdots + a_0 \]

Therefore,

\[
\begin{align*}
y_1 &= a_{n-1}x_1^{n-1} + a_{n-2}x_1^{n-2} + \cdots + a_0 \\
y_2 &= a_{n-1}x_2^{n-1} + a_{n-2}x_2^{n-2} + \cdots + a_0 \\
&\vdots \\
y_n &= a_{n-1}x_n^{n-1} + a_{n-2}x_n^{n-2} + \cdots + a_0 \\
\end{align*}
\]

\(n\) equations

or

\[
\begin{pmatrix}
y_1 \\
y_2 \\
\vdots \\
y_n \\
\end{pmatrix} =
\begin{pmatrix}
1 & x_1 & x_1^2 & \cdots & x_1^{n-1} \\
1 & x_2 & x_2^2 & \cdots & x_2^{n-1} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
1 & x_n & x_n^2 & \cdots & x_n^{n-1} \\
\end{pmatrix}
\begin{pmatrix}
a_0 \\
a_1 \\
\vdots \\
a_{n-1} \\
\end{pmatrix}
\]

Although the problem is well defined, it is tedious to solve \((a_0 \cdots a_{n-1})\) from a large sized \(n \times n\) matrix.

\[ \bar{y} = A_{n\times n} \bar{a} \]

The common methods to fit \(P_{n-1}\) polynomial passing through ‘n’ data points, or \(P_n\) through \((n + 1)\) data points:

**Newton’s divided-difference scheme**

Consider 2 data points

Let a line pass through \((X_0, Y_0)\) & \((X_1, Y_1)\):
\[
\begin{align*}
Y - Y_0 &= \frac{Y_1 - Y_0}{X - X_0} = \frac{X_1 - X_0}{X_1 - X_0} \\
or \quad Y &= Y_0 + \frac{Y_1 - Y_0}{X_1 - X_0} (X - X_0) \\
or \quad Y &= a_0 + a_1(X - X_0)
\end{align*}
\]

where \(a_0 = Y_0\)

\[a_1 = \frac{Y_1 - Y_0}{X_1 - X_0} = Y(X_1, X_0) \text{ defined as Newton First Divided Difference (N1DD)}\]

Similarly, define

\[Y[X_2, X_1, X_0] \equiv \text{Newton 2nd divided difference}\]

\[= \frac{Y[X_2, X_1] - Y[X_1, X_0]}{X_2 - X_0} \quad \text{(N2DD)}\]

\[Y[X_n, X_{n-1}, \ldots, X_0] = \frac{Y[X_n, X_{n-1}, \ldots, X_1] - Y[X_{n-1}, X_{n-2}, \ldots, X_0]}{X_n - X_0} \quad \text{(NnDD)}\]

Take 3 data points \((X_0, X_1, X_2)\):

\[Y(X) \equiv P_2(X) = a_0 + a_1(X - X) + a_2(X - X_0)(X - X_1)\]

By fitting \(P_2(X)\) to three data points, the three coefficients can be determined as

\[a_0 = Y_0, \quad a_1 = \frac{Y_1 - Y_0}{X_1 - X_0} \equiv Y[X_1, X_0]\]

and \[a_2 = \frac{Y[X_2, X_1] - Y[X_1, X_0]}{X_2 - X_0} \equiv Y[X_2, X_1, X_0]\]

Similarly for \((n+1)\) data

\[Y(X) \text{ or } P_n(X)\]

\[= a_0 + a_1(X - X_0) + a_2(X - X_0)(X - X_1) + \cdots + a_n(X - X_0)(X - X_1) \cdots (X - X_{n-1})\]

where \(a_0 = Y_0\)

\[a_1 = Y[X_1, X_0] = \frac{Y_2 - Y_0}{X_1 - X_0} \quad \text{(1st divided difference)}\]

\[a_n = Y[X_n, X_{n-1} \cdots X_0] \quad \text{(n-th divided difference)}\]
(Substitute $x = x_0, x_1, x_2 \ldots x_n$ in $P_n(x)$ to explore the sequence of polynomial)

In the tabular form,

<table>
<thead>
<tr>
<th>$i$</th>
<th>$X_i$</th>
<th>$Y_i$</th>
<th>$1^{st}$</th>
<th>$2^{nd}$</th>
<th>$\ldots$</th>
<th>$n^{th}$</th>
</tr>
</thead>
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<tr>
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<td>$\vdots$</td>
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<tr>
<td>$n-1$</td>
<td>$X_{n-1}$</td>
<td>$Y_{n-1}$</td>
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<tr>
<td>$n$</td>
<td>$X_n$</td>
<td>$Y_n$</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Note: Top row (circles) provides all NDD coefficients, $a_0, a_1, a_2 \ldots$

2. **Lagrangian Interpolation**

$$ y(x) = \sum_{k=0}^{n} l_k(x) y_k \quad (n + 1 \text{ data}) $$

Lagrangian coefficient of the $k^{th}$ term

Function must be a linear combination of $y_k$.

$l_k(x)$ must not depend on $y_k$.

$l_k(x)$ is defined as

$$ l_j(x_i) = \delta_{ij} \quad \text{(Kronecker delta)} $$

$$ = 1 \text{ when } i = j \text{ and } 0 \text{ when } i \neq j $$

Propose, $l_j(x) = C_j(x-x_0)(x-x_1)\ldots(x-x_{j-1})(x-x_{j+1})\ldots(x-x_n)$, and

$$ = 0 \quad (x \neq x_j) $$

$$ = 1 \quad (x = x_j) $$

Therefore, $C_j = (x_j-x_0)^{-1}(x_j-x_1)^{-1}\ldots(x_j-x_{j-1})^{-1}(x_j-x_{j+1})^{-1}\ldots(x_j-x_n)^{-1}$

and,$$ l_j(x) = \frac{(x-x_0)(x-x_1)\ldots(x-x_{j-1})(x-x_{j+1})\ldots(x-x_n)}{(x_j-x_0)(x_j-x_1)\ldots(x_j-x_{j-1})(x_j-x_{j+1})\ldots(x_j-x_n)} $$

The interpolating function is as follows:

$$ Y_n(x) = \sum_{k=0}^{n} l_k(x)Y_k \equiv P_n $$

where

$$ l_j(x) = \prod_{i=0}^{n} \frac{x-x_i}{(x_j-x_i)}_{(i \neq j)} $$
Suppose 2 data points: \((X_0, Y_0)\) and \((X_1, Y_1)\)

\[ Y_1(x) = l_0(x)Y_0 + l_1(x)Y_1 \]

\[ l_0 = \frac{x-x_1}{x_0-x_1}, \quad l_1 = \frac{x-x_0}{x_1-x_0} \]

or \[ Y_1(x) = \left(\frac{x-x_1}{x_0-x_1}\right)Y_0 + \left(\frac{x-x_0}{x_1-x_0}\right)Y_1 \]

(Since \(Y_1(x)\) is unique, it cannot be different from Newton-Divided difference formula; only forms are different)

Suppose there are 3 data points: \((X_0, Y_0), (X_1, Y_1),\) and \((X_2, Y_2)\)

\[ Y_2(x) = l_0(x)Y_0 + l_1(x)Y_1 + l_2(x)Y_2 \]

\[ l_0(x) = \frac{(x-x_1)(x-x_2)}{(x_0-x_1)(x_0-x_2)}; \quad l_1(x) = \frac{(x-x_0)(x-x_2)}{(x_1-x_0)(x_1-x_2)}, \Rightarrow l_2(x) = \frac{(x-x_0)(x-x_1)}{(x_2-x_0)(x_2-x_1)} \]

\[ Y(x) = \frac{(x-x_1)(x-x_2)}{(x_0-x_1)(x_0-x_2)}Y_0 + \frac{(x-x_0)(x-x_2)}{(x_1-x_0)(x_1-x_2)}Y_1 + \frac{(x-x_0)(x-x_1)}{(x_2-x_0)(x_2-x_1)}Y_2 \]

\[ = \text{same as NDDE or } aX^2 + bX + c \]

\[ \text{Ex.} \quad \begin{array}{c|c|c|c|c}
X_1 & X_2 & X & X_3 \\
-1 & 0 & 0.5 & 1.0 \\
\end{array} \]

\[ Y(t^0 c) \quad \begin{array}{c|c|c|c|c}
 & 10.1 & 11.3 & ? & 11.9 \\
\end{array} \]

\[ Y_2(x) = C_0 + C_1x + C_2x^2 \] (unique)

3 data points and 3 eqns to solve \(C_s\):

\[ \begin{bmatrix} 1 & -1 & 1 \\ 1 & 0 & 0 \\ 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} C_0 \\ C_1 \\ C_2 \end{bmatrix} = \begin{bmatrix} 10.1 \\ 11.3 \\ 11.9 \end{bmatrix}, \Rightarrow \text{Solve by any previously learnt method to obtain} \]

\[ C_0 = 11.3, \quad C_1 = 0.9, \quad \text{and} \quad C_2 = -0.3 \Rightarrow Y(0.5) = 11.675 \]

\[ \text{NDDE} \]

\[ 1^\text{st DD: } Y[X_0, X_1] = \frac{11.3-10.1}{0+1} = 1.2 \]

\[ 2^\text{nd DD: } Y[X_0, X_1, X_2] = \frac{11.9-11.3}{1-0} = 0.6 \]

\[ 1^\text{st DD: } Y[X_0, X_1] = \frac{11.3-10.1}{0+1} = 1.2 \]

\[ 2^\text{nd DD: } Y[X_0, X_1, X_2] = \frac{11.9-11.3}{1-0} = 0.6 \]
Therefore, \( Y_2(x) = a_0 + a_1(x-x_0) + a_2(x-x_0)(x-x_1) \)

\[
a_0 = Y_0 = 10.1, \quad a_1 = \text{FDD} = 1.2, \quad a_2 = \text{SDD} = -0.3
\]

\[= 10.1 + 1.2(x+1) - 0.3(x+1)x\]

- (Same as before, check) \( Y(0.5) = 11.675 \)

(2) Lagrange \( Y_2(x) = \sum_{k=0}^{2} l_k Y_k; \quad l_j(x) = \prod_{i=0,i\neq j}^{2} \frac{(x-x_i)}{(x_j-x_i)} \)

\[
l_0(x) = \frac{(x-x_1)(x-x_2)}{(x_0-x_1)(x_0-x_2)}; \quad l_1(x) = \frac{(x-x_0)(x-x_2)}{(x_1-x_0)(x_1-x_2)}, \text{etc.}
\]

\[
Y_2(x) = \frac{(x-0)(x-1)}{-1 \times -2} \times 10.1 + \frac{(x+1)(x-1)}{1 \times -1} \times 11.3 + \frac{(x+1)x}{2 \times 1} \times 11.9
\]

(Same as before, check) \( Y(0.5) = 11.675 \)

**Note:** ⇒ If ‘n’ is large, (> 4), the polynomial shows oscillation. In principle, one uses ‘piece-wise’ interpolation for large # of data points.

⇒ Less smooth if data points are less or sparse.

⇒ ‘Problem’ at the end points.

⇒ NDD uses the previous calculations, if an extra point is to be included in finding a new polynomial, unlike each coefficient has to be recalculated in ‘LI’. However, it is easy to program ‘LI’.

**Error analysis:** For (n+1) data points, \( P_n(\text{order } n) \) is the unique polynomial to pass through (n+1) data points. This polynomial can be used to predict \( P_n(X) \) at a new data points ‘X’. How much error can be expected in this prediction/interpolation? From engineering point of view, how much confidence an user has in the interpolated functional value? Well, in such case one should use an additional data \((\xi, Y(\xi))\) over the range \((X_0 \cdots X_n)\) and check the convergence in the re-interpolated value at \( P_{n+1}(X) \). Note, now you have (n+2) data points including \( \xi \).

Theoretically, it can be shown using Taylor’s series that the error in the interpolation using \( P_n(X) \) for (n+1) data is

\[
y^{n+1}(\xi)\frac{(x-x_0)(x-x_1)\cdots(x-x_n)}{n+1!}
\]

where \((x_0 < \xi < x_n)\)

additional data pt.
You should have also noted that
\[ y[x_0, x_1] = \frac{y(x_1) - y(x_0)}{x_1 - x_0} = y' \] (accurate to the 1st order)
\[ y[x_0, x_1, x_2] = \cdots = y'' \] (accurate to the 2nd order)
and
\[ y[\xi, x_0, x_1, \cdots x_n] = \frac{y[\xi, \cdots x_{n-1}] - y[x_0, \cdots x_n]}{\xi - x_n} = y^{n+1}(\xi) \]

Therefore, the error calculated is nothing but \( R_{n+1} \) (remainder) of the Taylor’s series. For more on this, read the book by Ferziger.
Lecture #13

Similar to the Newton’s Divided Difference and Lagrangian interpolation schemes, there is the **Newton’s interpolation formula** that makes use of 'Δ' operator (Forward Difference Operator)

\[ \Delta y(x) = y(x + \Delta x) - y(x) : ~ \text{Forward – difference operator} \]

\[
\begin{align*}
E y(x) &= y(x + \Delta x) : \text{Shift Operator} \\
E^2 y(x) &= E[y(x + \Delta x)] = y(x + 2\Delta x) \\
E^n y(x) &= y(x + n\Delta x)
\end{align*}
\]

Therefore, \( \Delta y(x) = E y(x) - y(x) = (E - 1)y(x) \)

or \( E = 1 + \Delta \)

or \( E^\alpha = (1 + \Delta)^\alpha = 1 + \alpha\Delta + \frac{\alpha(\alpha - 1)}{2!} \Delta^2 + \cdots \frac{\alpha(\alpha - 1) \cdots (\alpha - n + 1)}{n!} \Delta^n + \cdots \)

or \( E^\alpha y(x_0) = y(x_0 + \alpha\Delta x) = (1 + \Delta)^\alpha y(x_0) \)

\[\begin{align*}
= y_0 + \alpha\Delta y_0 + \frac{\alpha(\alpha - 1)}{2!} \Delta^2 y_0 + \cdots \frac{\alpha(\alpha - 1) \cdots (\alpha - n + 1)}{n!} \Delta^n y_0 + \]

If \( \alpha = \frac{x-x_0}{\Delta x} \)

| y(x) = y(x_0 + \alpha\Delta x) = y_0 + \alpha(\Delta y_0) + \frac{\alpha(\alpha - 1)}{2!} \Delta^2 y_0 + \cdots \frac{\alpha(\alpha - 1) \cdots (\alpha - n + 1)}{n!} \Delta^n y_0 + R | \]

\[ R = \frac{\alpha(\alpha - 1)(\alpha - n)}{(n+1)!} \Delta^{n+1} y(\xi) \quad \text{where} \ x_0 < \xi < x_n \]

Newton Forward-Difference Interpolation formula

In general

\[ \begin{align*}
\Delta y_i &= y(x_i + \Delta x) - y(x_i) = y_{i+1} - y_i \\
\Delta^2 y_i &= \Delta(\Delta y_i) = y_{i+2} - 2y_{i+1} + y_i
\end{align*} \]

Similar to ‘Δ’, \( \nabla \) has been defined as backward difference operator:

\[ \nabla y_i = y_i - y_{i-1} \quad \text{or} \quad \nabla y(x) = y(x_n + \alpha\Delta x), \quad \text{where} \ \alpha = \frac{x-x_0}{\Delta x} \]

And, therefore, there is another Newton’s interpolation formula! Again, note that all interpolating functions are one and the same, but written in different forms. Considering that the Newton’s interpolation formula resembles Taylor’s series, it can also be used for error analysis. **To this end, we have learnt how to approximate \( f(x) \) or \( y(x) \) with \( P_n(x) \). We will see later \( f'(x) \) or \( y'(x) \) and \( f''(x) \) or \( y''(x) \) will be approximated with \( P'_n(x) \) and \( P''_n(x) \), respectively.**
Splines

We have earlier noted that a high order polynomial \((n \geq 4)\) often shows oscillation. Therefore, a piece-wise polynomial \((n \leq 3)\) is usually preferred for most engineering applications.

→ ‘Spline’ is a piece-wise cubic polynomial \((y = ax^3 + bx^2 + cx + d)\) fitting 2 data points in segments or pieces. Is it unique? No. Because there are two extra degrees of freedom. In other words, two extra constraints or conditions may be imposed.

→ Let us define the problem:

\[ S_i = a_i x^3 + b_i x^2 + c_i x + d_i \text{ is the spline fitting the data } x_i \text{ and } x_{i+1}. \text{ Thus, it is a higher order polynomial for two data points.} \]

Each spline \((S_i)\) is a piece-wise cubic.
Curves must pass through the points \((x_i \text{ & } x_{i+1})\)
\(f'_i\) and \(f''_i\) are continuous at all ‘knots’, i.e, curve is smooth and curvature is the same at all nodes.

\[
\begin{align*}
S_{i-1}(x_i) &= S_i(x_i) \quad \equiv S^+ = S^- \\
S'_{i-1}(x_i) &= S'_i(x_i) \quad \equiv S'^+ = S'^- \\
S''_{i-1}(x_i) &= S''_i(x_i) \quad \equiv S''^+ = S''^-
\end{align*}
\]

Therefore, for \(n\) data points there are \((n-1)\) spline segments or \(4(n-1)\) unknown quantities (coefficients) to be determined:

Equations: \(y_i = S_i(x_i) : n\)

\[ S^+ = S^- : (n - 2) \quad : \text{only interior pts.} \]

\[ S'^+ = S'^- : (n - 2) \]

\[ S''^+ = S''^- : (n - 2) \]

\[ 4n - 6 \]

You have two BCs specified at the end data points or knots.

Therefore, there are as many \((4n-4)\) equations as # of unknowns.

The problem is now well defined:
\[ S_i(x) = \sum_{i=0}^{3} a_i x^i = ? \]

Note that \( S_i''(x) \) is a piece-wise linear and continuous (i.e. \( S_i''(x) = 6a_i x + 2b_i \))

\[ S_i''(x) \] (linear) \[ \begin{array}{c}
\uparrow \\
S_i(x) \end{array} \]

\[ \begin{array}{c}
\downarrow \\
S_i(x) \equiv \text{cubic} \\
\end{array} \]

Therefore, \( S_i(x) = \sum_{k=0}^{1} l_k(x) y_k \) \hspace{1em} (Lagrange interpolation)

\[ = \frac{x-x_{i+1}}{x_i-x_{i+1}} S''(x_i) + \frac{x-x_i}{x_{i+1}-x_i} S''(x_{i+1}) \]

On integrating twice, \( S_i(x) = \left( \frac{x^3}{6} - x_i \frac{x^2}{2} \right) S''(x_i) + \left( \frac{x^3}{6} - x_i \frac{x^2}{2} \right) S''(x_{i+1}) + c_1 x + c_2 \)

Apply the conditions

\[ S_i(x_i) = y_i \text{ and } S_i(x_{i+1}) = y_{i+1} \]

\[ \rightarrow S_i(x) = \frac{S''(x_i)(x_{i+1} - x)^3}{6\Delta_i} + \frac{S''(x_{i+1})(x - x_i)^3}{6\Delta_i} + \left( \frac{y_i - \Delta_i}{\Delta_i} S''(x_i) \right) (x_{i+1} - x) \]

\[ + \left( \frac{y_{i+1} - \Delta_i}{\Delta_i} S''(x_{i+1}) \right) (x - x_i) \]

Apply another condition:

\[ S_{i-1}'(x_i) = S_i'(x_i) \text{ on the following} \]

\[ S_i'(x) = -\frac{S''(x_i)(x_{i+1} - x)^2}{2\Delta_i} + \frac{S''(x_{i+1})(x - x_i)^2}{2\Delta_i} - \left( \frac{y_i - \Delta_i}{6\Delta_i} S''(x_i) \right) \]

\[ + \left( \frac{y_{i+1} - \Delta_i}{\Delta_i} S''(x_{i+1}) \right) \]

On re-arrangement it can be shown

\[ \frac{\Delta_{i-1}}{6} S''(x_{i-1}) + \frac{\Delta_i}{3} S''(x_i) + \frac{\Delta_i}{6} S''(x_{i+1}) \]

\[ = \frac{y_{i+1} - y_i}{\Delta_i} - \frac{y_i - y_{i-1}}{\Delta_{i-1}} \]

\[ i = 2, n - 1 \text{ (interior nodes)} \]
If $S''(x_i)$ and $S''(x_n)$ are pre-known as boundary conditions, we have

$$A\bar{x} = \bar{b} \text{ or } AS''(x) = \bar{b} \text{ where A is the tridiagonal matrix}$$

For a ‘natural’ spline, $S''(x_1) = S''(x_n) = 0 \text{ OR } S''(1) = S''(n) = 0$

If $\Delta_i = \Delta_{i-1}$ (equally spaced data)

$$\begin{align*}
\frac{1}{6} [S''(x_{i-1}) + 4S''(x_i) + S''(x_{i+1})] &= \left(\frac{y_{i+1} - 2y_i + y_{i-1}}{\Delta^2}\right)
\end{align*}$$

Call subroutine Tridiag$(n, 2, \frac{1}{6}, \frac{2}{3}, \frac{1}{6}, \bar{b})$

# of eqns coefficients of $\bar{A}$

RHS or b vector

$S''(x_i), \quad i = 2, n - 1$ are now known on solving the set of eqns.

Thus, $S_i(x)$ is determined from the boxed equation on the preceding page 3.

**Example:**

<table>
<thead>
<tr>
<th>0</th>
<th>1.67</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.5</td>
<td>0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Fit a cubic natural spline.

Use above

$$\begin{align*}
\frac{1}{6} S''(x_1) + \frac{2}{3} S''(x_2) + \frac{1}{6} S''(x_3) &= \frac{0 - 2 \times 1.67 + 0}{2.5^2}
\end{align*}$$

(You have only one linear algebraic eqn)

$$S''(x_2) = -0.8016 \quad i = 2 \text{ (middle node only)}$$

$$S_1(x) = -0.05344(x + 2.5)^3 + 1.002(x + 2.5) \quad S_2(x) = 1.667 - 0.4x^2 + 0.0533x^3 \quad \{ \text{Ans.} \}$$
Numerical Differentiation

Given a continuous $f(x)$, numerical differentiation can be performed to determine gradient $f'(x_i)$ at $x_i$. Fit a polynomial (usually $P_{1-3}$) and then determine $P_{1-3}'$ to estimate $y'_i$, depending on desired order of accuracy or error. Taylor’s series can be conveniently used to derive $f'$ or $f''$ because the series terms contain $f'$ or $f''$.

**Taylor’s series:**

given $f(x + h) = f(x) + hf'(x) + h^2/2 f''(x) + \cdots$ (1)

\[
f(x - h) = f(x) - hf'(x) + h^2/2 f''(x) - \cdots \tag{2}
\]

\[
\begin{align*}
  f'(x_i) &= \frac{f(x_{i+1}) - f(x_i)}{h} + 0(h^2) \quad \text{: Forward difference Scheme (FDS)} \\
  f'(x_i) &= \frac{f(x_i) - f(x_{i-1})}{h} + 0(h^2) \quad \text{: Backward difference Scheme (BDS)} \\
  f'(x_i) &= \frac{f(x_{i+1}) - f(x_{i-1})}{2h} + 0(h^3) \quad \text{: Central difference Scheme (CDS)}
\end{align*}
\]

Richardson’s extrapolation technique can be used to take 3 data pts.

\[
f(x_i + 2h) = f(x) + 2hf'(x) + 4(\frac{h^2}{2}) f''(x) + \cdots \tag{3}
\]

\[
f(x_i - 2h) = f(x) - 2hf'(x) + 4(\frac{h^2}{2}) f''(x) + \cdots \tag{4}
\]

Use 1 an 3 : Multiply eq(1) by 4 and subtract from 3 to eliminate $f''(x_i)$

\[
\begin{align*}
  f''(x_i) &= \frac{4f(x_{i+1}) - 3f(x_i) - f(x_{i+2})}{2h} + 0(h^3) \quad \text{: FDS} \\
  \text{Similarly 2 and 4 will give} \\
  f''(x_i) &= \frac{-4f(x_{i-1}) + 3f(x_i) + f(x_{i-2})}{2h} + 0(h^3) \quad \text{: BDS}
\end{align*}
\]

You will see later in the course that although BDS and FDS are also 2nd order accurate like CDS, such equations are used at the boundary points or end points only to discretize Neumann
or mixed or flux (gradient) terms: \(-k \frac{\partial T}{\partial x}\) or \(-D \frac{\partial C}{\partial x}\) or \(-\mu \frac{\partial v}{\partial x}\), whereas CDS is invariably used at interior nodes.

Higher order \(f'(x_i)\) can also be obtained as CDS:

\[
\begin{align*}
\text{4 data points} \quad f'(x_i) &= \frac{-4f(x_{i+2}) - 8f(x_{i-1}) + 8f(x_{i+1}) + 4f(x_{i+2})}{12h} + 0(h^4) \\
\text{(See the book by Ferziger)}
\end{align*}
\]

Similarly, use eqns 1 & 2 to obtain

\[
\begin{align*}
f''(x_i) &= \frac{f(x_{i+1}) - 2f(x_i) + f(x_{i-1})}{h^2} + 0(h^3) \\
&= f''(x_{i-1}) = f''(x_{i+1})
\end{align*}
\]

Why? (You have 2nd order polynomial between 3 data points)

You should note that similar to \(f'(x_i)\), FDS and BDS or formulae can also be derived for \(f''(x_i)\) using three points or manipulating Taylor’s series or equations 1-4. However, these equations are seldom or in fact, never used for most of chemical engineering problems. Why not? Because the N-S or species or thermal energy balance equations (PDEs) are 2nd order, with the 1st order (flux) boundary condition. Therefore, CDS for \(f''(x_i)\), applied at interior nodes, suffices.

To this end, apply Richardson’s extrapolation technique to obtain even higher order \(f''\)

\[
f''(x_i) = \frac{-f(x_{i-2}) + 16f(x_{i-1}) - 30f(x_i) + 16f(x_{i+1}) - f(x_{i+2})}{12h^2} + 0(h^4)
\]

(Five data points)

Note the notations:

\(f(x_i)\) and \(y_i(x_i)\); \(f'\) and \(f''\), and \(y'\) and \(y''\).

Summary at a glance:

\[
f(x) \approx P_n(x), f'(x) \approx P'_n(x), f''(x) \approx P''_n(x)
\]
Lecture #14-15

Numerical Integration

Similar to numerical differentiation, the integration of \( f(x) \), i.e., \( \int f(x)dx \) may be performed by approximating \( f(x) \approx P_n(x) \), usually \( n \leq 3 \). Therefore, first calculate \( y_i(x_i) \) from \( f(x) \), then fit a polynomial through the 'n' data points and determine \( \int P_n dx \) or area under the approximated curve. Considering usual oscillations set in the fitted polynomial for \( n \geq 4 \), piece-wise integration is performed. Detailed method and analysis are as follows.

\[ P_n(x) \text{ is the interpolating } f^n \text{ between } (x_0, \ldots, x_n) \]

It can be shown/proposed that

\[ \int_a^b f(x)dx = \sum_{k=0}^n w_k f(x_k); \quad f(x_k) = y(x_k) \]

where, \( n \) is the number of segments between 'a' and 'b'

and \( w_i \) is the respective weight at \( x_i \). It is also known as Quadrature formula. Let us look at the proposed formula differently. Apply Lagrange interpolation between \((n + 1)\) data points or \( n \) segments:

\[ P_n(x) = \sum_{k=0}^n l_k(x)y_k \quad (y_k \equiv y(x_k) \equiv y_k(x_k)) \]

\[ \int_a^b f(x)dx = \int_a^b \sum_{k=0}^n l_k(x)y_kdx = \sum_{k=0}^n \int_a^b l_k(x)y_kdx \]

\[ = (b - a) \sum_{k=0}^n C^k y_k; \quad C^k = \frac{1}{(b-a)} \int_a^b l_k(x)dx \]

- It is the same as the Quadrature formula ; \( n \equiv \text{parameter(degree of polynomial)} \)

(It can be shown \( \sum_{k=0}^n C^k = 1 \) (put \( f(x) = 1 \))

Therefore, we can have a table as follows:
Newton-Cotes Coefficients (ends points included)

<table>
<thead>
<tr>
<th>n</th>
<th>N</th>
<th>NC₀ⁿ</th>
<th>NC₁ⁿ</th>
<th>NC₂ⁿ</th>
<th>...</th>
<th>NCⁿᵖ</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>.0183Δ''''f''</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td></td>
<td></td>
<td>.0035Δ''''f''''</td>
</tr>
<tr>
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<td>8</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td></td>
<td>.00016Δ''''f''''</td>
</tr>
<tr>
<td>4</td>
<td>90</td>
<td>7</td>
<td>32</td>
<td>12</td>
<td>32</td>
<td>7</td>
<td>...</td>
</tr>
<tr>
<td>5</td>
<td>288</td>
<td>19</td>
<td>75</td>
<td>50</td>
<td>50</td>
<td>75</td>
<td>19</td>
</tr>
</tbody>
</table>

These are called closed N-C formula because they use functions at the end points also (a, b). Note, n or the number of segments is usually 1 or 2 or 3, or the degree of polynomial is 1 or 2 or 3, respectively. Readers may have recognized that n = 1 corresponds to Trapezoidal rule with \( \frac{1}{2} \) coefficients of \( y_k \); n = 2 corresponds to Simpson’s \( \frac{1}{3} \) rd rule with \( \frac{1}{6}, \frac{2}{3}, \frac{1}{6} \) coefficients, etc. For more details, you can refer the book by Ferziger or SKG.

The error in the numerical integration can be calculated from the remainder term of the polynomial:

\[
\Rightarrow l = \int (\text{error}) dx \Rightarrow \text{where} \ 'error' = \frac{y^{n+1}(\xi)}{n+1!} (x - x_0)(x - x_1) \cdots (x - x_n) \\
\text{for (n + 1) data points}
\]

\[
\Rightarrow \text{SKG’s book uses Newton’s Interpolation formula to determine the various integration formulae:}
\]

\[
y(x) = y(x_0 + a\Delta x) = y_0 + a(\Delta y_0) + \frac{a(a-1)(\Delta^2 y_0)}{2!} + \cdots + \frac{a(a-1)(a-2)a-\cdots(a-n)(\Delta^{n+1} y_0)}{n+1!} \\
R_n
\]

To obtain the different methods for integration, viz. Trapezoidal’s rule, Simpson’s \( \frac{1}{3} \) rd, etc, two approaches must give the identical results because polynomial of the highest degree that can fit to (n + 1) data points is unique.

Take n = 1

\[
\int_a^b f(x) dx = (b - a) \sum_{k=0}^{n} c_k^n f(x_k) \\
= (b - a) \left[ \frac{1}{2} y_a + \frac{1}{2} y_b \right] \\
= \frac{(b-a)}{2}(y_a + y_b)
\]
\[
\text{or } = \frac{(b-a)}{2} (f(a) + f(b))
\]

(Trapezoidal rule)

\[
n = 2
\]

\[
\int_a^b f(x) \, dx = \frac{(b-a)}{6} [f(a) + 4f \left( \frac{a+b}{2} \right) + f(b)]
\]

\[
\text{Simpson's } \frac{1}{3} \text{ rd formula (higher order accurate)}
\]

(Note: \( P_2 \equiv (a + bx + ax^2) \equiv \text{parabola} \))

\[
= \frac{\Delta x}{3} [f(a) + 4f \left( \frac{a+b}{2} \right) + f(b)] \quad \Delta X = \frac{b-a}{2}
\]

\[
n = 3
\]

\[
\int_a^b f(x) \, dx = \frac{(b-a)}{8} [f(a) + 3f(c) + 3f(d) + f(b)]
\]

\[
= \frac{3\Delta x}{8} [ \text{ ditto } ], \quad \Delta x = \frac{(b-a)}{3}
\]

- Simpson's \( \frac{3}{8} \) th formula.

In actual practice, applying a single Cotes formula over the entire range is rarely done. Considering large error for large '\( \Delta X \)' interval is broken into sub-intervals & then applying piece-wise quadrature formula and summing it over.

\[
\int_{X_{i-1}}^{X_i} f(x) \, dx = \frac{h}{2} [f(X_{i-1}) + f(X_i)]
\]

\[
h = \frac{(b-a)}{n} \quad (n + 1 \text{ data points or } n \text{ segments})
\]
Therefore,
\[
\int_a^b f(x) \, dx = \sum_{i=1}^{n} \frac{h}{2} \left[ f(x_{i-1}) + f(x_i) \right]
\]
\[
= \frac{h}{2} \left[ f(x_0) + 2 \sum_{k=1}^{n-1} f(x_k) + f(x_n) \right] \}
\]
\[
= \frac{(b-a)}{n} \left[ \sum_{k=0}^{n} f(x_k) - \frac{1}{2} [f(a) + f(b)] \right] \}
\]

\[\text{Trapezoidal rule}\]

\[\text{Simpson's 1/3rd rule:}\]
(intervals must be even or data points must be odd),

<table>
<thead>
<tr>
<th>n</th>
<th>N</th>
<th>NC$_0^n$</th>
<th>NC$_1^n$</th>
<th>NC$_2^n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>6</td>
<td>1</td>
<td>4</td>
<td>1</td>
</tr>
</tbody>
</table>

\[
f_a^b f(x) \, dx = \left( \frac{b-a}{6} \right) \left( f(a) + 4f(c) + f(b) \right)
\]
\[
h = \frac{b-a}{2}
\]

(Note that all even nodes ‘$X_k$’ are summed/counted twice in calculating total area)

What do you do if $n \equiv \text{odd}$ or data are even? Apply the method to one data less so that $n = \text{even}$. Add the area corresponding to the left-over segment, calculated using Trapezoidal rule!

\[\text{One open NC method is popular:}\]
Mid-point rule, the method is frequently applied when the $f^n$ is discontinuous at end points: a or b or both.

\[
f_a^b f(x) \, dx = (b - a) \left[ f \left( \frac{a+b}{2} \right) \right]
\]
ex. $\int_0^1 \frac{1}{1-x^2} \, dx$  \hspace{0.5cm} (Note $f(1) \rightarrow \infty$)

**Example:**

Consider the classical heat transfer/transport problem of SS heat transfer at constant wall temperature in the fully developed region of a tubular laminar parabolic flow, often discussed in TP lectures. The dimensionless SS temperature $\theta(z, r)$ in the fluid is analytically derived. See the solution above. Determine the 'mix-cup' temperature at $z = 0.5$.

**Sol:** In a flow-system, mix-cup temperature is the radially emerged temperature, taking into consideration the total heat (cal) carried away by the flowing fluid in unit time across the cross-section of the tube.

$$
\bar{T} = \left( \frac{\int_0^R \rho C_p v(r') T(2\pi r') \, dr'}{\int_0^R \rho C_p v(r') 2\pi r' \, dr'} \right) \frac{kg/m^3 \cdot \text{cal/kg} - K}{K} \hspace{1cm} (Note: dq = v2\pi rdr \frac{m^3}{s})
$$

$$
\bar{Q} = \int_0^R v2\pi rdr \hspace{1cm} \text{at a ref. temperature}
$$

In the dimensionless quantities,

$$
\bar{\theta}(z) = \frac{\int_0^1 \theta(r, z)(1 - r^2) \, rdr}{\int_0^1 (1 - r^2) \, rdr}
$$

Simpson’s $\frac{1}{3}$ rule can be applied by taking odd number (5) of data points over $r \equiv (0, 1)$. Therefore # of segment = 4, step size, $h = \frac{1-0}{4} = 0.25$, $\Delta r \equiv h = 0.25$; $r_i = i\Delta r$
Numerical integration is performed for both numerator and denominator terms.

\[ I = \int_0^1 f(r)dr / \int_0^1 \Phi(r)dr \]

where \( f(r) = \theta(r, z)(1 - r^2)r \) \& \( \Phi(r) = (1 - r^2)r \)

For both functions,

\[ I = \frac{h}{3} \left[ f(X_0) + 4 \sum_{k=1,3,5}^{n-1} + 2 \sum_{k=2,4}^{n-2} + f(X_n) \right] \]

\[ = \frac{h}{3} \left[ f(X_0) + 4 \sum_{1,3} + 2 \sum_{2} + f(X_4) \right] \]

Best way is to prepare a table for calculations:

<table>
<thead>
<tr>
<th>( k )</th>
<th>( r_k )</th>
<th>( \theta_k )</th>
<th>( (1 - r_k^2)r_k )</th>
<th>( \theta_k(1 - r_k^2)r_k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>-1.7083</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1</td>
<td>0.25</td>
<td>-1.7698</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>-1.9427</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.75</td>
<td>-2.1917</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.00</td>
<td>-2.4583</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

\[ \sum \text{Add} \quad \sum \text{Add} \]

Show,

\[ \bar{\theta}_{\text{mix-cup}}(0.5) \equiv -1.9976 = \frac{T - T_w}{r_w} \]

(wall is colder than bulk fluid)

What does decide the # of data points ‘n’ or the step size ‘h’? It is the level of desired accuracy. Repeat the entire calculations for \( n = 9 \) and check your requirement of an improved \( \bar{\theta}_{\text{mix-cup}} \) from the previous value -1.9976. Sometimes you have to decrease ‘n’ or increase ‘h’ if you have exceeded accuracy limit!

**Error Analysis**

Let us take the simplest Trapezoidal rule applied to one segment over \((a,b)\).

Start from Newton’s Difference Interpolation formula:
\[
f(x) = f(x_0) + a\Delta f(x_0) + \frac{a(a - 1)}{2!}\Delta^2 f(x_0) + \cdots R_n
\]

\[
R_n = \frac{a(a-1)\cdots(a-n)}{n+1!}\Delta^{n+1}f(\xi) \quad \text{where } x_0 < \xi < x
\]

\[
\alpha = \frac{x-x_0}{h} \quad \text{or } dx = h\,d\alpha ; \quad x_0 = a,
\]

If there is only one segment, \( h = (b-a) \)

\[
I = \int_a^b f(x)\,dx = h\int_0^1 \left( f(x_0) + a\Delta f(x_0) + \frac{a(a-1)}{2!}\Delta^2 f(x_0) \right)\,dx
\]

\[P_1 = (ax + b)\]

\[= h\left[ f(a) + \frac{1}{2} (f(b) - f(a)) + \left( \frac{\alpha^3}{6} - \frac{\alpha^2}{4} \right) \int_0^1 h^2 f''(\xi) \right]
\]

\[= h\left[ \frac{f(a)+f(b)}{2} \right] - \frac{1}{12} h^3 f''(\xi) \quad (f''(\xi) = \frac{\Delta^2 f(\xi)}{2h})
\]

Therefore, error on one segment is \( \frac{1}{2} h^3 f''(\xi) \) or \( 0(h^3) \)

If there are \( n \) segments between (a & b) error should also be summed up to

\[
\frac{1}{12} h^3 \sum_n f''(\xi) = \frac{1}{12} h^2 f''(\xi)(b-a) \quad \text{or } 0(h^2)
\]

\[\text{Note: } f''(\xi) = \frac{\sum f''(\xi)}{n} = \frac{h\sum f''(\xi)}{(b-a)}.
\]

Similarly, for the error estimation of Simpson's 1/3 rule start with \( P_2 = ax^2 + bx + c \), or

\[
R_n = \frac{a(a-1)(a-2)\Delta f(\xi)}{3!} \quad \text{over one segment or 3 data pts.}
\]

to show that error \( \equiv 0(h^5)f''''(\xi) \) and if summed over 'n' segments error \( = 0(h^4)f''''(\xi) \).

Simpson's 3/8 rule: \begin{align*}
\text{error(one segment)} & \equiv 0(h^5) \\
\text{error( segments)} & \equiv 0(h^4)
\end{align*}

A common question is asked: Show that Simpson's 1/3 rule gives the error corresponding to a cubic interpolating function, although it is based on a parabola or a quadratic polynomial. See Chhapra and Cannale's book for the details.

\[\text{Mid-Term}\]
Lecture #15-16

1st order ODE

A set of ODEs takes the following form:

\[
\begin{align*}
\frac{dy_1}{dt} &= f_1(t, y_1, y_2 \ldots y_n) \\
\vdots \\
\frac{dy_n}{dt} &= f_n(t, y_1, y_2 \ldots y_n)
\end{align*}
\]

or \( \frac{dy}{dt} = \bar{f}(t, \bar{y}) \)

Requires initial conditions to solve \( \bar{y} \).

\[
t = 0, \ y_1 = y_{10} \ldots y_n = y_{n0}, \ etc \ or \ \bar{y} = \bar{y}_0
\]

Note that ODEs can also be 1st order on x (space) & \( \frac{dy}{dx} = \bar{f}(x, \bar{y}) \) with \( x = 0, \ \bar{y} = \bar{y}_0 \).

⇒ We explore numerical solution to ODEs starting with Euler’s forward and backward methods. These methods are basics, and also set the tone for the stability analysis. Let us begin with one ODE.

**Euler’s Method**

\[
\frac{dy}{dx} = f(x, y) ; \ y(x_0) = y_0
\]

or \( \frac{y_{n+1} - y_n}{h} = f(x_n, y_n) + O(h^2) \)

(This is the general ‘discretization’ of a derivative at the ‘n’ th grid. Recall the lecture on numerical differentiation. We have used FDS.)

or \( y_{n+1} = y_n + hf(x_n, y_n) + O(h^2) \)

**Note:** The RHS terms are known to be 1st order accurate or have 2nd order error.

From the previous calculations, start from \( y(x = 0) = y_0 \rightarrow y_1 \rightarrow y_2 \ldots etc \). Therefore, you march forward and the method is called Euler’s forward or explicit method. Think carefully. The method is all about taking a linear slope/tangent at \( (x_n, y_n) \) and moving on to \( (x_{n+1}, y_{n+1}) \).
Graphically,

It is all about calculating true derivatives (gradients) at $x_n$ as you march forward:

$$
\begin{align*}
    y'_0 &= f(x_0, y_0) \\
    y'_1 &= f(x_1, y_1) \\
    \vdots \\
    y'_n &= f(x_n, y_n)
\end{align*}
$$

It is clear that smaller is ‘$h$’ (step-size), less is the error, or accuracy is higher: $O(h^2)$. However, there is a price for long CPU time. Also, stability may become an issue. Let us look at the stability aspect of the method.

$$
\frac{dy}{dx} = f(x, y) = f(x_0 + \Delta x, y_0 + \Delta y)
$$

$$
= f(x_0, y_0) + (y - y_0) \left( \frac{df}{dy} \right)_{x_0,y_0} + (x - x_0) \left( \frac{df}{dx} \right)_{x_0,y_0} + O(\Delta x^2, \Delta y^2)
$$

Multi-variable Taylor series can be applied to estimate gradient $y'(x_0, y_0)$:

$$
\begin{align*}
    \frac{dy}{dx} &= \alpha y + \beta x + \gamma \\
    \text{gives exponential solution} \\
    \Delta &\text{for linear solution}
\end{align*}
$$

Model equation for testing stability. (Note: Stability is governed by the homogeneous part of the solution)

Let us look at differently: Introduce perturbation or find true value, $\bar{y}$.

Therefore, $\frac{d\bar{y}}{dx} = \alpha \bar{y} + \beta x + \nu$

or, $\frac{d\xi}{dx} = \alpha(y - \bar{y}) = \alpha \xi$ ( $\xi = y - \bar{y}$)

We have the same inference: error satisfies homogeneous part of the solution. The equation describes how ‘$\xi$’ can grow because of a small perturbation.

At $x = x_0$, $y = y_0 \Rightarrow$ exact solution: $y = y_0 e^{\alpha x}$ If $\alpha > 0$, $f^n$ grows, $\alpha < 0$, $f^n$ is bounded.
Now Apply Euler’s method:

\[ y_{n+1} - y_n = hf(x_n, y_n) = h y'_n = h(\alpha y_n) \]

\[ y_{n+1} = y_n(1 + \alpha h) \]

\[ y_1 = y_0(1 + \alpha h), \ y_2 = y_0(1 + \alpha h)^2 \]

\[ y_n = y_0(1 + \alpha h)^n \Rightarrow \text{Numerical solution} \]

If \( \alpha > 0 \) function grows or unbounded
If \( \alpha < 0 \) function may be bounded 

Let us write, \( \alpha = \alpha_r + i\alpha_i \)

\[ y_n = y_0(1 + \alpha_r h + i\alpha_i h)^n \]

For function to be bounded

\[ |(1 + \alpha_r h) + i\alpha_i h| < 1 \]

\[ (1 + \alpha_r h)^2 + \alpha_i^2 h^2 < 1 \]

\[ 0 > \alpha_r h > -2 \] if \( \alpha_i = 0 \) for stability

Note: \( \alpha = -ve \), the exact solution is always bounded! Therefore, Euler’s forward/explicit numerical method is conditionally stable. Example:

\[ \frac{dy}{dx} = -y \ (x = 0, y = 1) \Rightarrow y = e^{-x} \]

Numerical sol^o: exact solution: 'bounded (theoretical)solution'

\[ \alpha = -1; \ \alpha_r = -1, \ \alpha_i = 0 \]

\[ 0 > \alpha_r h > -2 \] for stability

or \[ h < +2 \]

\[ \Rightarrow y_{n+1} - y_n = hf(x_n, y_n) = -hy_n \Rightarrow y_n = (1 - h)^n \]

Plot to see that oscillations start creeping in \( h > 2 \)
**Backward or Implicit Euler:**

\[
\frac{dy}{dx} = f(x, y), \quad y(x_0) = y_0
\]

\[
y_{n+1} - y_n = f(x_{n+1}, y_{n+1}) + 0(h^2) \quad \text{(Note this BDS may require iteration)}
\]

(Note this BDS may require iteration), maybe NR method; you can not march!

\[
y_{n+1} = y_n + h f(x_{n+1}, y_{n+1})
\]

Test it on the model eq\(n\)

\[
\frac{dy}{dx} = \alpha y
\]

for the stability analysis

\[
y_{n+1} = y_n + h(\alpha y_{n+1})
\]

\[
y_{n+1} = y_n / (1 - \alpha h)
\]

\[
y_{n+1} = y_0 (1 - \alpha r h - i\alpha_i h)^n
\]

For \(f^n\) to be bounded \(|(1 - \alpha_r h - i\alpha_i h)| > 1\)

or \((1 - \alpha_r h)^2 + \alpha_i^2 h^2 > 1\)

or \(|(1 - \alpha_r h)| > 1\) if \(\alpha_i = 0\)

Clearly, \(0 > \alpha_r h > 2\)

**Draw the region:**

\[
\Rightarrow \begin{cases} 
\text{For all } (\alpha_r h) \text{ in the left half of the plane } \alpha_r < 0 \text{ and } \alpha_i h \\
\text{the method is unconditionally stable} \\
\text{For all } h \text{ outside the circle} \\
\text{the method is stable (or } \alpha_r h > 2) 
\end{cases}
\]

It is clear the stability region for the implicit Euler is much more larger than that of the explicit Euler.

**Notes:** Error decreases with decreasing step sizes (h): \(O(h^n)\), however, at the expense of CPU time. This is not surprising. The actual ‘issue’ is with increasing step sizes. There is a tendency to speed up computation by taking large step-size. An explicit method like Euler Forward may not permit or allow you to do so, even if the level of desired accuracy may be acceptable. Instability may set in at large ‘h’. On the other hand, Euler Backward or an implicit method permits you to use relatively larger ‘h’ without instability, yielding a bounded solution.
‘Error’ must not be mixed up with the ‘instability’. A method may be relatively higher order accurate, but may show instability at small step-size. In general, implicit methods are more stable than explicit methods, but require iterations to compute \( y_{n+1} \). Examples:

\[
\frac{dy}{dx} = f(x, y) = \alpha y^2
\]

**Explicit:** \( y_{n+1} - y_n = h\alpha y_n^2 \)

**Implicit:** \( y_{n+1} - y_n = h\alpha y_{n+1}^2 \)  
(requires iterations or NR method?)

⇒ "A method is stable if it produces a bounded solution when it is supposed to and is unstable if it does not." Therefore, while solving \( \frac{dy}{dx} = -y \), if the numerical method produces a stable solution, it is stable, else unstable. On the other hand, there is no instability ‘issue’ with \( \frac{dy}{dx} = +y \) because the exact solution itself is unbounded. Therefore, both Euler Forward(explicit) or Backward(implicit) will produce an unbounded solutions!

Get back to \( \frac{dy}{dx} = -y (\alpha = -1) \) and \( y_n = (1 + h)^{-n} \)

Error increases with increasing ‘\( h \)’ but the solution remains stable. Compare to Forward Euler when \( \alpha < 2 \) for a stable solution.

⇒ Trapezoidal rule (\( O(h^2) \)):

\[
y_{n+1} - y_n = \frac{h}{2} [f(x_n, y_n) + f(x_{n+1}, y_{n+1})]
\]

(Implicit method)

It can also be tested on the model equation:

\[
\frac{dy}{dx} = \alpha y
\]

or

\[
y_{n+1} - y_n = \frac{\alpha h}{2} [y_n + y_{n+1}]
\]

\[
y_{n+1} = y_n \left(\frac{1 + \alpha h/2}{1 - \alpha h/2}\right)
\]

or

\[
y_n = y_0 \left(\frac{1 + \alpha h/2}{1 - \alpha h/2}\right)^n
\]
For stability \( \left| \frac{1 + \alpha h/2}{1 - \alpha h/2} \right| < 1 \) or

Each method has a stability region for selecting the step-size, 'h' for calculation without instability. See the textbooks for details.
Lecture #17

Single Step Methods

Forward or Backward Euler is the simplest single step method to solve ODEs. The methods are 1st order accurate. A general higher order method can be derived considering that it is all about choosing a suitable gradient at \((x_n, y_n)\) or \((t_n, y_n)\) to calculate \(y_{n+1}(x_{n+1})\):

\[
\frac{dy}{dt} = f(t, y); \quad y(0) = y_0
\]

\[y_{n+1} = y_n + h\phi(t_n, y_n, h)\quad (h = \text{step size} = \Delta t)\]

It is all about finding: \(\phi(t_n, y_n, h) = \left(\frac{dy}{dt}\right)_{t_n, y_n} = ?\)

Propose as

\[y_{n+1} = y_n + h[ak_1 + bk_2] \quad \text{(1)} \Rightarrow \text{general method.}\]

Here, \(k_1\) and \(k_2\) are the slopes with weights \(a\) & \(b\) respectively (Forward Euler may be considered to assume \(a = 1, b = 0\) and \(k_1 = y'_n, y_n\), whereas Backward Euler assumes \(a = 0, b = 1, k_2 = y'_{n+1}, y_{n+1}\) )

Here,

\[
k_1 = f(t_n, y_n)\]
\[
k_2 = f(t_n + ph, y_n + q(hk_1))
\]

Thus, the model has 4 parameters; \(a, b, p, q\).

Thus \(k_2\) (slope) is calculated at \((t_n + ph)\), fraction less than \((t_n + h)\) or \(t_{n+1}\), as \(x\) coordinate, and \(y_n + q(hk_1)\), fraction less than \((y_n + hk_1)\) or \(y_{n+1}\), as \(y\) coordinate.

\[-\text{Taylor multi-variable series applied on } k_2(t, y) \text{ with } \Delta t = ph, \Delta y = qhk_1\]

Substituting in (1)

\[y_{n+1} = y_n + h[af(t_n, y_n) + bf(t_n, y_n)] + h^2[bpf_t(t_n, y_n) + bqf_y(t_n, y_n)] + 0(h^3) \quad \text{(2)}\]
Also, restart from \( \frac{dy}{dt} = f(t, y(t)) \) as a total derivative on \( t \).

or \( y_{n+1} = y_n + hf + \frac{h^2}{2!}f' + 0(h^3) \): (Single variable(t) Taylor – Series)

where, \( f' = \frac{df}{dt}(t_n, y_n) = \left[ \frac{\partial f}{\partial t} + \frac{\partial f}{\partial y} \cdot \frac{dy}{dt} \right]_{t_n, y_n} = [f_t + fyf] \)

On substitution,

\[ y_{n+1} = y_n + hf + \frac{h^2}{2}f(t_n, y_n) + \frac{h^2}{2}fyf + 0(h^3) \quad (3) \]

Thus, model equation (2) can be equated with the fundamental equation (3) derived for \( y_{n+1} \):

\[
\begin{align*}
(\alpha + b &= 1) \\
bp &= 1/2 \\
bq &= 1/2
\end{align*}
\]

Case 1: \( a = 1/2 \), \( b = 1/2 \). \( p = q = 1 \)

\[
y_{n+1} = y_n + \frac{h}{2} \left[ f(t_n, y_n) + f(t_n + h, y_n + hy') \right] + 0(h^3)
\]

Write differently,

\[
y_{n+1}^* = y_n + hf(x_n, y_n) \quad \text{predictor full step}
\]

\[
y_{n+1} = y_n + \frac{h}{2} \left[ f(t_n, y_n) + f(t_n + h, y_{n+1}^*) \right] \quad \text{corrector full step}
\]

Look at graphically,

Therefore, first predict \( y_{n+1}^* \) and then correct as \( y_{n+1} \) by taking the average of the slopes, \( k_1 \) and \( k_2 \) : \( y_{n+1} = y_n + h\bar{k} \)
This method is called Heun’s improved method or modified Euler method or Runge-Kutta (RK-2) method.

**Case 2:** $a = 0, b = 1, \quad p = q = \frac{1}{2}$

$$y_{n+1} = y_n + h\left[f\left(t_n + \frac{h}{2}, y_n + \frac{h}{2}y'_n\right)\right]$$

Write differently,

$$y_{n+1/2} = y_n + \frac{1}{2}h y'_n \quad \text{(Euler predictor $\frac{1}{2}$ step)}$$

$$y_{n+1} = y_n + h\left[f\left(t_n + \frac{h}{2}, y_{n+1/2}'\right)\right] : \text{ Mid-point corrector full step}$$

Graphically,

- This method is called midpoint method.

**3. RK-4**

$$y_{n+1} = y_n + \frac{h}{6}[k_1 + 2k_2 + 2k_3 + k_4] + O(h^5)$$

$$\bar{k} = \text{avg of four slopes with more weights at mid points.}$$

$$k_1 = f(x_n, y_n)$$

$$k_2 = f\left(x_n + \frac{h}{2}, y_n + k_1 \frac{h}{2}\right) \quad \text{or} \quad f\left(x_{n+1/2}, y_{n+1/2}'\right)$$

$$y_{n+1/2} : \text{ Euler predictor } \frac{1}{2} \text{ step}$$

$$k_3 = f\left(x_n + \frac{h}{2}, y_n + k_2 \frac{h}{2}\right) \quad \text{or} \quad f\left(x_{n+1/2}, y_{n+1/2}''\right)$$

$$y_{n+1/2} : \text{ Backward Euler } \frac{1}{2} \text{ step correction}$$
\[ k_4 = f(x_n + h, y_n + k_3 h) \text{: Mid point predictor full step} \]
\[ y_{n+1} \]

Write differently,

\[ y_{n+1/2}^* = y_n + \frac{h}{2} f(x_n, y_n) \text{: EP 1/2 step} \]
\[ y_{n+1/2}^{**} = y_n + \frac{h}{2} f(x_{n+1/2}^*, y_{n+1/2}^*) \text{: BE 1/2 step corrector} \]
\[ y_{n+1}^{**} = y_n + hf(x_{n+1/2}^*, y_{n+1/2}^{**}) \text{: Mid point predictor full step.} \]
\[ y_{n+1} = y_n + \frac{h}{6} \left[ f(x_n, y_n) + 2f(x_{n+1/2}^*, y_{n+1/2}^*) + 2f(x_{n+1/2}^*, y_{n+1/2}^{**}) + f(x_{n+1}, y_{n+1}) \right] \text{: Simpson full step corrector.} \]

Graphically,

\[ \bar{k} = (k_1 + 2k_2 + 2k_3 + k_4)/6 \]

**Notes:**

1. RK-4 is a 4th order accurate method!

2. The method is explicit (does not require iterations to calculate \( y_{n+1} \)). You can march ahead from \( x_n \) to \( x_{n+1} \). Yet, considering that it makes use of the value \( y_{n+1} \) at \( x_{n+1} \) ahead of \( x_n \) via a predictor step, the method possesses some ‘characteristics’ of an implicit method. Therefore, the method also produces a stable solution at a relatively larger step size.

3. Coding (program) is simple.

4. Even if two or more number of simultaneous ODEs are coupled, the method is explicitly applied w/o requiring iterations,
(5) Considering that the method is explicit, non-linearity is not an issue.

(6) Considering that the method is explicit, the implementation is identical for a system of ODEs.

See example below:

Solve: \[ \frac{dy_1}{dt} = -100y_1 \quad \text{with} \quad y_1(0) = 2 \quad \text{choose} \quad h = \Delta t = 0.02 \]

\[ \frac{dy_2}{dt} = 2y_1 - y_2 \quad y_2(0) = 1 \]

Write alternatively, solve \[ \frac{dy}{dt} = f(x, y); \quad y(t_0) = y_0 \]

or \[ \begin{bmatrix} y_1' \\ y_2' \end{bmatrix} = \begin{bmatrix} -100 & 0 \\ 2 & -1 \end{bmatrix} \begin{bmatrix} y_1 \\ y_2 \end{bmatrix}; \quad \begin{bmatrix} y_1 \\ y_2 \end{bmatrix}_0 = \begin{bmatrix} 2 \\ 1 \end{bmatrix} \]

or \[ \begin{bmatrix} y_1' \\ y_2' \end{bmatrix} = \begin{bmatrix} -100y_1 \\ 2y_1 - y_2 \end{bmatrix}; \quad \begin{bmatrix} y_1 \\ y_2 \end{bmatrix}_0 = \begin{bmatrix} 2 \\ 1 \end{bmatrix} \]

\[ \bar{k}_1 = \begin{bmatrix} k'_1 \\ k''_1 \end{bmatrix} = \begin{bmatrix} -100 \times 2 \\ 2 \times 2 - 1 \end{bmatrix} = \begin{bmatrix} -200 \\ 3 \end{bmatrix} \]

\[ \bar{k}_2 = \begin{bmatrix} k'_2 \\ k''_2 \end{bmatrix} \Rightarrow \bar{k}_2 = f(t_{n+1/2}, y_n + \frac{1}{2} \bar{k}_1 h) \]

= \begin{bmatrix} 0.01, & 2 + \frac{1}{2} (-200) \times 0.02 \\
0.01, & 1 + \frac{1}{2} (3) \times 0.02 \end{bmatrix} = \begin{bmatrix} 0.01, & 0.00 \\
0.01, & 1.03 \end{bmatrix} = \begin{bmatrix} 0.00 \\
1.03 \end{bmatrix} \]

\[ \bar{k}_3 = \begin{bmatrix} k'_3 \\ k''_3 \end{bmatrix} \Rightarrow \bar{k}_3 = f(t_{n+1/2}, y_n + \frac{1}{2} \bar{k}_2 h) \]

= \begin{bmatrix} 0.01, & 2 + 0 \times \frac{0.02}{2} \\
0.01, & 1 - 1.03 \times \frac{0.02}{2} \end{bmatrix} = \begin{bmatrix} 0.01, & 2.000 \\
0.01, & 0.9897 \end{bmatrix} = \begin{bmatrix} -100 \times 2 \\
2 \times 2 - 0.9897 \end{bmatrix} = \begin{bmatrix} -200 \\
3.0103 \end{bmatrix} \]

\[ \bar{k}_4 = \begin{bmatrix} k'_4 \\ k''_4 \end{bmatrix} \Rightarrow \bar{k}_4 = f(t_{n+1}, y_n + h \bar{k}_3) \]
\[ f[0.02, 2 - 0.02 \times 200] = f[0.02, 1 + 0.02 \times 3.0103] = f[0.02, 1.060206] \]

\[ \begin{bmatrix} -100 \times 2 \\ 2 \times -2 - 1.060206 \end{bmatrix} = \begin{bmatrix} 200 \\ -5.060206 \end{bmatrix} \]

\[ \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \begin{bmatrix} 2 \\ 1 \end{bmatrix} + \frac{0.02}{6} \begin{bmatrix} -200 + 2 \times 0 - 2 \times 200 + 200 \\ 3 - 2 \times 1.03 + 2 \times 3.0103 - 5.060206 \end{bmatrix} \]

\[ \begin{bmatrix} 0.66667 \\ 1.00633 \end{bmatrix} \] Ans.

⇒ How to choose h? Choose a reasonable ‘h’ depending on the physics of the problem. Solve and re-do the calculation for \( h/2 \) and check the convergence. Sometimes, one may have to increase the step-size if the accuracy can be relaxed.

⇒ There are R-K-Mersen or R-K-Fehlberg automatic step-size control method where ‘h’ is adjusted (either \( h \to 2h \) or \( h \to \frac{h}{2} \)) depending upon the error in the RK-4 solution relative to that from error in a higher order method proposed by Mersen or Fehlberg.

**In summary**, the single step methods to solve 1st order ODE(s) are all about finding a relatively “accurate” slope or \( \tan \theta \) to reach the target at “h” step forward. The difference between the methods is the computation of the slopes, viz.,

\( (t_n, y_n) \) or \( (t_{n+1}, y_{n+1}) \) or \( (t_{n+1/2}, y_{n+1/2}) \) or a combination of these?

Thus, the methods are called differently (explicit/implicit) and have different orders (1st/2nd/4th, etc) of accuracy and different stability regions (smaller or bigger):

\[ y_{n+1} = y_n + h \phi(t_n, y_n): \text{Forward Euler} \]

\[ y_{n+1} = y_n + h \phi(t_{n+1}, y_{n+1}): \text{Backward Euler} \]

\[ y_{n+1} = y_n + h [\phi(t_n, y_n) + (t_{n+1}, y_{n+1})]/2: \text{Trapezoidal Rule} \]

\[ y_{n+1} = y_n + h k: \text{RK-4 predictor-corrector} \]

*where, k is some weightage average of slopes calculated at some intermediate locations.*

**Note:** All methods predict/estimate the functional value, \( y_{n+1} \) linearly starting with initial condition, \( y_n \) at \( x_n \).
Example 1 (RK-4)

Consider a special (diameter = 10 cm) ball made of steel \( k = 40 \) \( W/m-K \), \( \rho = 8000 \) \( kg/m^3 \), \( C_p = 400 \) \( J/kg-K \). The initial temperature of the ball is 300 K. It is immersed in a large oil tank at 400 K. The convective heat transfer coefficient, \( h \) at the sphere surface is 3000 \( W/m^2-K \). Assume that there is no radial temperature gradient inside the ball. Use the R-K-4 numerical technique to solve the governing first order energy balance equation for predicting the temperature of the sphere at \( t = 1 \) min after it was immersed in the oil tank. Use \( \Delta t = 10 \) s. Repeat calculations for \( \Delta t = 5 \) s. Draw graphical depiction of the slopes comprising all stages of the RK method. Do calculations up to 4 digits after decimal. Calculate the rate of temperature-decrease at \( t = 0, 0.5 \) and 1.0 min.

The energy balance (transient/unsteady equation):

\[
\rho C_p \frac{dT}{dt} = -hA_s (T - T_o)
\]

\((kg/m^3 \cdot J/kg-K \cdot \frac{K}{s}) = \frac{J}{s} - m^2 - k \ (400 - T) \ K \left( \frac{4\pi R^2}{3\pi R^3} \right) m^2 m^{-3}
\]

\[
8000 \times 400 \times \frac{dT}{dt} = +3000 \times \frac{3}{0.05} (400 - T)
\]

\[
\frac{dT}{dt} = +0.05625 (400 - T) = f(t, T)
\]

\( \Delta T = h = 10 \) or 5 s

\( k_1 = f(0, 300) = +0.05625(400 - 300) = 5.6250 \)

\( k_2 = f(5, 300 + \frac{5.625 \times 5}{328.125}) = +0.05625(400 - 328.125) = 4.0429 \)

\( k_3 = f(5, 300 + \frac{4.0429 \times 5}{320.2145}) = 0.05625(400 - 320.2145) = 4.4879 \)
\[ k_4 = f(10, 300 + 4.4879 \times 10) = 0.05625(400 - 344.879) = 3.1005 \]

\[ \bar{k} = \frac{1}{6} (5.6206 + 2 \times 4.0429 + 2 \times 4.4879 + 3.1005) = 4.2979 \]

\[ T = 300 + 4.2979 \times 10 = 342.9795 \text{ K} \text{ Ans.} \]

March for the next time steps \( t = 20, 30, 40, 50, 60 \text{ s} \), each time using the calculated values from the previous time steps (viz. 342.9795, etc). Repeat the entire calculations for \( \Delta t = 5 \text{ s} \).

⇒ In a 20-25 min quiz or examination, such problem can be solved for one time step using calculator. One requires to write a code to solve such problem for a long time or several steps calculations.

⇒ Rate at \( t = 0, 0.5 \) and 1.0 min

\[
\left. \frac{dT}{dt} \right|_0 = 0.05625(400 - T) = 0.05625 \times 100 = 5.6250 \text{ k/s}
\]

(Note: Once the functional values or temperatures are determined or known, the derivatives can also be calculated using the formulae you learnt! But, here is the analytical solution.)

Plot the graph as done in the previous lecture and approximately draw the steps for \( k_1, k_2, k_3, k_4, \bar{k} \), and functional values \( (T_n, T^*_n, T^{**}_n, T^{***}_n, T_{n+1}) \) on y-axis.

⇒ From the chemical engineering point of view, temperature-gradient in (steel) sphere was neglected considering a large thermal conductivity of the material, \( k \gg h'R' \) or small Biot #. Therefore, the lump body approach was used to determine the sphere temperature, and the resulting energy balance equation is derived to be a 1st order ODE, else.

**Ex2.** Consider a steady-state 1D reactive flow of a gaseous species, A in a long quartz tubular reactor (ID = D, length = L) \( (\text{Re} > 5000) \) radiated by UV light. The average velocity in the tube is \( \bar{V} \). The species \( \text{A} \) is converted to B by the 1st order homogeneous reaction \( (r = kC_A) \), as it flows in the tube. The inlet concentration of A is \( C_{Ao} \). Determine the axial concentration profiles of A in the reactor. The reaction is exothermic: \( (-\Delta H; \text{cal/mol}) \).

Inlet temperature is \( T_o \)
A species balance can be derived as follows, neglecting radial concentration profiles \( (\text{Pe}, r \gg 1) \)

\[
\frac{\partial C_A}{\partial t} + \bar{V} \frac{\partial C_A}{\partial x} = D_x \frac{\partial^2 C_A}{\partial x^2} - k C_A \quad (\text{mol}/S - m^3)
\]

or,

\[
\bar{V} \frac{dC_A}{dx} = D_x \frac{d^2 C_A}{dx^2} - k C_A \quad - (1)
\]

Note that the reaction is exothermic and the rate constant is temperature dependent. Write down the energy-balance eqn:

\[
\ddot{\rho} \ddot{C}_p \left( \frac{\partial T}{\partial t} + \bar{V} \frac{\partial T}{\partial x} \right) = k \frac{\partial^2 T}{\partial x^2} + k C_A (-\Delta H) \quad (\text{cal}/S - m^3)
\]

Further approximation can be made if mass/ thermal diffusion terms are neglected \( (V \nabla C_A \gg DV^2 A, V \nabla T \gg \alpha V^2 T) \), considering a large axial Pe, x # for mass as well as thermal transport. The equations (1-2) are modified as

\[
\bar{V} \frac{dC_A}{dx} = -k C_A = -k_0 \exp\left(-\frac{E}{RT}\right) C_A \quad - (3)
\]

\[
\bar{V} \frac{dT}{dx} = \frac{k_0 \exp\left(-\frac{E}{RT}\right)}{\bar{V} \ddot{C}_p} (-\Delta H) C_A \quad - (4)
\]

or

\[
\frac{dy_1}{dx} = f_1(y_1, y_2) = -\frac{k_0 \exp\left(-\frac{E}{Ry_2}\right) y_1}{\bar{V}} = \frac{A}{y_2} y_1
\]

\[
\frac{dy_2}{dx} = f_2(y_1, y_2) = \frac{k_0 \exp\left(-\frac{E}{Ry_2}\right) (-\Delta H) y_1}{\bar{V} \ddot{C}_p} = \frac{C}{y_2} y_1
\]

The two 1st order equations are coupled and the right hand side terms have non-linear dependence on \( y_1 \) and \( y_2 \). RK-4 can be applied without any problem, with the conditions:

\[
X = 0; \ y_1 = y_{10} \quad \text{and} \quad y_2 = y_{20}. \quad \text{You can choose a step-size of } \Delta x = L/10.
\]

**Notes:** - If the axial diffusion terms are not neglected, the governing equations will assume a form of 2nd order ODE, which will be discussed in the next lecture as Boundary Value Problems.

- There are higher-order RK methods and even implicit RK method discussed in literature to solve ODE or initial value problem.
There are two commonly used multi-step methods for solving ODEs (Note: RK-4 is a single step multi-stage method): \textbf{Adams-Bashforth} and \textbf{Adams-Moulten}. These methods use a polynomial on the derivatives of a function, passing through the single or multi-points.

**Adams-Bashforth (Explicit)**

\[
\frac{dy}{dt} = f(y, t) \equiv f(y(t), t)
\]

\[t = 0, \quad y(0) = y_0\]

Solve for \(y(t) = \) ?

\[
\begin{align*}
&\{t_0 \quad t_1 \quad t_n \quad t_{n+1} \} \\
&\{y_0 \quad y_1 \quad y_n \quad y_{n+1} \quad : \text{solve} \} \\
&\{y'_0 \quad y'_1 \quad y'_n \quad y'_{n+1} \quad : \text{gradient} \}
\end{align*}
\]

We have,

\[y_{n+1} = y_n + \int_{t_n}^{t_{n+1}} y'dt\]

\[
\text{extrapolated value between } t_n \text{ and } t_{n+1}
\]

Define \(\alpha = \frac{t-t_n}{h}:\) \[y_{n+1} = y + h \int_0^1 y'(\alpha)d\alpha \quad (0 \leq \alpha \leq 1) \quad - (1)\]

Fit a \(j^{th}\) order polynomial of \(y'_n\) through \(X_n\) and \(X_{n-j}\) \((j + 1 \text{ pts preceding } X_n)\) using \textbf{backward difference formula} \((\forall y_i = y_i - y_{i-1})\).

\[y'(\alpha) = \left[1 + \alpha \nabla + \frac{\alpha(\alpha + 1)}{2!} \nabla^2 + \ldots + \frac{\alpha(\alpha + 1)\ldots(\alpha + j - 1)}{j!} \nabla^j \right]y'_n + R(\xi)\]

(Thus, \(y'(\alpha)\) is the polynomial between \((X_n, X_{n-1}, X_{n-2} \ldots X_{n-j})\), substituting in \((1)\)

\[y_{n+1} = y_n + h \left[1 + \frac{1}{2} \nabla + \frac{5}{12} \nabla^2 + \frac{3}{8} \nabla^3 + \ldots C_j \nabla^j \right]y'_n + h \int_0^1 R(\xi)d\xi\]

\(j = 0: \) you have fitted a constant polynomial of the derivative \((y')\)

\[
\begin{array}{c}
\bullet \quad \bullet \quad \bullet \quad \bullet \\
\bullet \quad \bullet \quad \bullet \quad \bullet \\
\bullet \quad \bullet \quad \bullet \quad \bullet \\
\bullet \quad \bullet \quad \bullet \quad \bullet \\
\bullet \quad \bullet \quad \bullet \quad \bullet \\
\end{array}
\]

\[y'_{n+1} = y_n + hy'_n + \frac{h^2}{2} y''(\xi) \quad (y_n < \xi < y_{n+1})\]

(Recognize it as the Euler 1\textsuperscript{st} order formula/explicit)

\(j = 1, \) you have fitted a line (linear polynomial) between \(X_n\) and \(X_{n-1}\)

\[
\begin{array}{c}
\bullet \quad \bullet \quad \bullet \quad \bullet \\
\bullet \quad \bullet \quad \bullet \quad \bullet \\
\bullet \quad \bullet \quad \bullet \quad \bullet \\
\bullet \quad \bullet \quad \bullet \quad \bullet \\
\bullet \quad \bullet \quad \bullet \quad \bullet \\
\end{array}
\]

\[y'_{n+1} = y_n + h \left[y'_n + \frac{1}{2} \nabla y'_n \right] + \frac{5}{12} h^3 f''(\xi)\]
\[
= y_n + \frac{h}{2} [3f(y_n) - f(y_{n-1})] \quad - 2^{\text{nd}} \text{ order (Adam – Bashforth)}
\]

\[j = 2, \quad \text{you have a quadratic polynomial between } (X_n, X_{n-1}, X_{n-2})\]

Therefore, by taking different numbers of points preceding \( t_n \) or \( X_n \) one can get a set of working formulae having different \( O(h^m) \)

\[
y_{n+1} = y_n + h \sum_{m=1}^{k} \beta_{km} f_{n+1-m}
\]

\[
\begin{array}{cccc}
\beta_{1m} & 1 & & \\
2\beta_{2m} & 3 & -1 & \\
12\beta_{3m} & 23 & -16 & 5
\end{array}
\]

\( j = 1 \) (linear)

\( j = 2 \) (quadratic)

⇒ From the above description, it is clear that the method has a ‘starting’ problem because only one condition is known: \( y(0) = y_0 \). In practice one starts with the Euler’s forward/explicit approach to calculate \( y_1 \), then use \( 2^{\text{nd}} \) order method to predict \( y_2 \), and then use \( (y_0, y_1, y_2) \) to calculate \( y_3 \). Use of the preceding ‘3’ data-points gives \( 3^{\text{rd}} \) order accurate method.

⇒ Similar to the Adams-Bashforth (explicit), there is Adams-Moulton (Implicit) method based on forward difference interpolation formula. For details, refer the textbooks.
Lecture #19

Instability and stiffness for a system of ODEs

In the previous lectures, we have shown that a system of ODEs (IVP) \( y'_i = f_i(y_1 \cdots y_m) \) \( i = 1,2,\cdots m \) with \( y_i(0) = y_0 \) can be written as the coupled ODEs: \( \vec{y}'_i = A\vec{y} \), where \( A \) is the Jacobian matrix.

It is also clear that for the \( m \times m \) matrix \( A \), there are \( m \) eigenvalues: \( A\phi_k = \lambda_k\phi_k \), where \( \phi_k \) is the eigenvector corresponding to \( \lambda_k \) eigenvalue. Now, make use of linear transformation: one can construct a matrix, \( S \) whose columns are the eigenvectors of \( A \) such that \( S^{-1}AS = \Lambda \), where \( \Lambda \) is the diagonal matrix of the elements which are \( \lambda_k \) of \( A \), as \( \begin{bmatrix} \lambda_1 & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & \lambda_k \end{bmatrix} \).

Then one can write,

\[ \vec{z}'' = S^{-1}\vec{y}' = S^{-1}A\vec{y} = (S^{-1}AS)S^{-1}\vec{y} = \Lambda\vec{z} \]

or \( z'_k = \lambda_k z_k, \quad k = 1,2,\cdots n \) — cannonical form.

where, \( z'_k \) are uncoupled linear ODEs. Therefore, all (stability) characteristics of single ODE will also be shown by the system of ODEs.

We have also seen earlier shown that a general solution to the system of ODEs can be written as \( C_1 e^{\lambda_1 t} \{ \} + C_2 e^{\lambda_2 t} \{ \} + \cdots \), where the terms in the parenthesis are the eigenvectors corresponding to the eigenvalues. In such case, the growth or decay of the function depends on \( \lambda_{\min} - \lambda_{\max} \). A large numerical value of \( \lambda_{\max} \) will cause the function to grow or decay at a faster rate than that corresponding to
\( \lambda_{\text{min}} \). In other words, small change in ‘t’ will cause a large change/variation in \( y(\lambda_{\text{max}}) \). Solving such type of system of ODEs is numerically not trivial because a fine grid or step-size \( \Delta t \) or \( h \) is required to accurately predict change in \( y(\lambda_{\text{max}}) \), whereas a coarse grid can be used to predict \( y(\lambda_{\text{min}}) \).

- Such equations are called stiff ODEs. In general, 
  \[
  \text{Stiff ratio (SR)} = \frac{\lambda_{\text{max}}}{\lambda_{\text{min}}} > 10
  \]
  represents a system of stiff ODEs.

- Examples:
  (1) A common example is the boundary layer problem in hydrodynamics or heat or mass transport. Functional value changes sharply within the boundary layer, from that at the surface to that in the potential region far from the surface. Therefore, a numerical computation of the functional values in the boundary layer (bottom region), in principle, requires fine grid size, \( \Delta x_1 \), while that in the potential region (top region) requires coarse grid size, \( \Delta x_2 \). However, the sets of the conservation equations in two regions are coupled through some interfacial boundary conditions, and therefore, must be solved simultaneously using \( \Delta x_1 \), which is CPU-wise extensive!

(2) A combination of series and parallel chemical reactions with low and high rate constants:

\[
\frac{d\vec{y}}{dt} = \begin{bmatrix} -100 & 0 \\ 2 & -1 \end{bmatrix} \vec{y}; \quad \vec{y}(0) = [2 \quad 1]^T
\]

on coefficient matrix ‘A’: \((-100 - \lambda)(-1 - \lambda) = 0 \Rightarrow \lambda_1 = -100, \lambda_2 = -1\)

\[
\lambda_1 = -100: \quad \begin{bmatrix} -100 & 0 \\ 2 & -1 \end{bmatrix} \begin{bmatrix} Y_1 \\ Y_2 \end{bmatrix} = 100 \begin{bmatrix} Y_1 \\ Y_2 \end{bmatrix} \quad (\text{Note: } SR = 100)
\]

\[
2X_1 = -99X_2 \Rightarrow Y^{(1)} = \begin{bmatrix} 1 \\ -2/99 \end{bmatrix}
\]

\[
\lambda_2 = -1: \quad \begin{bmatrix} -100 & 0 \\ 2 & -1 \end{bmatrix} \begin{bmatrix} Y_1 \\ Y_2 \end{bmatrix} = -1 \begin{bmatrix} Y_1 \\ Y_2 \end{bmatrix}
\]

\[-100Y_1 = -Y_1 \text{ and } 2Y_1 - Y_2 = -Y_2 \Rightarrow Y^{(2)} = \begin{bmatrix} 0 \\ 1 \end{bmatrix}
\]

GS: \( \vec{Y} = C_1 e^{-100t} \begin{bmatrix} 1 \\ -2/99 \end{bmatrix} + C_2 e^{-t} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \)
or

\[
\begin{align*}
Y_1 &= C_1 e^{-100t} \\
Y_2 &= \frac{-2}{99} C_1 e^{-100t} + C_2 e^{-t}
\end{align*}
\]

Apply:

\[
\bar{Y} = \frac{103}{99} 2 e^{-100t} - \frac{4}{99} e^{-t} \]

\text{Analytical solution.}

To solve numerically, a fine grid size \( \Delta t \) will be initially required to accurately predict a fast decay in the functional value of \( y_1 \), which can be relaxed or step-size can be increased only during the later part of calculations.

In other words, time change in \( y_2 \) is gradual (slow). Therefore, one would have used a coarse grid size for \( y_2 \) but for a rapid change in \( y_1 \) during initial time of calculations which requires fine grid sizes.

\( \Rightarrow \) SKG's book has given one good example of stiff equations

\[
\begin{align*}
\frac{dy_1}{dt} &= 77.27(y_2 - y_1 y_2 + y_1 - 8.375 \times 10^{-6} y_1^2) \\
\frac{dy_2}{dt} &= \frac{-y_2 - y_1 y_2 + y_3}{77.23} \\
\frac{dy_3}{dt} &= 0.161(y_1 - y_3)
\end{align*}
\]

\( \bar{y}(0) = [4 \quad 1.1 \quad 4]^T \)

In this case, stiffness changes with time, requiring \textbf{adaptive mesh sizes}: coarse when \( f_n \) values slowly change and fine when they change rapidly.

\( \Rightarrow \) If you use one \textbf{fixed} fine step-size throughout the calculations, it is a wastage of CPU time.
**Gear’s Technique:** Used to solve stiff ODEs, based on multiple steps but using predictor-corrector approach:

Predictor *(explicit)*: \( \bar{y}_{n+1} = \bar{a}_1 y_n + \bar{a}_2 y_{n-1} + \cdots + \bar{a}_k y_{n-(k-1)} + h \bar{\beta}_0 y_n' \)

Corrector *(implicit)*: \( y_{n+1} = \alpha_1 y_n + \alpha_2 y_{n-1} + \cdots + \alpha_k y_{n-(k-1)} + h \beta_0 y_n' \)

You should note that this method also has a "starting" problem, similar to the previously discussed multi-step methods.

**Predictor Table**

<table>
<thead>
<tr>
<th>( k )</th>
<th>( \bar{a}_1 )</th>
<th>( \bar{a}_2 )</th>
<th>( \bar{a}_3 )</th>
<th>( \ldots )</th>
<th>( \bar{a}_6 )</th>
<th>( \bar{\beta}_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>\ldots</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>\ldots</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>(-3/2)</td>
<td>(6/2)</td>
<td>(-1/2)</td>
<td>\ldots</td>
<td>0</td>
<td>(6/2)</td>
</tr>
<tr>
<td>\vdots</td>
<td>\vdots</td>
<td>\vdots</td>
<td>\vdots</td>
<td>\ldots</td>
<td>\vdots</td>
<td>\vdots</td>
</tr>
<tr>
<td>6</td>
<td>\vdots</td>
<td>\vdots</td>
<td>\vdots</td>
<td>\ldots</td>
<td>\vdots</td>
<td>\vdots</td>
</tr>
</tbody>
</table>

**Corrector Table**

<table>
<thead>
<tr>
<th>( k )</th>
<th>( \alpha_1 )</th>
<th>( \alpha_2 )</th>
<th>( \alpha_3 )</th>
<th>( \ldots )</th>
<th>( \alpha_6 )</th>
<th>( \beta_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\frac{4}{3})</td>
<td>0</td>
<td>0</td>
<td>\ldots</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>(-\frac{1}{3})</td>
<td>0</td>
<td>\ldots</td>
<td>0</td>
<td>(2/3)</td>
</tr>
<tr>
<td>3</td>
<td>(\frac{18}{11})</td>
<td>(-\frac{9}{11})</td>
<td>(\frac{2}{11})</td>
<td>\ldots</td>
<td>0</td>
<td>(\frac{6}{11})</td>
</tr>
<tr>
<td>\vdots</td>
<td>\vdots</td>
<td>\vdots</td>
<td>\vdots</td>
<td>\ldots</td>
<td>\vdots</td>
<td>\vdots</td>
</tr>
<tr>
<td>6</td>
<td>\vdots</td>
<td>\vdots</td>
<td>\vdots</td>
<td>\ldots</td>
<td>\vdots</td>
<td>\vdots</td>
</tr>
</tbody>
</table>

The first row (\( k = 1 \)) of each table represents \( j = 0 \) (no previous data in the interpolating function); the second row (\( k = 2 \)) represents \( j = 1 \) (one preceding data in the interpolating function or a linear function), and the third row (\( k = 3 \)) represents \( j = 2 \) (two preceding data in the interpolating function or a quadratic function or parabola), etc.

**Quiz II**
Lecture #20

BVP (Boundary Value Problems)/2\textsuperscript{nd} order ODEs

In this lecture, we will learn how to apply finite difference (direct) methods to solve BVPs. Such problems are common in 1 D steady-state heat and mass transport in solid or fluid. The general form of the BVP assumes a 2\textsuperscript{nd} order ODE:

\[
\frac{d^2 y}{dx^2} = f(x, y, y') \quad \text{with two boundary conditions}
\]

required at two ends of the domain \((x = 0\) and \(x = L\) or \((0,1))\).

A general form of BVP can also be written as:

\[
A(x) \frac{d^2 y}{dx^2} + B(x) \frac{dy}{dx} + C(x) y + D(x) + E = 0; \quad (A(x) \neq 0)
\]

The required boundary conditions at two ends of the domain can assume any form: Dirichlet or Danckwarts or Neumann. That is, either functional value or gradient or mixed condition can be specified:

\[y = c, \text{ or } y' = c, \text{ or } ay' + by = c.\]

Let us solve a general BVP equation:

\[
A(x) \frac{d^2 y}{dx^2} + B(x) \frac{dy}{dx} + C(x) y + D(x) + E = 0;
\]

\[
0 \quad 1 \quad 2 \quad i-1 \quad i \quad i+1 \quad N-1 \quad N
\]

\textbf{Step 1:} divide the domain into \(N\) equal steps/grids or grids. Therefore, there are \((N+1)\) nodes.

\textbf{Step 2:} discretize the equation or each terms of the equation at \(i^{th}\) grid. In this course, we will discretize the terms using 2\textsuperscript{nd} order accurate method (recall numerical differentiation).

\[
A(x_i) \frac{y_{i-1} - 2y_i + y_{i+1}}{h^2} + B(x_i) \frac{y_{i+1} - y_{i-1}}{2h} + C(x_i) y_i + D(x_i) + E = 0
\]

\textbf{Step 3:} Arrange the terms:

\[
\left(\frac{A(x_i)}{h^2} - \frac{B(x_i)}{2h}\right) y_{i-1} - \left(\frac{2A(x_i)}{h^2} - C(x_i)\right) y_i + \left(\frac{A(x_i)}{h^2} + \frac{B(x_i)}{2h}\right) y_{i+1} = -D(x_i) - E
\]

or

\[
a_i y_{i-1} + b_i y_i + c_i y_{i+1} = d_i \quad \text{← discretized form of equation}
\]
In principle, this equation should be valid for $i = 0 \cdots N$. However, there may be problem (!) at the boundary nodes $i = 0$ and $N$, because $y_{-1}$ and $y_{N+1}$ may not be known or defined or calculated. You should carefully inspect the given boundary conditions and decide to apply the discretized equation over $(i = 0 \cdots N)$ or $(i = 1 \cdots N)$or $(i = 1 \cdots N - 1)$or $(i = 0 \cdots N - 1)$ so that the number of equations is the same as that many unknowns ($y_i$). For the moment, let us take the simplest boundary conditions, $y(0) = y_0$ and $y(N) = y_N$.

Apply the discretized equation over $i = 1 \cdots N - 1$ as

\[
\begin{align*}
    i = 1: & \quad a_1 y_0 + b_1 y_1 + c_1 y_2 = d_1 \\
    i = 2: & \quad a_2 y_1 + b_2 y_2 + c_2 y_3 = d_2 \\
    & \vdots \\
    i = N - 1: & \quad a_{N-2} y_{N-3} + b_{N-2} y_{N-2} + c_{N-2} y_{N-1} = d_{N-2} \\
    i = N: & \quad a_{N-1} y_{N-2} + b_{N-1} y_{N-1} + c_{N-1} y_N = d_{N-1}
\end{align*}
\]

Step 4: Apply the BCs and bring the terms containing $y_0$ and $y_N$ to RHS:

\[
\begin{align*}
    b_1 y_1 + c_1 y_2 = (d_1 - a_1 y_0) = d_1' \\
    a_2 y_1 + b_2 y_2 + c_2 y_3 = d_2 \\
    & \vdots \\
    a_{N-2} y_{N-3} + b_{N-2} y_{N-2} + c_{N-2} y_{N-1} = d_{N-2} \\
    a_{N-1} y_{N-2} + b_{N-1} y_{N-1} = (d_{N-1} - c_{N-1} y_N) = d_{N-1}'
\end{align*}
\]

There are exactly $(N-1)$ unknown and $(N-1)$ equations. Notably, set of equations can be written as

\[A\bar{y} = \bar{b}\]

where

\[
A = \begin{bmatrix}
    b_1 & c_1 & 0 \\
    a_2 & b_2 & c_2 & 0 \\
    0 & a_{N-2} & b_{N-2} & c_{N-2} \\
    0 & 0 & a_{N-1} & b_{N-1}
\end{bmatrix}
\]

is the tridiagonal matrix.

Step 5: Call Thomas Algorithm (learnt earlier) to invert such matrix:

You should be able to clearly recognize that while preparing to call tridiagonal matrix, the following coefficients were changed:

\[d_1' = d_1 - a_1 y_0 : 1^{\text{st}} \text{row } (i = 1)\]

The other coefficients remained the same: ($i = 2, N-2$)

\[
a_i = \frac{A(x_i)}{h^2} - \frac{B(x_i)}{2h} ; \quad b_i = C(x_i) - \frac{2A(x_i)}{h^2}
\]
\[ c_i = \frac{A(x_i)}{h^2} + \frac{B(x_i)}{2h}; \quad d_i = -D(x_i) - E; \]

Also, \(d_{N-1}\) was changed as \(d'_{N-1} = d_{N-1} - c_{N-1}Y_N\) : last row \((i = N - 1)\)

⇒ Let us consider another example where the BVP equation is the same. At boundary, \(y(0) = y_0\) (also same as before). However, at the other boundary, gradient is specified instead of functional value: \(y_N' = 0\).

The boundary condition \(y_N'\) can be discretized as \(\frac{Y_{N+1} - Y_{N-1}}{2h} = 0\) \((0(h^2))\) or \(Y_{N+1} = Y_{N-1}\)

Considering that \(Y_N\) is NOT known in this case, the coefficients \((a_i, b_i, c_i, d_i)\) are extended to the rows: \(i = 1 \ldots N\), i.e., the matrix A will have ‘N’ rows and the 1st & last row will be modified as

\[ d_1 = d_1 - a_1Y_0 \quad \text{(same as before)} \]

and \[ a_N = a_N + c_N; \quad \text{why?} \]

because the \(N\)th equation

\[ a_NY_{N-1} + b_NY_N + c_NY_{N+1} = d_N \]

is modified as

\[ a_NY_{N-1} + b_NY_N + c_NY_{N-1} = d_N \]

on substitution of the bc.

Finally, call \(\text{Tridiagonal (}N, a, b, c, d, Y; \ i = 1, N\)\)

⇒ It is recommended that you should do your best to keep consistency between the order of methods used to discretize the equation and boundary conditions. Also note that, 2nd order discretization method is reasonably good/accurate for engineering calculations. If you use a higher order method, the coefficient matrix A will no more be tridiagonal that is easy and fast to invert.

Ex: Consider the steady-state one dimensional heat conduction in a fine (length \(L\), cross-section \(A\), perimeter \(P\)), whose one end is at a constant temperature \(T_f\) and the other end is insulated. The ambient temperature is \(T_a\) and the convective heat transfer coefficient at the fix surface is \(h\).

Solve the steady-state temperature profiles in the fin.

An energy balance over ‘\(A\Delta x\)’ control volume will result in the following differential equation:

\[ \rho C_P \left( \frac{dT}{dt} + \nabla T \right) = k \nabla^2 T + \left\{ \begin{array}{c} \text{cal} \left/ \frac{S - m}{m^2} \right. \cdot \frac{m^2}{(A \Delta x)} \right\} \nabla x + \left\{ \begin{array}{c} \text{cal} \left/ \frac{S - m^2}{m^3} \right. \cdot \frac{m^3}{(A \Delta x)} \right\} \nabla x \]

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Note that there is no source or sink of heat as such in the fin. However, considering 1D axial heat transfer, heat dissipated from the fin surface is homogenously distributed within the $CV: S = -h(T - T_a)a_s$ where $a_s$ is the surface area per unit volume of the fin.

$$k \frac{dT}{dx^2} - \frac{h(T-T_a)P}{A} = 0$$

or \( \frac{dT}{dx^2} + BT + C = 0 \) where $B = \frac{-hP}{kA}$, $C = \frac{hP}{kA}T_a$ and choose $\Delta h = L/10$

BC: \( T(x = 0) = T_f \); \(-k\nabla T(x = L) = 0 \) or \( \frac{dT}{dx} = 0 \) (insulation)

Discretize the equation using the 2nd order method.

Soln:

\[
\frac{d^2T}{dx^2} + BT + C = 0
\]

\[
\frac{T_{i-1} - 2T_i + T_{i+1}}{h^2} + BT_i + C = 0
\]

\[
T_{i-1} + (Bh^2 - 2)T_i + T_{i+1} = -Ch^2
\]

\( i = 1, N \)

Prepare the tridiagonal matrix

\[
a_i = 1, \quad b_i = (Bh^2 - 2), \quad c_i = 1, \quad d_i = -Ch^2, \quad i = 1, N
\]

Apply BC/discretize BC:

\[
T_0 = T_f(i = 0), \quad T_{N+1} = T_{N-1} (i = N)
\]

Therefore, 1st & last row will be modified as

\[
d_1 = d_1 - a_1 T_f
\]

\[
a_N = a_N + c_N
\]

How? 1st row is modified as \((Bh^2 - 2)T_1 + T_2 = -Ch^2 - T_f\)

Last row is modified as \(T_{N-1} + (Bh^2 - 2)T_N + T_{N-1} = -Ch^2\)

Therefore, you have the tridiagonal matrix $A$. Call the subroutine as:

\[
\text{Tridiagonal} (N, a, b, c, d, y)
\]

(Note that the total number of equations is $N$)

As an example, take the fin-problem of heat transfer: $L = 1 \text{ cm}$, width of the fin = $0.1 \text{ cm}$, $T_f = 100^\circ C$, $T_a = 30^\circ C$, $h = 100 \text{ W/m}^2K$, $k = 20 \text{ W/m} - K$. Take $\Delta h = 0.1 \text{ cm}$, write a programming code to obtain the solution and plot the temperature profiles:
Calculate the rate of heat-loss/dissipation to atmosphere from the fin.

Note: \( Q \) (cal/s) = \( \int h A \ (T(x) - T_a) \ dx = \sum h A \ (T_i - T_a) \Delta x, \ i = 0, n \), where \( n \) is the number of nodes of the computational domain. Use Simpson’s 1/3 integration or Trapezoidal formula. Recall your knowledge of heat transfer. \( Q \) can also be calculated by determining the heat leaking into the fin at \( x = 0 \), viz. \( Q = \ -k A \frac{dT}{dx} \). You can calculate the derivative by the 2\textsuperscript{nd} order FDS using \( i = 0, 1 \) and \( 2 \) nodes. With a sufficient number of nodes or grids, two computations must produce the same results (cal/s). You should revisit Heat Transfer taught at the UG level. You can also calculate the fin-efficiency.

**Ex:** Consider the catalytic oxidation of \( SO_2 \) into \( SO_3 \) under the constant temperature and pressure conditions, over a spherical (diameter \( d_p = 1 \) mm) pt-dispersed porous carbon catalyst. \( SO_2 \) in air (1\%) diffuses (\( D = 1 \times 10^{-9} \) m\(^2\)/s) into the pores of the catalyst and is oxidized to \( SO_3 \) by a pseudo-zero\textsuperscript{th} order reaction, \( r = 0.01 \) moles s\(^{-1}\) m\(^3\). The convective film mass transfer coefficient is \( k_m = 0.1 \) m/s. Determine the steady-state concentration profiles of \( SO_2 \) within the pellet.

**Sol:**

\[ P, T = \text{constant} \]

\[ \frac{\partial C_A}{\partial t} + \nabla C_A = D_{pore} \nabla^2 C_A - k \]

or \( \frac{D_{pore}}{r^2} \frac{d}{dr} \left( r^2 \frac{dC_A}{dr} \right) = k \quad (0 \leq r \leq r_p) \)

continue in the next lecture………
Lecture #21

(continued.....from the previous lecture)

or \( D_p \frac{d^2 C_A}{dr^2} + \frac{2D_p}{r} \frac{dC_A}{dr} - k = 0 \)

or \( \frac{d^2 y}{dr^2} + \frac{2 dy}{r dr} + A = 0 \); \( A = \left( \frac{-k}{D_p} \right) \)

\[ \left( h = \frac{r_p}{N} \right) \]

**BCs.** \( r = 0 \) \( \frac{dC_A}{dr} = 0 \) (symmetric)

\( r = r_p \) \(- D_p \frac{dC_A}{dr} = k_m (C_A - C_b) \)

Discretized eqn:

\[ \frac{y_{i+1} - 2y_i + y_{i-1}}{h^2} + \frac{2}{r_i} \frac{y_{i+1} - y_{i-1}}{2h} + A = 0 \quad - (1) \]

\( (r_i = ih) \)

Discretized BCs:

\( r_i = 0 \) \( \frac{y_1 - y_{-1}}{2h} = 0 \)

\( (i = 0) \)

\( y_{-1} = y_1 \)

\( r_i = r_p \) \( - D_p \frac{y_{N+1} - y_{N-1}}{2h} = k_m (y_N - C_b) \)

\( (i = N) \)

\( y_{N+1} = \left( y_{N-1} - \frac{2h}{D_p} k_m y_N + \frac{2hk_m}{D_p} C_b \right) \)

Before you re-arrange the terms, you should realize that there is a clear discontinuity at \( r_i = 0 \) (or 1st node). Therefore, you cannot proceed without removing discontinuity. One way of doing this is to approximate \( \frac{1}{r} \frac{dy}{dr} \bigg|_{i=0} \) as \( \frac{d^2 y}{dr^2} \bigg|_{i=0} \) because \( \forall y = 0 \) at \( r = 0 \)

or \( \frac{y_{i+1} - 2y_0 + y_{i-1}}{h^2} + 2 \frac{y_{i+1} - 2y_0 + y_{i-1}}{h^2} + A = 0 \)

or \( \left( 3 \frac{d^2 y}{dr^2} + A \right) = 0 \)

or \( \frac{3}{h^2} y_{i+1} - 2y_0 + y_{i-1} + A = 0 \) at \( i = 0 \)

Eq. (1) is applied over the next nodes, i.e., \( i = 1 \cdots N \) without any discontinuity

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Arrange the terms now,

\[
\begin{align*}
&\ y_{-1} + \left( \frac{Ah^2}{3} - 2 \right) y_0 + y_1 = -A & r = 0 \\
&\left( \frac{1}{h^2} - \frac{1}{r_1h} \right) y_0 - \frac{2}{h^2} y_1 + \left( \frac{1}{h^2} + \frac{1}{r_1h} \right) y_2 = -A & r = 1 \\
&\left( \frac{1}{h^2} - \frac{1}{r_2h} \right) y_1 - \frac{2}{h^2} y_2 + \left( \frac{1}{h^2} + \frac{1}{r_2h} \right) y_3 = -A & r = 2 \\
&\vdots \\
&\left( \frac{1}{h^2} - \frac{1}{r_Nh} \right) y_{N-1} - \frac{2}{h^2} y_N + \left( \frac{1}{h^2} + \frac{1}{r_Nh} \right) y_{N+1} = -A & r = N
\end{align*}
\]

Apply the BCs (i = 0 and i = N)

1st row: \( \left( \frac{Ah^2}{3} - 2 \right) y_0 + 2y_1 = -A \)

Last row: \( \frac{2}{h^2} y_{N-1} - \left( \frac{2}{h^2} + \frac{2hkm}{Dp} \times \left( \frac{1}{h^2} + \frac{1}{r_Nh} \right) \right) y_N = -A - \frac{2hkm}{Dp} \left( \frac{1}{h^2} + \frac{1}{r_Nh} \right) \)

From the ‘preparation of tridiagonal matrix’ point of view,

\[ a_0 = 1, b_0 = \left( \frac{Ah^2}{3} - 2 \right), c_0 = 1, d_0 = -A \]

and

\[ a_i = \frac{1}{h^2} - \frac{1}{r_ih}, b_i = -\frac{2}{h^2}, c_i = \frac{1}{h^2} + \frac{1}{r_ih}, d_i = -A; \quad i = 1 - N \]

However, on the substitution of BCs,

\[ c_0 = c_0 + a_0 \quad (1\text{st row } @ i = 0) \]

\[ a_N = a_N + c_N, \quad b_N = b_N - c_N \frac{2hkm}{Dp}, \quad d_N = d_N - c_N \frac{2hkm}{Dp} \cdot \]

Therefore, \( A\tilde{X} = B \). There are \( N + 1 \) equations to solve \( (N + 1) \) unknown \( (Y_0 \cdots Y_N) \) and \( A \) is the tridiagonal matrix.

\textbf{call Tridiagonal} \( (N + 1, a, b, c, d, y) \) \( i = 0 \cdots N \)

Write a programming code to solve the SS profiles of \( C_A(r) \) for different \( r_p = 0.25, 0.5 \) and 1 mm, \( k_m = 0.01, 0.1, 0.5 \) m/s and \( D_p = 10^{-7}, 10^{-9}, 10^{-11} \) m²/s.

Plot the profiles and interpret the results.
Recall the course on chemical reaction engineering. Once SS $C_A(r)$ is calculated, you can calculate the (total) effectiveness factor considering both inter- and intraphase diffusion resistances by computing the total rate of the consumption of the species, $A$ within the catalyst and that corresponding to the bulk (gas) phase concentration. The computations may require numerical integration (maybe, Simpson’s $1/3$rd method) to calculate the volume-average quantities and/or numerical differentiation (may be, $2^{nd}$ order BDS) to calculate the flux at the surface of the sphere.

Ex. Consider the steady-state 1D reactive flow (Re > 5000) of a gaseous species $A$ in a long quartz tubular reactor (1D = D, length = L) radiated by UV light. Velocity in the tube is $\bar{V}$.

The species $A$ is converted into $B$ by the $1^{st}$ order homogeneous reaction $(r = kC_A)$, as it flows in the tube. The inlet concentration of A is $C_{A_0}$. Determine the axial concentration profiles $C_A(X) = ?$. The reaction takes place under isothermal conditions and $\Delta H \approx 0$.

\[ \frac{dC_A}{dt} + V \cdot \nabla C_A = D \nabla^2 C_A + (r_A) \]

BC. \[ X = 0 \quad C_A = C_{A_0} \quad X = L \quad \nabla C_A = 0 \quad \text{or} \quad \frac{dC_A}{dx} = 0 \quad \text{(long tube approximation)} \]

\[ \frac{dC_A}{dx} + B \frac{d^2C_A}{dx^2} + C C_A = 0, \quad B = -\frac{D}{\bar{V}}; \quad C = \frac{k}{\bar{V}}, \quad \Delta h = \frac{L}{N} \]
\[ \frac{y_{i+1} - y_{i-1}}{2h} + B \frac{y_{i+1} - 2y_i + y_{i-1}}{h^2} + Cy_i = 0, \quad i = 1, N \]

Discretize BCs: \( y_0 = C_{Ao} \); \( \frac{y_{N+1} - y_{N-1}}{2h} = 0 \Rightarrow y_{N+1} = y_{N-1} \)

Collect the terms:
\[ \left( \frac{B}{h^2} - \frac{1}{2h} \right)y_{i-1} - \left( \frac{2B}{h} - C \right)y_i + \left( \frac{B}{h^2} + \frac{1}{2h} \right)y_{i+1} = 0, \quad i = 1, N \]

Prepare the tridiagonal matrix:
\[
a_i = \left( \frac{B}{h^2} - \frac{1}{2h} \right), \quad b_i = \left( \frac{2B}{h} - C \right), \quad c_i = \left( \frac{B}{h^2} + \frac{1}{2h} \right), \quad d_i = 0; \quad i = 1, N
\]

On substitution of BCs,
\[
d_1 = d_1 - a_1 C_{Ao} \quad (i = 1, \text{ 1st row})
\]
\[
a_N = a_N + c_N \quad (i = N, \text{ last row})
\]

You have \( A\bar{y} = \bar{b} \), where \( A \) is the tridiagonal matrix.
\[
\bar{y} = 1, N
\]

call Tridiagonal (\( N, a, b, c, d, y \))

Plot (numerical solutions using reasonable values for \( D, \bar{V}, k, C_{Ao}, L \))
**Partial Differential Equations (PDEs)**

**Parabolic equations**

1D: \[ A \frac{\partial y}{\partial t} + B \frac{\partial^2 y}{\partial X^2} + \left( \frac{B}{r} \frac{\partial}{\partial r} \left( r \frac{\partial y}{\partial r} \right) \right) + \frac{B}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial y}{\partial r} \right) + C \frac{\partial y}{\partial X} + Dy + E = 0 \]

Such time dependent 1D (spatial) equations are common in heat/mass/momentum transport. The PDE representing conservation of transport variables usually contains a convective term \((V \cdot \nabla T)\) and a diffusion term, \((\alpha \nabla^2 C)\), besides the unsteady-state or transient term \((\rho C_p \frac{\partial T}{\partial t} \text{ or } \frac{\partial c}{\partial t} \text{ or } \rho \frac{\partial \vec{v}}{\partial t})\). Therefore,

\[
\begin{align*}
\frac{\partial C_A}{\partial t} + V_X \frac{\partial C_A}{\partial X} &= D \frac{\partial^2 C_A}{\partial X^2} - k C_A \\
\text{or } \rho C_p \left( \frac{\partial T}{\partial t} + V_X \frac{\partial T}{\partial X} \right) &= k \frac{\partial^2 T}{\partial X^2} + (kC_A)(-\Delta H) \\
\text{or } \rho \left( \frac{\partial V_X}{\partial t} + V_X \frac{\partial V_X}{\partial X} \right) &= \mu \frac{\partial^2 V_X}{\partial X^2} - \left( \frac{dp}{dX} \right) + \rho g_X \\
\text{or } \rho C_p \frac{\partial T}{\partial t} &= \frac{k}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T}{\partial r} \right) \\
\text{or } \frac{\partial C_A}{\partial t} &= \frac{D}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_A}{\partial r} \right) - k C_A
\end{align*}
\]

are all examples of the time-dependent 1D parabolic PDE. You may refer the book by Ferziger for the exact mathematical definition of different types of PDE including parabolic, elliptic or hyperbolic.

⇒ **Why ‘Parabolic’?** Because we march on time ‘endlessly’ covering the space.

⇒ **Note:** If you drop the time-dependent equation (or the unsteady-state or transient term), what do you get? A boundary value problem (BVP), which we covered in the previous lectures.

⇒ **Message is clear.** Solving 1D parabolic PDE is not different from solving BVP. The procedure for discretization in the space remains the same as before; it is to be repeated on every time step as you march by refreshing the numerical values from the previous step. In fact, you may like to copy and paste the programming code for BVP and nest it within the time loop. The graphical representation of the numerical calculation is as follows.

**March on time**

\[
\begin{array}{c}
t = 2 \\
t = 1 \\
t = 0 \\
0 & i & i + 1 & 1 \\
i - 1 & i & i + 1 & \\
i - 1 & i & i + 1 & \\
\end{array}
\]

\[ X \]
Take a general case:

\[ A \frac{\partial y}{\partial t} + B \frac{\partial y}{\partial x} = C \frac{\partial^2 y}{\partial x^2} + D \quad \text{(or} \quad A \frac{\partial y}{\partial t} = f(y_x, y_{xx}, D)) \]

\[
\begin{align*}
t &= 0 & y &= 0 & \text{for all} \ L > X > 0 \\
t &= 0^+ & X &= 0 & y &= y_0 \quad ; \quad X &= L \quad \frac{\partial y}{\partial X} = 0
\end{align*}
\]

**Steps**

Discretize 'X' -terms as before. On time, apply trapezoidal rule for integration:

\[
A \frac{y_i^{t+1} - y_i^t}{\Delta t} = \frac{1}{2} \left[ -B \left( \frac{y_{i+1} - y_{i-1}}{2h} \right)^t - B \left( \frac{y_{i+1} - y_{i-1}}{2h} \right)^{t+1} \right] + C \left( \frac{y_{i+1} - 2y_i + y_{i-1}}{h^2} \right)^t + C \left( \frac{y_{i+1} - 2y_i + y_{i-1}}{h^2} \right)^{t+1} + D
\]

(Note: 'D' is a const. \( \frac{D^{t+1} - D^t}{2} = D! \) – This method is better known as Crank-Nicolson.

Also note that you have used a 2nd order accurate scheme on both time and X.

Collect all terms on \((t + 1)\) on the LHS and \(t\) on the RHS as

\[
Ay^{(t+1)} = d^{(t)}
\]

\[
\frac{1}{2} \left( -\frac{C}{h^2} - \frac{B}{2h} \right) y_{i-1}^{t+1} + \left( \frac{A}{\Delta t} + \frac{2C}{h^2} \right) y_i^{t+1} + \frac{1}{2} \left( -\frac{C}{h^2} + \frac{B}{2h} \right) y_{i+1}^{t+1} = \frac{1}{2} \left( \frac{C}{h^2} + \frac{B}{2h} \right) y_{i-1}^t + \left( \frac{A}{\Delta t} - \frac{C}{h^2} \right) y_i^t + \frac{1}{2} \left( \frac{C}{h^2} - \frac{B}{2h} \right) y_{i+1}^t + D \quad \text{for} \quad i = 1, N
\]

*Note:* All terms on RHS are known/calculated from the previous time step.
(3) Apply BCs on both sides \((t + 1)\) and \((t)\):

- \(i = 0\)  \(y_{(0)} = y_0\) for all \(t\) \((t + 1 \text{ and } t)\)
- \(i = N\)  \(y_{N+1} = y_{N-1}\) for all \(t\) \((t + 1 \text{ and } t)\)

1\(^{st}\) row will change as:

\[
\begin{align*}
\left\{ \begin{array}{l}
\left( \frac{A}{\Delta t} + \frac{C}{h^2} \right) y_1^{t+1} + \frac{1}{2} \left( - \frac{C}{h^2} + \frac{B}{2\Delta h} \right) y_2^{t+1} = \\
\left( \frac{C}{h^2} + \frac{B}{2\Delta h} \right) y_0 + \left( \frac{A}{\Delta t} - \frac{C}{h^2} \right) y_1^t + \frac{1}{2} \left( \frac{C}{h^2} - \frac{B}{2\Delta h} \right) y_2^t + D
\end{array} \right. \quad (i = 1)
\end{align*}
\]

Last row will change as:

\[
\begin{align*}
- \frac{C}{h^2} y_{N-1}^{t+1} + \left( \frac{A}{\Delta t} + \frac{C}{h^2} \right) y_N^{t+1} = \frac{C}{h^2} y_{N-1}^t + \left( \frac{A}{\Delta t} - \frac{C}{h^2} \right) y_N^t + D \quad (i = N)
\end{align*}
\]

The other rows \((2 \cdots N - 1)\) will remain the same. Again, the coefficient matrix is a tridiagonal one:

\[Ay^{(t+1)} = d^{(t)}\]

You have prepared the tridiagonal matrix as follows:

\[
\begin{align*}
a_i &= -\frac{1}{2} \left( \frac{C}{h^2} + \frac{B}{2\Delta h} \right), \quad b_i = \left( \frac{A}{\Delta t} + \frac{C}{h^2} \right), \quad c_i = \frac{1}{2} \left( - \frac{C}{h^2} + \frac{B}{2\Delta h} \right), \quad d_i = \frac{1}{2} \left( \frac{C}{h^2} + \frac{B}{2\Delta h} \right) y_{i-1}^t + \\
&\left( \frac{A}{\Delta t} - \frac{C}{h^2} \right) y_i^t + \frac{1}{2} \left( \frac{C}{h^2} - \frac{B}{2\Delta h} \right) y_{i+1}^t + D; \quad i = 1, N
\end{align*}
\]

on application of BCs  \(d_1 = d_1 - a_1y_0, i = 1\)

Note that \(y_0\) is substituted for \(y_{i-1}^t\) before applying BC.

\[
\begin{align*}
a_N &= a_N + c_N \quad (\text{last row, } i = N) \\
d_N &= \frac{C}{h^2} y_{N-1}^t + \left( \frac{A}{\Delta t} - \frac{C}{h^2} \right) y_N^t + D
\end{align*}
\]
(4) Start calculations: RHS is known from $t = 0$ (initial condition)

March on time and call

$\begin{align*}
Ay^{(1)} &= b^{(0)} \\
Ay^{(2)} &= b^{(1)} \\
\vdots \\
Ay^{(t+1)} &= b^{(t)}
\end{align*}$

Tridiagonal subroutine at every time step, & update $y_0 \to y^{(1)} \to y^{(2)} \to \ldots$

Tridiagonal $(N, a, b, c, d^t, y^{t+1})$

$\rightarrow i = 1, N$

Convince yourself that the SS values will be the same as solving the corresponding BVP by dropping the transient or unsteady-state term.

**Ex:**

Consider the SS flow of a liquid through a long tube. Reynolds number is 5000 and a radially flat velocity profile may be assumed. At certain time a tracer is injected into the liquid at the inlet. The dispersion coefficient of the tracer in the liquid may be assumed to be $D \text{ cm}^2/\text{s}$. Radial peclet number is large. Determine unsteady-state or transient axial concentration profiles, $C_A(t, X) = ?$

**Soln:**

Excluding radial term

$$\frac{\partial C_A}{\partial t} + V \cdot \nabla C_A = D \nabla^2 C_A + \dot{r}\phi$$

$$\frac{\partial C_A}{\partial t} + V \frac{\partial C_A}{\partial X} = D \frac{\partial^2 C_A}{\partial X^2};$$

(no reaction)

(neglecting radial term)

$t = 0, \ C_A = 0 \text{ for all } L > x > 0$ \quad (Pure liquid)

$0^+, \ X = 0; \ C_A = C_{A, in}$ \ (Inlet concentration of tracer)
\[ X = L, \ \nabla C_A = 0 \text{ (long – tube approximation) or } \frac{\partial C_A}{\partial x} = 0 \]

\[
\begin{align*}
\frac{\partial C_A}{\partial t} + V \frac{\partial C_A}{\partial x} &= D \frac{\partial^2 C_A}{\partial x^2} ; \quad V = \bar{V} \\
&= \frac{\partial}{\partial t} + V \frac{\partial}{\partial x}
\end{align*}
\]

\[ i = 0 \quad i = 1 \quad i = N \quad t = 1 \quad t + 1 \] \[ \Delta t' \]

\[
\frac{C_{A,i}^{t+1} - C_{A,i}^t}{\Delta t} = \frac{1}{2} \left[ D \left( \frac{C_{A,i+1} - 2C_{A,i} + C_{A,i-1}}{h^2} \right)^{t+1} + D \left( \frac{C_{A,i+1} - 2C_{A,i} + C_{A,i-1}}{h^2} \right)^t \right] \\
- \bar{V} \left[ \frac{C_{A,i+1} - C_{A,i-1}}{2h} \right]^{t+1} - \bar{V} \left[ \frac{C_{A,i+1} - C_{A,i-1}}{2h} \right]^t
\]

\[
\begin{align*}
\left( \frac{D}{2h^2} + \frac{\bar{V}}{4h} \right) C_{A,i-1}^{t+1} - \left( \frac{1}{\Delta t} + \frac{D}{h^2} \right) C_{A,i}^{t+1} + \left( \frac{D}{2h^2} - \frac{\bar{V}}{4h} \right) C_{A,i+1}^{t+1} \\
= - \left( \frac{D}{2h^2} + \frac{\bar{V}}{4h} \right) C_{A,i-1}^{t} - \left( \frac{1}{\Delta t} - \frac{D}{h^2} \right) C_{A,i}^{t} + \left( \frac{D}{2h^2} - \frac{\bar{V}}{4h} \right) C_{A,i+1}^{t}
\end{align*}
\]

\[ i = 1, N \]

\[ i = 0: \quad C_{A,0}^t = C_{A,0}^{t+1} = C_{A,in} \text{ (Inlet BC)} \]

\[ i = N: \quad C_{A,N+1}^{t+1} = C_{A,N-1}^{t+1} \text{ and } C_{A,N+1}^t = C_{A,N-1}^t \]

* Prepare the tridiagonal matrix

\[ a_i = \left( \frac{D}{2h^2} + \frac{\bar{V}}{4h} \right), \quad b_i = - \left( \frac{D}{h^2} + \frac{1}{\Delta t} \right), \quad c_i = \left( \frac{D}{2h^2} - \frac{\bar{V}}{4h} \right), \quad d_i \]

\[ = - \left( \frac{D}{2h^2} + \frac{\bar{V}}{4h} \right) C_{A,i-1}^t - \left( \frac{1}{\Delta t} - \frac{D}{h^2} \right) C_{A,i}^t - \left( \frac{D}{2h^2} - \frac{\bar{V}}{4h} \right) C_{A,i+1}^t \]

Apply BCs:

\[ d_1 = d_1 - a_1 C_{A,in} \quad : \text{Note that } C_{A,in} \text{ is substituted for } C_{A,i-1}^t \text{ in } d_1. \]

\[ a_N = a_N + c_N \]

\[ d_N = - \left( \frac{1}{\Delta t} - \frac{D}{h^2} \right) C_{A,N}^t - \left( \frac{D}{h^2} \right) C_{A,N-1}^t \]

You have \[ A y^{(t+1)} = d^{(t)} \]; \( A \equiv \) Tridiagonal matrix with \( i = 1, N \) rows
Call Tridiagonal (N, a, b, c, d, y)

Start with $t = 0$: $C_A(i = 0, N) = 0$ (pure solvent) or use a small concentration, $C_{Ai} \ll C_{A,inlet}$.

Solve for $y^{(1)}$ or $C_A^{(1)}$ at $t = 1$, recalculate RHS $d^{(2)}$ and keep on marching on time till a steady-state solution or at $t = t_{final}$ is reached.

Plot (use $L = 10$ cm, $C_{A,i} = 0.001$, $C_{A,inlet} = 1.0$, $\bar{V} = 0.1$ cm/s, $D = 0.01$ cm$^2$/s)

\[
\Rightarrow \frac{\partial C}{\partial x} = 0 \bigg|_{x=L}
\]

Note that

- Tridiagonal matrix is called at every time-step.
- $\vec{b}$ vector is updated with the recent most $C_A$ values.
- gradient at the exit must be flat (consistent with BC)
- There are two steps ($h$ & $\Delta t$). How do you choose them?
- No one knows! In general $\Delta t < \frac{\Delta x}{\bar{V}}, \frac{\Delta x^2}{D}$. Why??

One should choose a fixed $\Delta X$, and then refine '$\Delta t$' till there is a convergence in the solution. Again, use $\Delta X = \Delta X/2$, adjust '$\Delta t$' till the solution converges, and so forth!

Ex. Repeat the previous problem, assuming that some solute is irreversibly adsorbed at the tube-wall @ $kC_A$ rate.

Species balance equation:

\[
\frac{\partial C_A}{\partial t} + \bar{V} \cdot \nabla C_A = D \nabla^2 C_A - (kC_A)a, \text{ where } a \text{ is the specific surface area per unit volume of the tube.}
\]

or \[
\frac{\partial C_A}{\partial t} + \bar{V} \frac{\partial C_A}{\partial x} = D \frac{\partial^2 C_A}{\partial x^2} - k'C_A;
\]
IC: \( t = 0 \quad C_A = C_{A,0} \),

BC \( 0^+, \ X = 0; \ C_A = C_{A,0}, \ X = L, \ \nabla C_A = 0 \Rightarrow \frac{\partial C_A}{\partial x} = 0 \)

\[
\frac{c_{A,i}^{t+1} - c_{A,i}^t}{\Delta t} = \frac{1}{2} D \left( \frac{C_{A,i+1}^{t} - 2C_{A,i}^{t} + C_{A,i-1}^{t}}{h^2} \right) + D \left( \frac{C_{A,i+1}^{t} - 2C_{A,i}^{t} + C_{A,i-1}^{t}}{h^2} \right) - \left( \frac{v}{2h} \right)^2 (C_{A,i}^{t+1} - C_{A,i-1}^{t})
\]

\[
\bar{V} \left( \frac{C_{A,i+1}^{t} - C_{A,i}^{t}}{2h} \right)^t - \left( k' c_{A,i}^{t+1} + k' c_{A,i}^{t} \right)
\]

Note: This is an extra term.

Re-arrange,

\[
\left( \frac{D}{2h^2} + \frac{\bar{V}}{4h} \right) C_{A,i-1}^{t+1} - \left( \frac{1}{\Delta t} + \frac{D}{h^2} + \frac{k'}{2} \right) C_{A,i}^{t+1} + \left( \frac{D}{2h^2} - \frac{\bar{V}}{4h} \right) C_{A,i+1}^{t+1} = - \left( \frac{D}{2h^2} + \frac{\bar{V}}{4h} \right) C_{A,i-1}^{t} - \left( \frac{1}{\Delta t} - \frac{D}{h^2} - \frac{k'}{2} \right) C_{A,i}^{t} - \left( \frac{D}{2h^2} - \frac{\bar{V}}{4h} \right) C_{A,i+1}^{t}
\]

\( i = 1, N \)

BCs:

\[
\begin{align*}
\text{BCs:} & \quad \begin{cases} 
(i = 0, \quad C_{A,0}^{t+1} = C_{A,0} \text{ (for all time steps)} \\
(i = N, \quad C_{A,N+1}^{t+1} = C_{A,N-1} \text{ and } C_{A,N+1}^{t} = C_{A,N-1} \text{ (last row)}) 
\end{cases}
\end{align*}
\]

Prepare tridiagonal matrix:

\[
\begin{align*}
a_i &= \left( \frac{D}{2h^2} + \frac{\bar{V}}{4h} \right) , \quad b_i = - \left( \frac{1}{\Delta t} + \frac{D}{h^2} + \frac{k'}{2} \right) , \quad c_i = \left( \frac{D}{2h^2} - \frac{\bar{V}}{4h} \right) , \quad d_i \\
&= - \left( \frac{D}{2h^2} + \frac{\bar{V}}{4h} \right) C_{A,i-1}^{t} - \left( \frac{1}{\Delta t} - \frac{D}{h^2} - \frac{k'}{2} \right) C_{A,i}^{t} - \left( \frac{D}{2h^2} - \frac{\bar{V}}{4h} \right) C_{A,i+1}^{t}
\end{align*}
\]

Apply BCs.

\[
d_1 = - \left( \frac{D}{h^2} + \frac{\bar{V}}{2h} \right) C_{A,1}^{t} - \left( \frac{1}{\Delta t} - \frac{D}{h^2} - \frac{k'}{2} \right) C_{A,1}^{t} - \left( \frac{D}{2h^2} - \frac{\bar{V}}{4h} \right) C_{A,2}^{t} : i = 1 \text{ (1st row)}
\]

(Note that this step is the same as \( d_1 = d_1 - a_1 C_{A,1}^{t} \))

\[
a_N = a_N + c_N \\
d_N = - \left( \frac{D}{h^2} C_{A,N-1}^{t} - \left( \frac{1}{\Delta t} - \frac{D}{h^2} - \frac{k'}{2} \right) C_{A,N}^{t} \right)
\]

\[A y^{(t+1)} = d^{(t)}; \ A \text{ is the tridiagonal matrix.}\]
Proceed as before with initial condition \( C_A(i = 1, N) = C_{A,i} \). Evaluate \( d^{(t)} \), solve for \( y^{(t+1)} \), evaluate \( d^{(t+1)} \), solve for \( y^{(t+2)} \) etc. Subroutine Tridiagonal \((N, a, b, c, d, y)\) is called at every time step. Plot qualitatively for the same conditions as before, use \( k = 0.1 \text{ s}^{-1} \).

The axial concentration profiles for different ‘\( t_s \)’ will be the similar as before; however increase in concentration with ‘\( t \)’ will be less than before because of the reactive/adsorptive wall.
Example: Consider a spherical \( d_p = 0.1 \text{ cm} \) steel pellet \( (k = 40 \text{ W/m-K}, \rho = 8000 \text{ kg/m}^3, C_p = 400 \text{ J/kg-K}) \). The initial temperature of the pellet is 300 K. It is immersed in a large oil tank at 400 K. The corrective heat transfer coefficient, \( h_f \) at the sphere surface is 3000 W/m\(^2\)K. Solve for unsteady-state temperature profiles in the sphere. Choose \( \Delta t = 1 \text{ s} \). Determine the average temperature in the sphere and the rate of which the surface temperature decreases at \( t = 20 \text{ s} \).

* Recall: There is a discontinuity at \( i = 0 \ (r = ih) \)

However, the grad \( \nabla T = 0 \) at \( r = 0 \). Therefore, \( \frac{1}{r} \frac{\partial T}{\partial r} \approx \frac{\partial^2 T}{\partial r^2} \)

\[
\rho C_p \frac{\partial T}{\partial t} = k \nabla^2 T + S_{\text{ext}} \\
\frac{\partial T}{\partial t} = \frac{\alpha}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T}{\partial r} \right) \quad r_p > r \geq 0
\]

IC: \( t = 0 \quad T = 300 \text{ K}(T_o) \quad \text{for all} \ r_p \geq r \geq 0 \)

BC: \( 0^+ \quad r = 0 \quad \nabla T = 0 \quad \text{or} \quad \frac{\partial T}{\partial r} = 0 \)

\[
r = r_p - k \frac{\partial T}{\partial r} = h(T - T_f) \\
\text{or} \quad k \frac{\partial T}{\partial r} = h(T_f - T)
\]
The equation is re-written as

\[ \frac{\partial r}{\partial t} = \alpha \frac{\partial^2 r}{\partial r^2} + \frac{2\alpha}{r} \frac{\partial r}{\partial r} \]

Apply Crank-Nicholson discretization scheme:

\[ \frac{T_{i+1}^t - T_i^t}{\Delta t} = \frac{1}{2} \left[ \alpha \left( \frac{\Delta T_i}{h^2} - \frac{2}{\Delta r} \frac{\partial^2 T_i}{\partial r^2} + \frac{2}{\Delta t} \frac{\partial T_i}{\partial t} \right) + \alpha \left( \frac{\Delta T_i}{h^2} - \frac{2}{\Delta r} \frac{\partial^2 T_i}{\partial r^2} + \frac{2}{\Delta t} \frac{\partial T_i}{\partial t} \right) \right] + \frac{2\alpha}{r_i} \left( \frac{T_{i+1}^t - T_{i-1}^t}{2h} \right) \]

Arrange:

\[ \left( \frac{\alpha}{h^2} - \frac{1}{\Delta t} \right) T_i^t - \left( \frac{\alpha}{h^2} - \frac{2}{\Delta r} \frac{\partial^2 T_i}{\partial r^2} + \frac{2}{\Delta t} \frac{\partial T_i}{\partial t} \right) T_i^{t+1} = \left( \frac{\alpha}{h^2} - \frac{2}{\Delta r} \frac{\partial^2 T_i}{\partial r^2} + \frac{2}{\Delta t} \frac{\partial T_i}{\partial t} \right) T_i^t \]

\[ (\alpha - \frac{1}{\Delta t}) T_i^t - (\alpha - \frac{\alpha}{2\Delta r}) T_i^{t+1} \quad i = 1, N \]

Note \( i = 0 \) requires a modified equation as (why?): \[ \frac{\partial r}{\partial t} = 3\alpha \frac{\partial^2 r}{\partial r^2} \]

The modified equation is discretized:

\[ \frac{r_i^{t+1} - r_i^t}{\Delta t} = \frac{3\alpha}{2} \left[ \left( \frac{3\alpha}{h^2} + \frac{1}{\Delta t} \right) r_i^t + \left( \frac{3\alpha}{h^2} - 1 \right) r_i^{t+1} \right] \quad i = 0 \]

\[ \left( \frac{3\alpha}{2h^2} \right) T_{i-1}^t - \left( \frac{3\alpha}{h^2} + \frac{1}{\Delta t} \right) T_0^t + \left( \frac{3\alpha}{2h^2} \right) T_1^t = \left( \frac{3\alpha}{h^2} - 1 \right) T_0^t - \left( \frac{3\alpha}{2h^2} \right) T_1^t \quad i = 0 \]

Prepare tridiagonal matrix:

\[ a_0 = \frac{3\alpha}{2h^2}, b_0 = -\left( \frac{3\alpha}{h^2} + \frac{1}{\Delta t} \right), c_0 = \frac{3\alpha}{2h^2} \]

\[ a_i = \frac{\alpha}{2h^2} - \frac{\alpha}{2\Delta r}, b_i = -\left( \frac{\alpha}{h^2} + \frac{1}{\Delta t} \right), c_i = \left( \frac{\alpha}{2h^2} + \frac{\alpha}{2\Delta r} \right), d_i = \frac{\alpha}{2\Delta r} - \frac{\alpha}{2h^2} \]

\[ = \left( \frac{\alpha}{2\Delta r} - \frac{\alpha}{2h^2} \right) T_{i-1}^t + \left( \frac{\alpha}{h^2} - \frac{1}{\Delta t} \right) T_{i-1}^t - \left( \frac{\alpha}{2h^2} + \frac{\alpha}{2\Delta r} \right) T_{i+1}^t \quad i = 1, N \]

Discretize BCs

1. \( r = 0 \Rightarrow \frac{\partial r}{\partial r} = 0 \Rightarrow i = 0; \quad T_{-1} = T_{+1} \)

2. \( r = r_p \quad k \frac{\partial r}{\partial r} = h_f (T_f - T) \quad i = N \)
\[
\frac{T_{N+1} - T_{N-1}}{2h} = \frac{h_f}{k} (T_f - T_N)
\]
or,
\[
T_{N+1} = T_{N-1} + \frac{2h_f h}{K} (T_f - T_N)
\]

Apply BC
\[
c_0 = c_0 + a_0 \\
d_0 = \left( \frac{3\alpha}{h^2} - \frac{1}{\Delta t} \right) T_0^t - \frac{3\alpha}{h^2} T_1^t \quad i = 0
\]
\[
a_N = a_N + c_N \\
d_N = -\frac{\alpha}{h^2} T_{N-1}^t + \left( \frac{\alpha}{h^2} - \frac{1}{\Delta t} \right) T_N^t + \left( \frac{\alpha}{2h^2} - \frac{\alpha}{2r_i h} \right) \frac{2h_f h}{k} T_N^t - \left( \frac{\alpha}{2h^2} + \frac{\alpha}{2r_i h} \right) \frac{2h_f h}{k} T_f
\]

Call Tridiagonal(N+1, a,b,c,d,y)

Solve \( Ay^{(t+1)} = d^{(t)} \), \( i = 0, N \) with initial condition: \( T = T_{ini} = 300 \)
\[
Ay^{(1)} = d^{(0)} \Rightarrow Ay^{(2)} = d^{(1)} \Rightarrow Ay^{(3)} = d^{(2)}, \quad \text{etc.}
\]

Once the functional values or \( y(t,r) \) or \( y_i \), \( i = 0, N \) are computed, the average temperature of the sphere at any time, \( t \) can be calculated as the volume-average quantity (why?), as follows:
\[
3 \sum r_i^2 \Delta r / R^3, \quad i = 0, N \text{ and } r_i = ih \]
(assuming the constant or average thermophysical properties i.e., \( \rho, C_p \) of the material). You can use the Simpson’s 1/3rd or Trapezoidal rule of integration.

Similarly, the rate of decrease of the surface temperature, viz. \( \frac{\partial T}{\partial t} \) at \( r = R \) at any time, \( t \) can be calculated using CDS as \( \frac{\gamma(t_{i+1}) - y(t_{i-1})}{2\Delta t} \) or BDS as \( \frac{4y(t_{i+1}) - 3y(t_i) - y(t_{i+2})}{2\Delta t} \) or FDS as \( \frac{-4y(t_{i-1}) + 3y(t_{i}) + y(t_{i+2})}{2\Delta t} \), depending upon the time, \( t \). Therefore, you must use FDS at the initial time, \( t = 0 \), etc.
**Example:** Consider the catalytic oxidation of $SO_2$ into $SO_3$ over a spherical Pt-dispersed porous carbon catalyst ($\text{radius} = r_p$). The atmospheric concentration of $SO_2$ is 1%. The rate of reaction is $r = k (= 0.1) C_A \text{ mole} / \text{s} - \text{m}^3$. The film mass transfer coefficient is $k_m (\text{m/s})$. Determine the time-development of concentration profiles within the catalyst. The pore diffusion coefficient of $SO_2$ is estimated to be $D \text{ m}^2 / \text{s}$.

![Diagram of concentration profile](image)

\[
\frac{\partial C_A}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_A}{\partial r} \right) - k C_A \quad (1)
\]

\[
t = 0 \quad C_A = C_{A0} \ll C_b \quad \text{for all } r_p \geq r \geq 0
\]

\[
0^+ \quad \nabla C_A = 0 \quad @ \quad r = 0
\]

\[
-D \frac{\partial C_A}{\partial r} = k_m (C_A - C_b) \quad @ \quad r = r_p
\]

Before you solve, two clarifications follow:

1. The steady-state solution of eq(1) is the same as that of the equation solved in the previous lectures for BVP. Therefore, one way of checking the present code for this unsteady-state 1D parabolic equation is to compare its SS solution with that from the BVP-code. In the latter lectures you will see that very often it is better to artificially introduce the transient term \( \nu \{ \frac{\partial T}{\partial t} , \frac{\partial C}{\partial t} , \frac{\partial V}{\partial t} \} \) in the BVPs and solve the entire time-profiles, even when one is asked to solve the SS solution only. This strategy is often followed for solving elliptic PDE.

2. You should also compare this mass transport example with the previous example on heat transfer. But for the non-homogenous term \( k C_A \), two equations are identically the same, including the IC and BCs.

**Recall:**
\[
\frac{\partial T}{\partial t} = \frac{\alpha}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T}{\partial r} \right) \\
\frac{\partial C_A}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_A}{\partial r} \right)
\]

**IC:** \( t = 0 \quad T = T_0 \quad C_A = C_{A_i} \) for all \( r_p > r > 0 \)

**BC 1:** \( r = 0 \quad \frac{\partial T}{\partial r} = 0 \quad \frac{\partial C_A}{\partial r} = 0 \)

**BC 2:** \( r = r_p \quad -k \frac{\partial T}{\partial r} = h_f(T-T_f) \quad -D \frac{\partial C_A}{\partial r} = k_m(C_A-C_b) \)

All it means is that their non-dimensionalized forms are identically the same:

\[
\frac{\partial \theta}{\partial \tau} = \frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial \theta}{\partial \xi} \right)
\]

where,

\[
\begin{align*}
\theta &= \frac{T-T_0}{T_f-T_o}, \quad \frac{C_A - C_{A_i}}{C_{A,b} - C_{A_i}} \\
\xi &= \frac{r}{r_p} \\
\tau &= \frac{t}{t_c}; \quad t_c = \frac{r_p^2}{\alpha}, \quad \frac{r_p^2}{D}
\end{align*}
\]

**IC:** \( \tau = 0 \quad \theta = 0 \)

**BC 1:** \( \xi = 0 \quad \frac{\partial \theta}{\partial \xi} = 0 \)

**2.** \( \xi = 1 \quad -\frac{\partial \theta}{\partial \xi} = A(\theta - 1) \), where \( A = \text{Nu} \) or \( \text{Sh} \)

Therefore, it is clear that their (non-dimensional) solutions will also be the same.

It also follows that one should non-dimensionalize the transport equations, as a good practice, before solving the equations. Apart from learning about transport phenomena from the analogy between heat, mass and momentum, there is a possibility that the non-dimensional forms of the conservation equations & the respective bcs being the same, the non-dimensionalized solutions will also be the same. In such cases or similar cases, the programming code written for one problem will be the same or similar, requiring small modifications.

Let us continue with the non-dimensionalized form of the present mass transport problem:

\[
\frac{\partial \theta}{\partial \tau} = \frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial \theta}{\partial \xi} \right) - B \theta - C \]

where \( B = kt_c, \quad C = kt_c \frac{c_{A_i}}{c_{A,b} - c_{A_i}} \)

Discretize:
\[
\frac{\theta_i^{\tau+1} - \theta_i^\tau}{\Delta \tau} = \frac{1}{2} \left[ \left( \frac{\theta_{i+1} - 2\theta_i + \theta_{i-1}}{\Delta \xi^2} \right)^{\tau+1} + \left( \frac{\theta_{i+1} - 2\theta_i + \theta_{i-1}}{\Delta \xi^2} \right)^\tau + \frac{2}{\xi_i} \left( \frac{\theta_{i+1} - \theta_{i-1}}{2\Delta \xi} \right)^{\tau+1} \right] - B(\theta_i^{\tau+1} + \theta_i^\tau) - C
\]

\[
i = 0, N
\]

@\(i = 0\) there is a discontinuity in the equation. Therefore,

\[
\frac{\theta_0^{\tau+1} - \theta_0^\tau}{\Delta \tau} = \frac{3}{2} \left[ \left( \frac{\theta_1 - 2\theta_0 + \theta_{-1}}{\Delta \xi^2} \right)^{\tau+1} + \left( \frac{\theta_1 - 2\theta_0 + \theta_{-1}}{\Delta \xi^2} \right)^\tau + \frac{B}{2} \left( \theta_0^{\tau+1} + \theta_0^\tau \right) \right] - C \quad \text{for } i = 0
\]

Apply BCs

\[
\begin{align*}
i & = 0 & \theta_{-1} = \theta_1 \\
& i = N & \frac{\theta_{N+1} - \theta_{N-1}}{2\Delta \xi} = A(\theta_N - 1) \quad \text{or} \quad \theta_{N+1} = \theta_{N-1} - 2A\Delta \xi(\theta_N - 1)
\end{align*}
\]

\[
i = 0: \quad \left( \frac{1}{\Delta \tau} + \frac{3\Delta \xi}{2} - B \right) \theta_0^{\tau+1} - \frac{3\Delta \xi}{2} \theta_0^\tau = \left( \frac{1}{\Delta \tau} - \frac{3\Delta \xi}{2} + \frac{B}{2} \right) \theta_0^\tau + \frac{3}{2\Delta \xi} \theta_1^\tau - C
\]

\[
i = N: \quad \left( \frac{1}{\Delta \xi^2} \right) \theta_{N-1}^\tau - \left( \frac{1}{\Delta \xi^2} + \frac{B}{2} + \frac{1}{\Delta \tau} \right) \theta_N^\tau = - \left( \frac{1}{\Delta \xi^2} \right) \theta_{N-1}^\tau - \left( \frac{1}{\Delta \tau} - \frac{1}{\Delta \xi^2} - \frac{B}{2} \right) \theta_N^\tau + C
\]

\[
i = 1, N - 1 \quad \left( \frac{1}{2\Delta \xi^2} - \frac{1}{2\Delta \xi \xi} \right) \theta_{i-1}^{\tau+1} - \left( \frac{1}{\Delta \tau} + \frac{1}{\Delta \xi^2} - \frac{B}{2} \right) \theta_i^{\tau+1} + \left( \frac{1}{2\Delta \xi^2} - \frac{1}{2\Delta \xi \xi} \right) \theta_{i+1}^{\tau+1} = \left( - \frac{1}{2\Delta \xi^2} + \frac{1}{2\Delta \xi \xi} \right) \theta_i^{\tau+1} - \left( \frac{1}{\Delta \tau} - \frac{1}{\Delta \xi^2} - \frac{B}{2} \right) \theta_i^\tau + \left( - \frac{1}{2\Delta \xi^2} - \frac{1}{2\Delta \xi \xi} \right) \theta_{i+1} + C
\]

Solve \( A\theta^{\tau+1} = d^\tau, i = 0, N \) with IC \( \theta = 0 @ \tau = 0 \)

(same as before, \( A \equiv \text{Tridiagonal matrix} \))

Here, we skipped the steps for preparing tridiagonal matrix and directly substituted discretized BCs into the discretized equations! As an exercise, prepare tridiagonal matrix and see if you get the same discretized equations post substitution of BCs, as before.

**Quiz III**
Lecture #24-25

Elliptic PDE (Method of Lines)

The model equations may be recognized by the following examples:

1. \[ k \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) + S = 0; \quad S \equiv \frac{I^2 R}{\eta} \text{ cal}/s - m^3 \]

2. \[ k \left( \frac{\partial^2 T}{\partial x^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) \right) + S = 0 \]

--- SS 2D temperature profiles in a (1) rectangular plate and (2) cylindrical wire because of uniform heating

3. \[ V_x \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} + \frac{D}{r} \left( \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right) \right) - kC \]

--- SS 2D concentration distributions of a solute in the reactive flow in a tube

4. \[ V_x \frac{\partial T}{\partial x} = \alpha \frac{\partial^2 T}{\partial x^2} + \alpha \frac{\partial^2 T}{\partial y^2} \]

- SS 2D temperature distributions in a flow through rectangular channel.

5. \[ \rho V_x \frac{\partial V_x}{\partial x} = \mu \left( \frac{\partial^2 V_x}{\partial x^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial V_x}{\partial r} \right) \right) - \frac{dp}{dx} \]

- SS 2D velocity profiles of an incompressible NF in a pressure-driven horizontal flow.

By now, you must have realized that we are referring to an elliptic PDE which describes a SS 2D (no time-dependent term) heat/mass/momentum transport. Why is the equation called elliptic? Because one has to solve the entire 2D space. Considering that there is the SS consideration, there is no ‘marching’ on time as such and the updating of the solutions from the previous time-step, as we earlier discussed for the parabolic PDEs. The solution in this case must be sought one-time only under SS conditions. You will see later that solving elliptic equations is computational extensive requiring iterations.

- The best way of understanding the numerical technique for solving an elliptic PDE is to directly take the example (1) above.
Ex: A rectangular plate \((L \times w \times t_h)\) fabricated from stainless steel \((k = 40 \ W/m - k, \ \rho = 8000 \ kg/m^3, \ C_p = 400 \ J/kg \ K)\) is uniformly heated using an electric power source \((100 \ W)\). The top and bottom ends are insulated, whereas the side surfaces are exposed to atmosphere \((T_a = 30^0 \ C, h = 100 \ W/m^2k)\). Determine the SS temperature profiles in the plate.

\[ S(W/m^3) = \frac{100 \ W}{L \times W \times t_h} \]

(heat source)

2D energy balance over \(\Delta x\Delta yt_h\)'CV under SS:

\[
\rho C_p \left( \frac{\partial T}{\partial t} + \mathbf{V} \cdot \nabla T \right) = k \nabla^2 T + S; \ W/m^3
\]

\[
SS, 0, solid
\]

\[
k \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) + S = 0; \ S = 100 \ W/m^3 \text{ of the plate volume}
\]

BCs: \(x = 0 \ \text{ for } w > y > 0 \); \(-k \frac{\partial T}{\partial x} = -h_f (T - T_a)\)

\[
= L \ \text{ for } w > y > 0 \ ; \ -k \frac{\partial T}{\partial x} = h_f (T - T_a)
\]

\[
y = 0 \ \text{ and } w \text{ for } L > x > 0, \ -k \frac{\partial T}{\partial y} = 0(\text{insulation})
\]
Computational molecule:

\[ (i-1) \quad (i,j) \quad (i+1) \quad (j+1) \]

Discretize equations over \((i,j)\). Note that it is a 2D problem. Therefore, one will have to discretize in both directions \((x,y)\) using steps \(\Delta x\) and \(\Delta y\), respectively. They need not be equal.

\[
k \left[ \left( \frac{\partial^2 T}{\partial x^2} \right)_{i,j} + \left( \frac{\partial^2 T}{\partial y^2} \right)_{i,j} \right] + S_{i,j} = 0
\]

\[
\left( \frac{T_{i-1,j} - 2T_{i,j} + T_{i+1,j}}{\Delta x^2} \right) + \left( \frac{T_{i,j-1} - 2T_{i,j} + T_{i,j+1}}{\Delta y^2} \right) + \frac{S_{i,j}}{k} = 0
\]

(As expected, when discretizing \(\frac{\partial^2 T}{\partial x^2}\), \(j\) is constant, and when discretizing \(\frac{\partial^2 T}{\partial y^2}\), \(i\) is constant)

There are two ways to arrange the discretized terms to

\[ A\vec{y} = \vec{b} \text{ form :} \]

(1) \[
\frac{1}{\Delta x^2} \left( T_{i-1,j} - 2T_{i,j} + T_{i+1,j} \right) = -\frac{1}{\Delta y^2} \left( T_{i,j-1} - 2T_{i,j} + T_{i,j+1} \right) - \frac{S_{i,j}}{k}
\]

(2) \[
\frac{1}{\Delta y^2} \left( T_{i,j-1} - 2T_{i,j} + T_{i,j+1} \right) = -\frac{1}{\Delta x^2} \left( T_{i-1,j} - 2T_{i,j} + T_{i+1,j} \right) - \frac{S_{i,j}}{k}
\]

Notes: 1. Although the linear algebraic equations have taken the form of \(A\vec{y} = \vec{b}\) in both cases, \(\vec{b}\) or RHS terms are not known. Therefore, in principle \(\vec{y}\) or \(\vec{T}\) cannot be solved by inverting the ‘matrix’ formed on LHS, the way we did in the previous cases. In other words, there is no way one can march in \(x\) or \(y\) direction and solve the unknown variables, because marching in either direction \((i\) or \(j\)) creates unknown variables in the other direction \((j\) or \(i\)). In fact, one has to solve the ‘entire space’ at one time (without marching). This is the problem in solving an elliptic PDE!

(2) The only way to solve an elliptic PDE or \(A\vec{y} = \vec{b}\), where \(A\) is the tridiagonal matrix, is by making guess for all variables \((T_{i,j})\) to start with, so that \(\vec{b}\) (RHS term) is known. Then, \(\vec{y}\) (which is similar to \(\vec{b}\)) can be solved. Next, compare the newly calculated values with the guess values and iterate till there is the convergence:
\[ Ay^{k+1} = b^k \]
b^0 = initial guess for \((T_{i,j})
\]
k = # of iterations.

(3) Either of the two discretized schemes (1) & (2) can be used to solve \(T_{i,j}\). In general, one should sweep the discretized set of equations in the direction the expected solution (functional value) is lesser stiff than in the other direction. In the present example, \(w \ll L\) and the y-ends are insulated. One should use scheme (1). The convergence will be relatively faster.

\[
\frac{1}{\Delta x^2} (T_{i-1,j} - 2T_{i,j} + T_{i+1,j}) = -\frac{1}{\Delta y^2} (T_{i,j-1} - 2T_{i,j} + T_{i,j+1})^g - \frac{S_{i,j}}{k} \tag{1}
\]

Prepare tridiagonal matrix:

\[
\begin{align*}
a(i,j) &= \frac{1}{\Delta x^2}, \\
b(i,j) &= -\frac{2}{\Delta x^2}, \\
c(i,j) &= \frac{1}{\Delta x^2}, \\
d(i,j) &= -\frac{1}{\Delta y^2} (T_{i,j-1} - 2T_{i,j} + T_{i,j+1})^g - \frac{S_{i,j}}{k}
\end{align*}
\]

\(i = 0, N\)

\(j = 0, M\)

The superscript "g" stands for the guess values. Once the initial guess is made, one can now march along 'j' direction, solving \(T_{i,j}\) at every 'jth' step as \(Ay_j = b\), where \(A\) is the tridiagonal matrix containing the discretized 'y' along 'i' direction for a fixed \(j\), and \(b\) is known from the guess.

Discretize BCs

\[
\begin{align*}
(i = 0), & \quad j: -k \frac{T_{1,j} - T_{-1,j}}{2\Delta x} = -h_f (T_{0,j} - T_a) \\
or & \quad T_{-1,j} = T_{1,j} - \frac{2h_f \Delta x}{k} (T_{0,j} - T_a) \\
(i = N), & \quad j: T_{N+1,j} = T_{N-1,j} - \frac{2h_f \Delta x}{k} (T_{N,j} - T_a)
\end{align*}
\]

\(j = 0, i: T_{i,-1} = T_{i,1}\)

\(j = M, i: T_{i,M+1} = T_{i,M-1}\)

Apply BCs

\(j = 0\)

\[ i = 0 \quad \oplus \quad i - 1 \quad i \quad i + 1 \quad N - 1 \quad N \]
\[
\begin{align*}
    c(0,0) &= c(0,0) + a(0,0) \\
    b(0,0) &= b(0,0) - \frac{2h_f \Delta x}{k} a(0,0) \\
    d(0,0) &= \frac{2}{\Delta y^2} (T_{0,0} - T_{0,1})^g - \frac{S_{0,0}}{k} - \frac{2h_f \Delta x}{k} T_a a(0,0) \\

    d(i,0) &= \frac{2}{\Delta y^2} (T_{i,0} - T_{i,1})^g - \frac{S_{i,0}}{k}, \quad i = 1, N - 1 \\

    a(N,0) &= a(N,0) + c(N,0) \\
    b(N,0) &= b(N,0) - \frac{2h_f \Delta x}{k} c(N,0) \\
    d(N,0) &= \frac{2}{\Delta y^2} (T_{N,0} - T_{N,1})^g - \frac{S_{N,0}}{k} - \frac{2h_f \Delta x}{k} T_a a(N,0)
\end{align*}
\]

\( \text{Tridiag}(N + 1, a, b, c, d, T_{i,0}) \) (\( i = 0, N \))

\( j = 1, M - 1 \)

\[
\begin{align*}
    c(0,j) &= c(0,j) + a(0,j) \\
    b(0,j) &= b(0,j) - \frac{2h_f \Delta x}{k} a(0,j) \\
    d(0,j) &= d(0,j) - \left( \frac{2h_f \Delta x}{k} T_a a(0,j) \right)
\end{align*}
\]

\( \Rightarrow \) No coefficients will change for the rows, \( i = 1, N - 1 \), because all of these correspond to interior nodes:
\[
\begin{align*}
a(N,j) &= a(N,j) + c(N,j) \\
b(N,j) &= b(N,j) - \left(\frac{2h_f \Delta x}{k}\right)c(N,j) \\
d(N,j) &= d(N,j) - \left(\frac{2h_f \Delta x}{k}\right)T_a c(N,j)
\end{align*}
\]

\[
\begin{align*}
\text{Tridiag}(N+1, a, b, c, d, T_{i,j}) & \quad (i = 0, N) \\
\end{align*}
\]

\[
\begin{align*}
c(0,j) &= c(0,j) + a(0,j) \\
b(0,j) &= b(0,j) - \frac{2h_f \Delta x}{k}a(0,j) \\
d(0,j) &= \frac{2}{\Delta y^2}(-T_{0,M-1} + T_{0,M})^g - \frac{S_{0,M}}{k} - \left(\frac{2h_f \Delta x}{k}\right)T_a a(0,j)
\end{align*}
\]

\[
\begin{align*}
d(i,j) &= -\frac{2}{\Delta y^2}(-T_{i,M-1} + T_{i,M})^g - \frac{s_{iM}}{k} \\
a(N,j) &= a(N,j) + c(N,j) \\
b(N,j) &= b(N,j) - \frac{2h_f \Delta x}{k}c(N,j) \\
d(N,j) &= \frac{2}{\Delta y^2}(-T_{N,M-1} + T_{N,M})^g - \frac{S_{N,M}}{k} - \frac{2h_f \Delta x}{k}T_a c(N,j)
\end{align*}
\]

\[
\begin{align*}
\text{Tridiag}(N+1, a, b, c, d, T_{i,j}) & \quad (i = 0, N) \\
\end{align*}
\]

You have, therefore, called Tridiagonal subroutine ‘M + 1’ times as you marched along ‘j’ direction. At the end, entire ‘x – y’ grids have been solved for \( T_{i,j} (i = 0, N; j = 0, M) \). Compare solved values with the guess values and keep iterating till there is a convergence.

⇒ Solving an elliptic PDE is indeed computational extensive because there is a convergence issue using the guesses.

⇒ There is another twist in solving an elliptic PDE. Do you update your guess values of \( \bar{b} \) (RHS terms) at ‘j’ with the ones solved at ‘j - 1’ as you march in y-direction, or do you wait till you have solved till ‘M’ (the last boundary)? This question should remind you of the G-S and Jacobi iterations. Choice is yours. A fast convergence is the criterion. Also, the relaxation factor, ‘w’ can be used to update the functional values in either case: \( T_{i,j} = wT'_{i,j} + (1 - w)T_{i,j} \), where \( T' \) and \( T \) are the new and old values, respectively.
**Lecture #25-26**

**Ex 2:** Consider the fully developed SS flow \((Re = 200)\) of an incompressible NF in a long horizontal tube \((L, D)\). The inlet temperature of the liquid is \(T_0\). The heat is supplied to the flowing liquid at constant flux \(q_w \left( \frac{W}{m^2} \right)\) through the tube walls. Determine the 2D \((r, x)\) SS temperature profiles in the tube.

Energy balance over \(2\pi r \Delta r \Delta X\) CV:

\[
\rho C_p V_x \nabla T = k \nabla^2 T + \frac{q_w}{\Delta r \Delta X} \quad (J \text{ or } \text{cal/s} - m^3)
\]

\[
V(r) \frac{\partial T}{\partial x} = \alpha \left( \frac{\partial^2 T}{\partial x^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) \right) \quad \alpha = \frac{k}{\rho c} ;
\]

**BC.** \(X = 0 \quad T(r) = T_0 \quad R \geq r \geq 0\)

\[
X = L \quad + \frac{\partial \theta}{\partial x} = 0 \quad \text{(long tube approximation)}
\]

\[
r = 0 \quad \frac{\partial \theta}{\partial r} = 0 \quad \text{(symmetric BC)}
\]

\[
r = R \quad - k \frac{\partial \theta}{\partial r} = -q_w \quad \left( \frac{W}{m^2} \right) \quad \left\{ L \geq z \geq 0 \right\}
\]

or \(k \frac{\partial \theta}{\partial r} = q_w\)

Let us non-dimensionalize the equation & BC

\[
\theta = \frac{T}{T_0}, \quad z = \frac{x}{L_c} \quad \text{where} \quad L_c = R P_e \quad \text{where} \quad P_e \text{(radial)} = \frac{U_{max} R}{\alpha}, \quad \xi = \frac{r}{R}
\]

\[
\frac{U_{max} (1 - \xi^2) \frac{\partial \theta}{\partial \xi}}{L_c} = \alpha \left( \frac{1}{L_c^2 \frac{\partial^2 \theta}{\partial z^2}} + \frac{1}{R^2 \frac{\partial^2 \theta}{\partial \xi^2}} + \frac{1}{R^2} \frac{1}{\xi} \frac{\partial \theta}{\partial \xi} \right)
\]

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or

\[
(1 - \xi^2) \frac{\partial \theta}{\partial z} = \frac{1}{Pe^2} \frac{\partial^2 \theta}{\partial \xi^2} + \frac{1}{\xi} \frac{\partial \theta}{\partial \xi}
\]

BCs:

\[
\begin{align*}
  z &= 0 & \theta &= 1 & + \frac{\partial \theta}{\partial z} &= 0 \bigg) 1 > \xi > 0 \\
  z &= \frac{L}{L_c} & \xi &= 0 & \frac{\partial \theta}{\partial \xi} &= 0 \\
  \xi &= 1 & \frac{\partial \theta}{\partial \xi} &= \left(\frac{q_w R}{k T_o}\right) = H(\text{constant}) & \text{for } \frac{L}{L_c} > z > 0
\end{align*}
\]

Before solving, let us consider another example on mass transport.

**Ex.** Consider the fully developed SS flow \((Re = 200)\) of an incompressible NF in a long horizontal tube \((L, D)\). The inlet concentration of the species A in the liquid is \(C_{Ao}\). The species are catalytically destroyed at the tube walls by the zero\(^{th}\) order chemical reaction \((k \text{ mole/s} - \text{m}^3)\). Determine the 2D \((r, X)\) SS concentration profiles in the tube.

Species balance over \((2\pi r \Delta r \Delta X)\) \(C, V\).

\[
V_x \frac{\partial C_A}{\partial X} = D \left( \frac{\partial^2 C_A}{\partial X^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_A}{\partial r} \right) \right) \quad \text{moles/s} - \text{m}^3
\]

\[
U_{\text{max}} \left(1 - \frac{r^2}{R^2}\right) \frac{\partial C_A}{\partial X} = D \left( \frac{\partial^2 C_A}{\partial X^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_A}{\partial r} \right) \right)
\]

\[
= D \left( \frac{\partial^2 C_A}{\partial X^2} + \frac{\partial^2 C_A}{\partial r^2} + \frac{1}{r} \frac{\partial C_A}{\partial r} \right)
\]

BCs. \(X = 0\) \(C_A = C_{Ao}\), \(X = L\) \(\frac{\partial C_A}{\partial x} = 0\) \((R > r > 0)\)

\(r = 0\) \(\frac{\partial C_A}{\partial r} = 0\) \(r = R\), \(- D \frac{\partial C_A}{\partial r} = k\) \((L > X > 0)\)

Let us non-dimensionalize the equation & BCs:
\[ \theta = \frac{C_A}{C_{A_0}}, \quad z = \frac{x}{L_c}, \quad \xi = \frac{r}{R}, \quad L_c = R P_e, \quad \text{where } P_e(\text{radial}) = \frac{U_{max} R}{D} \]

(Note that this 'P_e' is based on mass transport)

\[
(1 - \xi^2) \frac{\partial \theta}{\partial z} = \frac{1}{P_e^2} \frac{\partial^2 \theta}{\partial z^2} + \frac{\partial^2 \theta}{\partial \xi^2} + \frac{1}{\xi} \frac{\partial \theta}{\partial \xi}
\]

BC. \( z = 0, \quad \theta = 1 \); \( z = L/L_c, \quad \frac{\partial \theta}{\partial z} = 0 \)

\[ \xi = 0, \quad \frac{\partial \theta}{\partial \xi} = 0 \]; \( \xi = 1 \quad - \frac{\partial \theta}{\partial \xi} = \left( \frac{kR}{D C_{A_0}} \right) = M' \quad \text{(constant)} \)

⇒ It is clear that the non-dimensionalized equations and BCs of this (mass transport) and previous (heat transport) examples are the same. Therefore, you need to solve only one of the two. The dimensionless solutions will be the same. This situation should remind you of the recommendation that one should non-dimensionalize the equation before solving it. Several such analogous heat, mass, and momentum transport scenarios exist in chemical engineering applications.

⇒ In most cases, radial \( P_e(\text{mass or heat}) \text{ number} \) in laminar flow regime is of the order of 10 or higher. In such cases, the axial diffusion term can be neglected. In other words,

\[ \alpha \frac{d^2 T}{d x^2} << V_X \frac{\partial T}{\partial x} \text{ or } D \frac{d^2 C_A}{d x^2} << V_X \frac{\partial C_A}{\partial x} \quad \text{(See BSL book)} \]

If you neglect the axial diffusion term, the 2D elliptic PDE is modified/simplified to 1D parabolic PDE:

\[ V_X \frac{\partial T}{\partial x} = \frac{\alpha}{r} \frac{\partial}{\partial r} \left( \frac{r \frac{\partial T}{\partial r}}{\partial r} \right) \text{ or } V_X \frac{\partial C_A}{\partial x} = \frac{D}{r} \frac{\partial}{\partial r} \left( \frac{r \frac{\partial C_A}{\partial r}}{\partial r} \right) \]

This simplified PDE can be solved using the Crank-Nicholson technique described in the preceding lecture. In other words, one can numerically march in ‘X’ direction and solve in ‘r’ direction using Thomas Algorithm for the tridiagonal matrix built from the discretized ‘r’ terms. For now, let us revert to the original (full) non-dimensionalized elliptic PDE:

\[
(1 - \xi^2) \frac{\partial \theta}{\partial z} = \frac{1}{P_e^2} \frac{\partial^2 \theta}{\partial z^2} + \frac{\partial^2 \theta}{\partial \xi^2} + \frac{1}{\xi} \frac{\partial \theta}{\partial \xi}
\]

At \( \xi = 0 \), there is a discontinuity and you are solving an approximation:

\[
(1 - \xi^2) \frac{\partial \theta}{\partial z} = \frac{1}{P_e^2} \frac{\partial^2 \theta}{\partial z^2} + \frac{2 \partial^2 \theta}{\partial \xi^2}
\]
Discretize the main conservation equation:

\[
(1 - \xi_j^2)\frac{\theta_{i+1,j} - \theta_{i-1,j}}{2\Delta z} = \frac{1}{P_e^2} \frac{\theta_{i+1,j} - 2\theta_{i,j} + \theta_{i-1,j}}{\Delta z^2} + \frac{\theta_{i,j+1} - 2\theta_{i,j} + \theta_{i,j-1}}{\Delta \xi^2} + \frac{1}{\xi_j} \frac{\theta_{i,j+1} - \theta_{i,j-1}}{2\Delta \xi}
\]

or

\[
\left(\frac{1-\xi_j^2}{2\Delta z} + \frac{1}{p_e^2\Delta z^2}\right)\theta_{i-1,j} - \frac{2\theta_{i,j}}{p_e^2\Delta z^2} - \left(\frac{1-\xi_j^2}{2\Delta z} - \frac{1}{p_e^2\Delta z^2}\right)\theta_{i+1,j} = \left(\frac{1}{2\Delta \xi_j} - \frac{1}{\Delta \xi^2}\right)\theta_{i,j-1} + \frac{2\theta_{i,j}}{\Delta \xi^2} - \left(\frac{1}{2\Delta \xi_j} + \frac{1}{\Delta \xi^2}\right)\theta_{i,j+1}
\]

Discretize the approximated conservation equation at the line of symmetry:

\[
\left(\frac{1-\xi_j^2}{2\Delta z} + \frac{1}{p_e^2\Delta z^2}\right)\theta_{i-1,0} - \frac{2\theta_{i,0}}{p_e^2\Delta z^2} - \left(\frac{1-\xi_j^2}{2\Delta z} - \frac{1}{p_e^2\Delta z^2}\right)\theta_{i+1,0} = -\frac{2\theta_{i-1,0}}{\Delta \xi^2} + \frac{4\theta_{i,0}}{\Delta \xi^2} - \frac{2\theta_{i+1,0}}{\Delta \xi^2}
\]

\[
i = 1, N
\]

\[
\Delta z = 1/N, \quad \Delta \xi = \frac{L/L_c}{M}
\]

Note that RHS terms for all rows contain guess values for all \(\theta_{i,j}\) to begin with

Discretize BCs:

\[
i = 0, j = 0, M; \quad \theta_{0,j} = 1; \quad i = N, j = 0, M; \quad \theta_{N+1,j} = \theta_{N-1,j}
\]

\[
j = 0, i = 1, N; \quad \theta_{i,-1} = \theta_{i,1}; \quad j = M, i = 0, N; \quad \theta_{i,M+1} = \theta_{i,M-1} - 2M'\Delta \xi
\]

1st row of Tridiagonal matrix,

\[
i = 1 \quad -\frac{2\theta_{1,0}}{p_e^2\Delta z^2} - \left(\frac{1-\xi_0^2}{2\Delta z} - \frac{1}{p_e^2\Delta z^2}\right)\theta_{2,0} = -\frac{4\theta_{1,0}}{\Delta \xi^2} + \frac{4\theta_{1,0}}{\Delta \xi^2} - \left(\frac{1-\xi_0^2}{2\Delta z} + \frac{1}{p_e^2\Delta z^2}\right)\theta_{0,0}
\]

\[
= 1
\]

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middle rows, 
\[ i = 2, N - 1: \quad \left( \frac{1 - \xi_0^2}{2\Delta z} + \frac{1}{p_e^2 \Delta z^2} \right) \theta_{i-1,0} - \frac{2\theta_{i,0}}{p_e^2 \Delta z^2} - \left( \frac{1 - \xi_0^2}{2\Delta z} - \frac{1}{p_e^2 \Delta z^2} \right) \theta_{i+1,0} = -\frac{4\theta_{i,1}}{\Delta \xi^2} + \frac{4\theta_{i,0}}{\Delta \xi^2} \]

last row, \[ i = N: \quad \frac{2}{p_e^2 \Delta z^2} \theta_{N-1,0} - \frac{2\theta_{N,0}}{p_e^2 \Delta z^2} = -\frac{4\theta_{N,1}}{\Delta \xi^2} + \frac{4\theta_{N,0}}{\Delta \xi^2} \]

You have a tridiagonal matrix \( A \) in \( (A\theta_{i,0}^{k+1} = b_{i,0}^k) \) to invert

\[ j = 1, M - 1 \] (Visit the main conservation equation)

1st row,
\[ i = 1: \quad \frac{2\theta_{1,j}}{p_e^2 \Delta z^2} - \left( \frac{1 - \xi_j^2}{2\Delta z} - \frac{1}{p_e^2 \Delta z^2} \right) \theta_{2,j} = -\left( \frac{1 - \xi_j^2}{2\Delta z} + \frac{1}{p_e^2 \Delta z^2} \right) \theta_{0,j} \]
\[ \left( \frac{1}{2\Delta \xi_j} - \frac{1}{\Delta \xi^2} \right) \theta_{1,j-1} + \frac{2\theta_{1,j}}{\Delta \xi^2} - \left( \frac{1}{2\Delta \xi_j} + \frac{1}{\Delta \xi^2} \right) \theta_{1,j+1} \]

middle rows:
\[ i = 2, N - 1 \]: These are middle grids unaffected by BCs.

last row
\[ i = N \quad \frac{2}{p_e^2 \Delta z^2} \theta_{N-1,j} - \frac{2\theta_{N,j}}{p_e^2 \Delta z^2} = \left( \frac{1}{2\Delta \xi_j} - \frac{1}{\Delta \xi^2} \right) \theta_{N,j-1} + \frac{2\theta_{N,j}}{\Delta \xi^2} - \left( \frac{1}{2\Delta \xi_j} + \frac{1}{\Delta \xi^2} \right) \theta_{N,j+1} \]

Again, \( A\theta_{i,j}^{k+1} = b_{i,j}^k \); \[ i = 1, N \quad j = 1, M - 1 \]

\[ j = M \]

1st row,
\[ i = 1 \quad -\frac{2\theta_{1,M}}{p_e^2 \Delta z^2} - \left( \frac{1 - \xi_M^2}{2\Delta z} - \frac{1}{p_e^2 \Delta z^2} \right) \theta_{2,M} = -\left( \frac{1 - \xi_M^2}{2\Delta z} + \frac{1}{p_e^2 \Delta z^2} \right) \theta_{0,M} \]
\[ -\frac{2}{\Delta \xi^2} \theta_{1,M-1} + \frac{2\theta_{1,M}}{\Delta \xi^2} + 2M' \Delta \xi \left( \frac{1}{2\Delta \xi_M} + \frac{1}{\Delta \xi^2} \right) \]

middle rows, LHS (same as that of eq1), unaffected by BC =
\[ i = 2, N - 1 \quad \frac{2}{\Delta \xi^2} \theta_{i,M-1} + \frac{2\theta_{i,M}}{\Delta \xi^2} + 2M' \Delta \xi \left( \frac{1}{2\Delta \xi_M} + \frac{1}{\Delta \xi^2} \right) \]
last row,

\[ i = N, \quad \frac{2\theta_{N-1,M}}{p_e^2 \Delta z^2} - \frac{2\theta_{N,M}}{p_e^2 \Delta z^2} = -\frac{2}{\Delta \xi^2} \theta_{N,M-1} + \frac{2\theta_{N,M}}{\Delta \xi^2} + 2M' \Delta \xi \left( \frac{1}{2\Delta \xi \xi_M} + \frac{1}{\Delta \xi^2} \right) \]

Again, \[ A\theta_{i,M}^{k+1} = b_{i,M}^k \]

You have called the Thomas Algorithm (M+1) times to invert the tridiagonal A matrix to solve \[ \theta_{i,j}, \quad i = 1, N \]
\[ j = 0, M \] using the guess values on the RHS of the tridiagonal matrix.

You must have noted that we did not prepare the tridiagonal matrix, and instead directly substituted the BCs in the discretized equations! As an exercise, prepare the tridiagonal matrix by defining individual elements of rows for every ‘j’ viz a(i,j), b(i,j) ⋯, substitute BCs and see if you get the same equations for different ‘j’.

Now, this is the time to compare the solved \( \theta_{i,j} \) values with the guess values you made at the beginning of the iterations before starting the iterations.

⇒ From the programming point of view, you should be able to choose reasonable values of all variables including, D, V_{max}, M and \( p_e \), mass transport, or H and \( p_e \), heat transport.

⇒ As earlier noted, solving elliptic PDE is computational extensive, requiring guess values, iterations and convergence. Very often, one artificially inserts a transient term \( \left( \frac{\partial C_A}{\partial t} \right. \) or \( \rho C_p \frac{\partial T}{\partial t} \) or \( \rho \frac{\partial V}{\partial t} \) and seeks SS solutions, which is the focus of the last two lectures.
Lecture #26-27

Time – dependent 2D parabolic PDE: ADI Method

We are solving, for examples:

\[ \frac{\partial C_A}{\partial t} + V \cdot \nabla C_A = D \nabla^2 C_A + (-r_A) ; \ C_A(t, r, x) \]

or

\[ \rho C_p \left( \frac{\partial T}{\partial t} + V \cdot \nabla T \right) = k \nabla^2 T + (-r_A) (\Delta H) ; \ T(t, r, x) \]

**Note**: SS solution must be the same as that of the converged solution of the analogous 2D elliptic PDE \( \left( \frac{\partial c_A}{\partial t} = \frac{\partial \sigma}{\partial t} = 0 \right) \) discussed in the previous lectures.

Let us take a general case of the time-dependent 2D PDE:

\[ \frac{\partial \phi}{\partial t} = \phi_{XX} + \phi_X + \phi_{YY} + \phi_Y ; \phi(t, x, y) \]

with necessary IC and BCs.

Apply Crank-Nicholson method/scheme to discretize \( \phi_{XX}, \phi_{YY}, \phi_X, \) and \( \phi_Y \) terms, in the similar fashion solved the time-dependent 1D PDE on \( \phi(t, x) \):

\[ \left( \frac{\phi^{t+1} - \phi^t}{\Delta t} \right)_{i,j} = \frac{1}{2} \left[ \left( \frac{\phi_{i+1,j}^{t+1} - 2 \phi_{i,j}^{t+1} + \phi_{i-1,j}^{t+1}}{\Delta X^2} \right)^t + \left( \frac{\phi_{i+1,j}^{t+1} - \phi_{i-1,j}^{t+1}}{2 \Delta X} \right)^t \right] \\
+ \left( \frac{\phi_{i,j+1}^{t+1} - 2 \phi_{i,j}^{t+1} + \phi_{i,j-1}^{t+1}}{\Delta Y^2} \right)^t + \left( \frac{\phi_{i,j+1}^{t+1} - \phi_{i,j-1}^{t+1}}{2 \Delta Y} \right)^t \]

- This way the X-derivatives have been discretized implicitly on time, whereas the Y-derivatives have been discretized explicitly.
- Alternatively, one can discretize Y-derivatives implicitly on time, whereas X-derivatives can be discretized explicitly.
- Re-arranging the terms as \[ A \phi_x^{t+1} = \phi_y^t \] or \[ A \phi_y^{t+1} = \phi_x^t \] from either scheme, it is clear that ‘A’ will be a tridiagonal matrix, and one can proceed on time-step by solving \( \phi \) on X-Y plane:
\[
\left( \frac{1}{2\Delta X^2} - \frac{1}{4\Delta X} \right) \phi_{i-1,j}^{t+1} - \left( \frac{1}{\Delta t} + \frac{1}{\Delta X^2} \right) \phi_{i,j}^{t+1} + \left( \frac{1}{2\Delta X^2} + \frac{1}{4\Delta X} \right) \phi_{i+1,j}^{t+1} = \left( \frac{1}{4\Delta Y} - \frac{1}{2\Delta Y^2} \right) \phi_{i,j}^t - \left( \frac{1}{\Delta t} - \frac{1}{\Delta Y^2} \right) \phi_{i,j}^t - \left( \frac{1}{4\Delta Y} + \frac{1}{2\Delta Y^2} \right) \phi_{i,j+1}^t
\]

- This way you are ‘marching’ in ‘j’ direction and ‘sweeping’ in ‘i’ direction.

By the second scheme, if you ‘march’ in ‘i’ direction and ‘sweep’ in ‘j’-direction, you will get the following equation:

\[
\left( \frac{1}{4\Delta Y} - \frac{1}{2\Delta Y^2} \right) \phi_{i,j-1}^{t+1} + \left( \frac{1}{\Delta t} + \frac{1}{\Delta Y^2} \right) \phi_{i,j}^{t+1} - \left( \frac{1}{4\Delta Y} + \frac{1}{2\Delta Y^2} \right) \phi_{i,j+1}^{t+1} = \left( \frac{1}{2\Delta X^2} - \frac{1}{4\Delta X} \right) \phi_{i,j}^t + \left( \frac{1}{\Delta t} - \frac{1}{\Delta X^2} \right) \phi_{i,j}^t + \left( \frac{1}{2\Delta X^2} + \frac{1}{4\Delta X} \right) \phi_{i,j-1}^t
\]

- Both schemes will work and the Crank-Nicholson method will produce 2\(^{nd}\) order accuracy.

- Alternate Direct Implicit (ADI) method is an improved method producing 4\(^{th}\) order accuracy without any extra computational cost (for more, refer the book by Ferziger):

First discretize \(\phi_X\) and \(\phi_{XX}\) terms implicitly and \(\phi_Y\) and \(\phi_{YY}\) terms explicitly to solve \(\phi\) over half step \((\Delta t/2)\) and then discretize \(\phi_Y\) and \(\phi_{YY}\) terms implicitly and \(\phi_X\) and \(\phi_{XX}\) terms explicitly over the next half step:

**Step 1:**

\[
\left( \frac{\phi_{i,j}^{t+1/2} - \phi_i^t}{\Delta t/2} \right) = \frac{1}{2} \left[ (\phi_{XX} + \phi_X)^{t+1/2} + (\phi_{YY} + \phi_Y)^t \right]
\]

**Step 2:**

\[
\left( \frac{\phi_{i,j}^{t+1} - \phi_{i,j}^{t+1/2}}{\Delta t/2} \right) = \frac{1}{2} \left[ (\phi_{XX} + \phi_X)^{t+1/2} + (\phi_{YY} + \phi_Y)^{t+1} \right]
\]

or

\[
A\phi_{i,j}^{t+1/2} = \phi_{i,j}^t
\]

and

\[
B\phi_{i,j}^{t+1} = \phi_{i,j}^{t+1/2}
\]

The procedure can also be understood by the following illustration:
Ex: Consider 2D diffusion in a rectangular shaped solid porous carbon block. The block is initially soaked with moisture, say at concentration $C_o \, (\text{moles/m}^3)$. At $t = 0^+$ all four sides of the block are exposed to dry air (moisture concentration = $C_i \ll C_o$). We are interested in calculating the unsteady-state concentration profiles of moisture within the block, i.e. $C(t, x, y) = ?$. Pore diffusion coefficient for moisture in solid is $D_{pore}$.

\[ \frac{\partial C_A}{\partial t} + \nabla \cdot (\nabla C_A) = D_{pore} \nabla^2 C_A + \left( \frac{1}{\varphi_0} \right) \]  

\[ \frac{\partial C_A}{\partial t} = D_{pore} \left( \frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} \right) \]  

\[ t = 0 \quad C = C_o \quad \text{for } L \geq x \geq 0; w \geq y \geq 0 \]  

\[ 0^+ \quad C = C_i^* \quad \text{at } x = 0 \& L \text{ for } w > y > 0 \quad \text{and } \text{at } y = 0 \& w \text{ for } L > x > 0 \]  

($C_i^*$ is the solid phase moisture concentration at the surface of the block in equilibrium with $C_i$ in atmosphere).
Step 1: discretize \( 'i' \) implicitly and \( 'j' \) explicitly over \((t & t + 1/2)\)

\[
\frac{C_{i,j}^{t+1/2} - C_{i,j}^t}{\Delta t/2} = \frac{D_{\text{pore}}}{2} \left[ \left( \frac{C_{i+1,j} - 2C_{i,j} + C_{i-1,j}}{\Delta X^2} \right)^{t+1/2} + \left( \frac{C_{i,j+1} - 2C_{i,j} + C_{i,j-1}}{\Delta y^2} \right)^t \right] 
\]

\((\Delta X = L/N, \Delta y = W/M)\)

Arrange:

\[
D_{\text{pore}} \frac{\Delta t}{2\Delta X^2} C_{i-1,j}^{t+1/2} - \left( \frac{D_{\text{pore}}}{\Delta X^2} + \frac{2}{\Delta t} \right) C_{i,j}^{t+1/2} + D_{\text{pore}} \frac{\Delta t}{2\Delta X^2} C_{i+1,j}^{t+1/2} = \frac{D_{\text{pore}}}{2\Delta y^2} C_{i,j-1}^t + \left( \frac{D_{\text{pore}}}{\Delta y^2} - \frac{2}{\Delta t} \right) C_{i,j}^t - \frac{D_{\text{pore}}}{2\Delta y^2} C_{i,j+1}^t
\]

\[i = 1, N - 1\]

\[j = 1, M - 1\]

Step 2:

Discretize BCs: \( C_{o,j} = C_{N,j} = C^*; \ j = 0, M \)

\( C_{i,0} = C_{i,M} = C^*; \ i = 0, N \)

Prepare the tridiagonal matrix:

\[
a(i,j) = \frac{D_{\text{pore}}}{2\Delta X^2}; \quad b(i,j) = -\left( \frac{D_{\text{pore}}}{\Delta X^2} + \frac{2}{\Delta t} \right); \quad c(i,j) = \frac{D_{\text{pore}}}{2\Delta X^2}; \quad d(i,j) = -\frac{D_{\text{pore}}}{2\Delta y^2} C_{i,j-1} + \left( \frac{D_{\text{pore}}}{\Delta y^2} - \frac{2}{\Delta t} \right) C_{i,j} + \frac{D_{\text{pore}}}{2\Delta y^2} C_{i,j+1}
\]

\[i = 1, N - 1\]

\[j = 1, M - 1\]
Substitute BCs and the following coefficients will be modified:

\[
\begin{align*}
    d(1, j) &= d(1, j) - a(1, j)C^* \\
    d(N - 1, j) &= d(N - 1, j) - c(N - 1, j)C^*
\end{align*}
\]

Convince yourself that no other coefficients will change. This was actually an easy problem, when all four boundary conditions were simple, i.e., functional values were prescribed. Problems are complicated when you have ‘flux’/gradient or mixed boundary conditions; for example,

\[-D \frac{ac}{dx} = k_m(C - C_{atm})
\]

or \[\text{Flux (known)}\]

and/or \[-D \frac{ac}{dy} = kC \text{ or } k_m(C - C_{atm})\]

In such cases the other coefficients may also change. Revert to the previous step.

Tridiagonal \((N - 1, a, b, c, d, y(i, j)) \quad i = 1, N - 1\)

\[\Rightarrow\] You will be calling the subroutine ‘\(M - 1\)’ times as you ‘march’ along ‘\(j\)’ direction. Now, you have the values for \(C_{i,j}^{t+1/2} \quad i = 1, N - 1\)

Step3:

Now march along ‘\(i\)’ direction and ‘sweep’ along ‘\(j\)’ direction to solve for \(C_{i,j}^{t+1} \quad \text{from} \quad C_{i,j}^{t+1/2}\).

Arrange:

\[
\begin{align*}
    C_{i,j}^{t+1} - C_{i,j}^{t+1/2} &= \frac{D_{\text{pore}}}{2} \left[ \left( C_{i-1,j}^{t+1/2} - 2C_{i,j}^{t+1/2} + C_{i+1,j}^{t+1/2} \right) \frac{\Delta x^2}{2} + \left( C_{i,j}^{t+1/2} - 2C_{i,j}^{t+1/2} + C_{i,j+1}^{t+1/2} \right) \frac{\Delta y^2}{2} \right]
\end{align*}
\]

\[\text{explicit}\]

\[\text{implicit}\]

\[
\begin{align*}
    \frac{D_{\text{pore}}}{2\Delta y^2} C_{i,j-1}^{t+1} - \left( \frac{D_{\text{pore}}}{\Delta y^2} + \frac{2}{\Delta t} \right) C_{i,j}^{t+1} + \frac{D_{\text{pore}}}{2\Delta y^2} C_{i,j+1}^{t+1} &= -\frac{D_{\text{pore}}}{2\Delta x^2} C_{i-1,j}^{t+1/2} + \left( \frac{D_{\text{pore}}}{\Delta x^2} - \frac{2}{\Delta t} \right) C_{i,j}^{t+1/2} - \frac{D_{\text{pore}}}{2\Delta x^2} C_{i,j}^{t+1/2} ; \\
    j &= 1, M - 1 \\
    i &= 1, N - 1
\end{align*}
\]
Step 4:
Discretize the BCs: Same as before.

Prepare the tridiagonal matrix:

\[
a(i, j) = \frac{D_{pore}}{2\Delta y^2}; \quad b(i, j) = -\left(\frac{D_{pore}}{\Delta y^2} + \frac{2}{\Delta t}\right); \quad c(i, j) = \frac{D_{pore}}{2\Delta y^2}; \quad d(i, j) = -\frac{D_{pore}}{2\Delta x^2} C_{i-1,j}^{t+1/2} + \left(\frac{D_{pore}}{\Delta x^2} - \frac{2}{\Delta t}\right) C_{i,j}^{t+1/2} - \frac{D_{pore}}{2\Delta x^2} C_{i+1,j}^{t+1/2};
\]

\[
i = 1, N - 1; \quad j = 1, M - 1
\]

Substitute the discretized BCs, and only the following coefficients will be modified:

\[
d(i, 1) = d(i, 1) - a(i, 1)C^*; \quad d(i, M - 1) = d(i, M - 1) - c(i, M - 1)C^* \quad \left\{ \begin{array}{l} i = 1, N - 1 \\ j = 1, M - 1 \end{array} \right.
\]

Tridiagonal \((M - 1, a, b, c, d, y(i, j))\) \(j = 1, M - 1\)

⇒ You will be calling the subroutine \('N - 1'\) times as you 'march' along \('t'\) direction. Thus, you have solved for \(C_{i,j}^{t+1}\), \(i = 1, N - 1\) \(j = 1, M - 1\)

Recap (solving 2nd order ODE and PDEs at a glance)

<table>
<thead>
<tr>
<th>BVP: (A\phi_i = b) (Direct Method)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D parabolic: (A\phi_i^{t+1} = \phi_i^t) (Crank-Nicholson Method)</td>
</tr>
<tr>
<td>2D Elliptic: (A\phi_{i,j} = \phi_{j,i}^{\text{guess}}) or (A\phi_{j,i} = \phi_{i,j}^{\text{guess}}) (Method of Lines)</td>
</tr>
<tr>
<td>2D parabolic: (\text{(ADI Method)})</td>
</tr>
</tbody>
</table>

\[
A\phi_i^{t+1/2} = \phi_i^t \quad \text{or} \quad A\phi_j^{t+1/2} = \phi_j^t \quad \text{and} \quad B\phi_j^{t+1} = \phi_j^{t+1/2} \quad \text{or} \quad B\phi_i^{t+1} = \phi_i^{t+1/2}
\]

where, \(A\) and \(B\) are the Tridiagonal matrices.
Example: Consider the SS flow of a liquid through a long tube. Reynolds number is 180. At time $t = 0$, a tracer is injected into the liquid at inlet to the tube. Diffusion coefficient of tracer in the liquid is $D \text{ cm}^2 \text{/s}$. Determine the time profiles of the tracer concentrations $(r, x)$ in the tube, i.e. $C(t, r, x) =$?

Soln.

A species balance over $2\pi r \Delta r \Delta x'$ $CV$ yields the following eqn

$$
\frac{\partial c}{\partial t} + V(r) \frac{\partial c}{\partial x} = D \nabla^2 c + (-r_A)
$$

or

$$
\frac{\partial c}{\partial t} + V(r) \frac{\partial c}{\partial x} = D \left( \frac{\partial^2 c}{\partial x^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right) \right) \quad L > X > 0
$$

or

$$
\frac{\partial c}{\partial t} = \left( -V(r) \frac{\partial c}{\partial x} + D \frac{\partial^2 c}{\partial x^2} \right) + D \left( \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial r^2} \right)
$$

$t = 0 \quad C = 0 \quad L \geq x \geq 0$ and $R \geq r \geq 0$

$0^+ \quad C = C_o \quad @ \quad x = 0$

$\frac{\partial c}{\partial x} = 0 \quad @ \quad X = L \quad \{ \text{for all } R > r > 0 \}$

(long tube approximation)

$$
\frac{\partial c}{\partial r} = 0 \quad @r = 0 \quad (\text{symmetric})
$$

$$
= 0 \quad @r = R \quad (\text{non-reactive walls}) \quad \{ \text{for all } L > X > 0 \} 
$$
Note: You will encounter discontinuity at \( r = 0 \) in the radial diffusion terms while discretizing. Considering \( \nabla C = 0 \), you will be solving the approximated equation instead.

\[
\frac{\partial C}{\partial t} = (-V(r) \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2}) + 2D \frac{\partial^2 C}{\partial r^2} \quad \text{at } r = 0 \text{ for all } L > X > 0
\]

Discretize the approximated equation:

\[
\frac{C_{i,j}^{t+1/2} - C_{i,j}^t}{\Delta t/2} = \frac{1}{2} \left( (-V_j) \frac{C_{i+1,j} - C_{i-1,j}}{2\Delta X} + D \frac{C_{i+1,j} - 2C_{i,j} + C_{i-1,j}}{4\Delta X^2} \right)^{t+1/2}
\]

\[
+ 2D \left( \frac{C_{i,j+1} - 2C_{i,j} + C_{i,j-1}}{\Delta r^2} \right)^t \quad ; \quad j = 0 \}
\]

\[
\text{explicit}
\]

\[
\text{implicit}
\]

Arrange;

\[
\left( \frac{V_j}{4\Delta X} + \frac{D}{2\Delta X^2} \right) C_{i-1,j}^{t+1/2} - \left( \frac{2}{\Delta t} + \frac{D}{\Delta X^2} \right) C_{i,j}^{t+1/2} - \left( \frac{V_j}{4\Delta X} - \frac{D}{2\Delta X^2} \right) C_{i+1,j}^{t+1/2}
\]

\[
= -\left( \frac{D}{\Delta r^2} \right) C_{i,j-1}^t - \left( \frac{2}{\Delta t} - \frac{2D}{\Delta r^2} \right) C_{i,j}^t - \left( \frac{D}{\Delta r^2} \right) C_{i,j+1}^t \quad ; \quad j = 0 \}
\]

\[
i = 1, N
\]
Similarly, discretize the main equation:

\[
\frac{C_{i,j}^{t+1/2} - C_{i,j}^t}{\Delta t / 2} = \frac{1}{2} \left[ \left( -V_j \right) \frac{C_{i+1,j} - C_{i-1,j}}{2\Delta x} + D \left( \frac{C_{i+1,j} - 2C_{i,j} + C_{i-1,j}}{\Delta x^2} \right) \right]^{t+1/2} \\
+ D \left( \frac{1}{r_j} \frac{C_{i,j+1} - C_{i,j-1}}{2\Delta r} + \frac{C_{i+1,j} - 2C_{i,j} + C_{i,j-1}}{\Delta r^2} \right)^t \\
\text{for } j = 1, M \\
\text{and } \left( \frac{1}{r_j} \frac{C_{i,j+1} - C_{i,j-1}}{2\Delta r} + \frac{C_{i+1,j} - 2C_{i,j} + C_{i,j-1}}{\Delta r^2} \right)^t \\
\text{for } i = 1, N
\]

Arrange,

\[
\left( \frac{V_j}{4\Delta x} + \frac{D}{2\Delta x^2} \right) C_{i-1,j}^{t+1/2} - \left( \frac{2}{\Delta t} + \frac{D}{\Delta x^2} \right) C_{i,j}^{t+1/2} - \left( \frac{V_j}{4\Delta x} - \frac{D}{2\Delta x^2} \right) C_{i+1,j}^{t+1/2} \\
= \left( \frac{D}{4r_j \Delta r} - \frac{D}{2\Delta r^2} \right) C_{i,j-1}^{t} - \left( \frac{2}{\Delta t} - \frac{D}{\Delta r^2} \right) C_{i,j}^{t} \\
- \left( \frac{D}{4r_j \Delta r} + \frac{D}{2\Delta r^2} \right) C_{i,j+1}^{t}; \quad j = 1, M \\
\text{and } \left( \frac{D}{4r_j \Delta r} + \frac{D}{2\Delta r^2} \right) C_{i,j+1}^{t}; \quad i = 1, N
\]

Note: \( V_j = U_{\text{max}} \left( 1 - \frac{r_j^2}{R^2} \right) \); \( r_j = j\Delta r \)

Discretize BCs & IC

\[
t = 0, \quad C(i, j) = 0 \text{ or a small number } C_{\text{int}} \ll C_o \text{ (} N \geq i \geq 0 \text{ and } M \geq j \geq 0 \)
\]

\[
\begin{align*}
0^+ & \quad C(0, j) = C_o \\
\frac{c(N+1,j) - c(N-1,j)}{\Delta x} & = 0 \\
\text{or } & \quad C(N+1,j) = C(N-1,j)
\end{align*} \quad \text{for } M > j > 0
\]

\[
\begin{align*}
C(i, 1) & = C(i, -1) \\
C(i, M+1) & = C(i, M-1)
\end{align*} \quad \text{for } N > i > 0
\]

Prepare tridiagonal matrix

\[
\begin{align*}
\text{for } j = 0: \quad a(i, 0) & = \left( \frac{V_0}{4\Delta x} + \frac{D}{2\Delta x^2} \right); \quad b(i, 0) = -\left( \frac{2}{\Delta t} + \frac{D}{\Delta x^2} \right); \quad c(i, 0) = -\left( \frac{V_0}{4\Delta x} - \frac{D}{2\Delta x^2} \right); \quad d(i, 0) = \left( \frac{2D}{\Delta r^2} \right) C_{i,-1}^t - \left( \frac{2}{\Delta t} - \frac{2D}{\Delta r^2} \right) C_{i,0}^t - \left( \frac{D}{\Delta r^2} \right) C_{i,1}^t; \quad i = 1, N
\end{align*}
\]

Substitute BCs,

\[
d(1,0) = -\left( \frac{2D}{\Delta r^2} \right) C_{1,-1}^t - \left( \frac{2}{\Delta t} - \frac{2D}{\Delta r^2} \right) C_{1,0}^t - a(1,0)C_o
\]

\[
a(N,0) = a(N,0) + c(N,0)
\]
\[ d(N, 0) = -\left( \frac{2D}{\Delta r^2} \right) C_{N,1}^t - \left( \frac{2}{\Delta t} - \frac{2D}{\Delta r^2} \right) C_{N,0}^t \]

Tridiagonal \( (N, a, b, c, d, y^{t+1/2}(i, 0)); \ i = 1, N \)

Preparation of tridiagonal matrix... continue....

\[
a(i, j) = \left( \frac{V_j}{4\Delta X} + \frac{D}{2\Delta X^2} \right); \ b(i, j) = -\left( \frac{2}{\Delta t} + \frac{D}{\Delta X^2} \right); \ c(i, j) = -\left( \frac{V_j}{4\Delta X} - \frac{D}{2\Delta X^2} \right); \ d(i, j)
\]

\[
= \left( \frac{D}{4r_j \Delta r} - \frac{D}{2\Delta r^2} \right) C_{i,j-1}^t - \left( \frac{2}{\Delta t} - \frac{D}{\Delta r^2} \right) C_{i,j}^t
\]

\[
- \left( \frac{D}{4r_j \Delta r} + \frac{D}{2\Delta r^2} \right) C_{i,j+1}^t \quad j = 1, M\}
\]

\[ i = 1, N \}

Substitute BC \( (j = 1, M - 1) \)

\[ d(1, j) = d(1, j) - a(1, j)C_0 \]

\[ a(N, j) = a(N, j) + c(N, j) \]

Tridiagonal \( (N, a, b, c, d, y^{t+1/2}(i, j)); \ i = 1, N \)

\[ j = 1, M - 1 \}

You have called the tridiagonal subroutine \( 'M - 1' \) times for the interior nodes.

Substitute BC @ \( j = M \)

\[ d(1, M) = -\left( \frac{D}{\Delta r^2} \right) C_{1,M-1}^t - \left( \frac{2}{\Delta t} - \frac{D}{\Delta r^2} \right) C_{1,M}^t - a(1, N) . C_0 \]

\[ d(i, M) = -\left( \frac{2}{\Delta r^2} \right) C_{i,M-1}^t - \left( \frac{2}{\Delta t} - \frac{D}{\Delta r^2} \right) C_{i,M}^t \]

\[ a(N, M) = a(N, M) + c(N, M) \]

\[ d(N, M) = -\left( \frac{D}{\Delta r^2} \right) C_{N,M-1}^t - \left( \frac{2}{\Delta t} - \frac{D}{\Delta r^2} \right) C_{N,M}^t \]

Tridiagonal \( (N, a, b, c, d, y^{t+1/2}(i, M)); \ i = 1, N \)

(Therefore, you have called the Thomas Algorithm \( (M + 1) \) times while sweeping \( j = 0, M \) rows)
For the last time in this course, let us write down complete eqn

\[ Ay^{t+1/2} = d^t \quad \text{for } j = 0, i = 1, N \]

\[
\begin{pmatrix}
-\left( \frac{2}{\Delta t} + \frac{D}{\Delta x^2} \right) & -\left( \frac{V_0}{4\Delta X} + \frac{D}{2\Delta X^2} \right) & \cdots & \cdots & \cdots \\
\vdots & \ddots & \ddots & \ddots & \ddots \\
\vdots & & \ddots & \ddots & \ddots \\
-\left( \frac{2}{\Delta t} + \frac{D}{\Delta x^2} \right) & -\left( \frac{V_0}{4\Delta X} + \frac{D}{2\Delta X^2} \right) & \cdots & \cdots & \cdots \\
\end{pmatrix}
\begin{pmatrix}
Y_i \\
\end{pmatrix}^{t+1/2} =
\begin{pmatrix}
\vdots \\
d(1,0) \\
\vdots \\
\vdots \\
d(N,0) \\
\end{pmatrix}^t
\]

Similarly, you can write a set of equations for \( j = 1, M - 1 \) and \( j = M \) using the coefficient as above:

\[ j = 1, M - 1 \]

\[
\begin{pmatrix}
-\left( \frac{2}{\Delta t} + \frac{4}{\Delta x^2} \right) & -\left( \frac{V_j}{4\Delta X} + \frac{D}{2\Delta X^2} \right) & \cdots & \cdots & \cdots \\
\vdots & \ddots & \ddots & \ddots & \ddots \\
\vdots & & \ddots & \ddots & \ddots \\
-\left( \frac{2}{\Delta t} + \frac{D}{\Delta x^2} \right) & -\left( \frac{V_j}{4\Delta X} + \frac{D}{2\Delta X^2} \right) & \cdots & \cdots & \cdots \\
\end{pmatrix}
\begin{pmatrix}
Y_i \\
\end{pmatrix}^{t+1/2} =
\begin{pmatrix}
\vdots \\
d(i,j) \\
\vdots \\
\vdots \\
d(N,j) \\
\end{pmatrix}^t
\]
\[ j = M \]

\[
\begin{bmatrix}
-\left(\frac{2}{\Delta t} + \frac{4}{2\Delta x^2}\right) & -\left(\frac{V_M}{4\Delta X} - \frac{D}{2\Delta X^2}\right) & \cdots & \cdots & \cdots & \cdots \\
\cdots & \left(\frac{V_M}{4\Delta X} + \frac{D}{2\Delta X^2}\right) & -\left(\frac{2}{\Delta t} + \frac{D}{\Delta x^2}\right) & -\left(\frac{V_M}{4\Delta X} - \frac{D}{2\Delta X^2}\right) & \cdots & \cdots \\
\vdots & \vdots & \vdots & \vdots & \left(\frac{D}{\Delta x^2}\right) & -\left(\frac{2}{\Delta t} + \frac{D}{\Delta x^2}\right) \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\end{bmatrix}\begin{bmatrix} Y_i \end{bmatrix}^{t+1/2} \\
\begin{cases}
d(1,M) \\
\vdots \\
i = 2, N - 1 \\
\vdots \\
d(N,M) \\
\end{cases}
\]

Now, sweep in 'j' direction and march in 'i' direction for \((t + 1)\) based on the \(y(i,j)\) values you determined at \((t + 1/2)\) step (above)

\[Ay^{t+1}(i,j) = d^{t+1/2} \quad i = 1, N \]

\[j = 0\]

\[
\frac{C_{i,j}^{t+1} - C_{i,j}^{t+1/2}}{\Delta t/2} = \frac{1}{2}\left(\left(-V_j\right)\frac{C_{i+1,j} - C_{i-1,j}}{2\Delta X} + D\frac{C_{i+1,j} - 2C_{i,j} + C_{i-1,j}}{\Delta X^2}\right)^{t+1/2} \\
+ 2D\left(\frac{C_{i,j+1} - 2C_{i,j} + C_{i,j-1}}{\Delta r^2}\right)^{t+1} (i = 1, N)
\]
\( j = 1, M \)

\[
\frac{C_{i,j}^{t+1} - C_{i,j}^{t+1/2}}{\Delta t/2} = \frac{1}{2} \left[ \left( -V_j \right) \frac{C_{i+1,j} - C_{i-1,j}}{2\Delta X} + D \frac{C_{i+1,j} - 2C_{i,j} + C_{i-1,j}}{\Delta X^2} \right]^{t+1/2} \\
+ D \left( \frac{1}{r_j} \frac{C_{i,j+1} - C_{i,j-1}}{2\Delta r} + \frac{C_{i,j+1} - 2C_{i,j} + C_{i,j-1}}{\Delta r^2} \right)^{t+1} (i = 1, N)
\]

In this last lecture of the course, I leave it here for you to do the remaining part (arranging the terms and applying BCs for \( i = 1, (2 \cdots N - 1) \), \( N \) rows to invert the matrix) as you sweep in \('j' direction, as an exercise. The topic on ADI stops here.

**Note:**

1. The SS solution \( y(t,x,r) \) as \( t \to \infty \) of the time-dependent 2D parabolic equation must be the same as that of the corresponding 2D elliptic PDE you have learnt how to solve in the preceding lecture, using 'Method of Lines', i.e. for

\[
\frac{\partial C}{\partial t} + V \cdot \nabla C = D \nabla^2 C + (-r_A);
\]

\( C(t,x,r) \) as \( t \to \infty \) must be the same as that of

\[
V \cdot \nabla C = D \nabla^2 C + (-r_A) \Rightarrow C(x,r)
\]

2. A question arises. When asked to solve the elliptic (2D) PDE, should not or cannot we artificially insert the transient term \( \frac{\partial C}{\partial t} \) and seek the SS solution to the corresponding time-dependent 2D parabolic equation? Very often, yes. Recall that, solving elliptic PDE requires iterations and there is always a convergence issue. How many iterations? On the other hand, the parabolic equation does not require iterations, and you march on \('t' axis solving \( y(x,r) \) at every time step without iterations. Therefore, more than often the ADI method is preferred over 'Method of Lines' for solving an elliptic (2D) PDE. Insert the transient term and solve till you have SS solution.

3. Before closing this chapter, let us answer how we address non-linearity in the differential term, for example, \( V \frac{\partial V}{\partial x} \) of the NS equation? The answer is simple. By iterations! Guess velocity fields \( (V_g) \). Discretize the derivative term as before. Solve for velocity fields as before. Iterate
till there is convergence. Alternatively, Taylor’s series can also be used to approximate velocity fields by linearization, in which case guesses are required for the velocity gradients.

**End – Semester Exam**

[In a regular semester, these course materials are usually covered in 28 lectures of 1 h 15 min duration each, or 42 lectures of 50 min duration each. For record and due acknowledgement, most of these materials were part of my graduate level lectures from Prof. Hermann F. Fasel, AME, which I audited way back in 1995 at the University of Arizona, Tucson, USA. At Kanpur, I offer this course to graduate students only. To this end, you are welcome to send me any comments, or mistakes or errors you notice in the lectures, to my email id: vermanishith@gmail.com.]
Heterogeneous Chemical Reaction Engineering
Lecture 01

Chemical Reaction Engineering (heterogeneous reaction)

Recommended books:

- Chemical Engineering Kinetics by JM Smith, McGraw Hill, 2nd ed.
- Chemical Reactor Analysis and Design by Froment and Bischoff, Wily, 3rd ed.
- Chemical and Catalytic Reaction Engineering by James Carberry, Dover

The focus is on the catalytic reactions in multi-phase systems:

\[
\begin{align*}
&\text{s + g, s + l,} \\
&\text{s + l + g,} \\
&\text{l + g} \\
(2 - \text{or multi-phase systems})
\end{align*}
\]

eg. \( N_2 + 3H_2 \rightarrow 2NH_3 \)

(non-catalytic reaction: \( C + O_2 \rightarrow CO_2 \))

Review:

a) Representation of chemical reactions

\[ \sum_i n_i A_i = 0 \]

\( \text{stoichiometric coefficients} : \{ -ve \text{ for reactants} \}
\[ +ve \text{ for products} \]

\( e.g. \quad N_2 + 3H_2 \rightarrow 2NH_3 \)

\[ \Rightarrow 2NH_3 - 3H_2 - N_2 = 0 \quad \text{(representation)} \]

or

\[ \frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3 \]

\[ \Rightarrow NH_3 - \frac{1}{2}N_2 - \frac{3}{2}H_2 = 0 \quad \text{(representation)} \]

Both are stoichiometrically balanced equations, but do not show the path of the reactions.....to be discussed later)

b) Reaction rate \((\dot{r})\):

\[ aA + bB + ... \rightarrow qQ + sS + ... \]
\[ r = \frac{1}{v_i w} \frac{dN_i}{dt} \rightarrow \text{# of moles of the '}_i\text{' species at a time '}_t\text{' in a reactive system} \]

always + ve

, where

\[ \frac{dN_i}{dt} = \begin{cases} -\text{ve for reactants} \\ +\text{ve for products} \end{cases} \]

⇒ 'r' is defined in such a way that it is an intrinsic property of the reaction (specific to the reaction), and not species-specific; hence divided by 'w'.

\[ r = -\frac{1}{(aw)} \frac{dN_A}{dt} = -\frac{1}{(bw)} \frac{dN_B}{dt} = \frac{1}{(qw)} \frac{dQ}{dt} = \frac{1}{(sw)} \frac{dS}{dt} \]

Note that there is no indices 'i' for the rate of reaction

⇒ Therefore, the rate of the reaction can be measured by measuring any of the reactants or products.

\[ \text{or, } r = \frac{1}{2} \frac{+\text{ve}}{w} \frac{dNH_3}{dt} = -\frac{1}{w} \frac{dN_2}{dt} = -\frac{1}{3} \frac{dH_2}{dt} \]

c) Reactions: Elementary or non – elementary (definition)

\[ A + B \rightarrow C \]

If the above reaction represents only mass balance: - Non – elementary
If the reaction represents path of the reaction: - Elementary

eg. \[ N_2 + 3H_2 \rightarrow 2NH_3 \]

⇒ “One mole of \( N_2 \) collides with 3 moles of \( H_2 \) to produce 2 moles of \( NH_3 \)”: only mass balance (or stoichiometric balance) holds good; this is not a path of the reaction ⇒ It is a non – elementary reaction.

⇒ The actual path(s) of the reaction is/are elementary, and are called mechanistic steps.

Mechanism is nothing but the sequence of elementary reactions.
eg. \[ H_2 + Cl_2 \rightarrow 2HCl \]

Stoichiometrically (mass) balanced reaction

But, it is a non – elementary reaction. Physical chemistry tells us that this is not the path of the reaction. Actual paths are as follows:

\[
\begin{align*}
Cl_2 & \rightleftharpoons 2Cl \cdot \\
Cl \cdot + H_2 & \rightarrow H \cdot + HCl \\
\vdots & \\
\text{etc} & 
\end{align*}
\]

Sequence of elementary reactions, these are mechanistic steps or actual paths.

Revisit the book by Levenspiel or Fogler for certain rules/guidelines for a reaction to be elementary, which are necessary conditions, but not sufficient for a reaction to be elementary; the mechanism must be proposed from the knowledge of physical chemistry, and validated:

\[ \Rightarrow \text{Maximum 3 – body collision of the reactant or product species (molecularity cannot exceed } > 3 \text{). That is, for an elementary reaction, } aA + bB \rightarrow cC + dD \]

\[
a + b \leq 3; c + d \leq 3; \text{ and } a, b, c, d, \text{ are } + \text{ ve and whole numbers.}
\]

\[ \Rightarrow \text{If the reversible reaction is non – elementary, the forward reaction is also non – elementary, or vice –versa (note that no reaction is truly irreversible).}
\]

Some trivia:

1. \[
\begin{align*}
& k_1 \\
2A & \rightleftharpoons B \\
& k_2
\end{align*}
\]

\[
r \equiv (\text{measured experimentally}) = k_1 C_A^2 - k_2 C_B . \text{ Is it an elementary or non – elementary reaction? The answer is we do not know. The mechanism of the reaction is required. However, if it is an elementary reaction,}
\]

\[
r = k_1 C_A^2 - k_2 C_B, \text{ and not vice versa.}
\]

2. \[
\begin{align*}
& \frac{1}{2} A \rightleftharpoons B \\
& k_1 \\
& k_2
\end{align*}
\]

\[ \Rightarrow \text{Non – elementary, even if } r \text{ is measured experimentally as}
\]

\[
k_1 C_A^{0.5} - k_2 C_B.
\]

3. \[
2A \rightleftharpoons 4B \Rightarrow \text{Non – elementary, because the reversible reaction cannot be elementary.}
\]
4. \[ 2A \rightleftharpoons 0.5B \quad \Rightarrow \text{Same as above.} \]

5. \[ \frac{k_1}{k_2} \quad \Rightarrow r_{\text{exp}} = k_1 - k_2C_B \Rightarrow \text{Non-elementary.} \quad \text{Note: A zeroth order reaction is always non-elementary.} \]

6. \[ \text{If} \quad 2A \rightleftharpoons 4B + C \quad \text{is an elementary reaction, what will be the rate?} \quad \Rightarrow \text{Wrong question. This reaction can never be elementary.} \]
Lecture 02

d) Rate Expression

For an elementary reaction, \(aA + bB \rightarrow cC + dD\),

\[ r = r(C, T): \text{experimental observation} \]

where, \(C\) is the concentration of the reactant species.

\[ = f(T) \phi(C) \text{ or } f(T) \prod_i C_i^{\nu_i} \]

\([\text{two separate functions}]\)

eg. If \(2A + B \rightarrow A_2B\) is an elementary reaction \(r = kC_A^2C_B\)

\[ \text{or, } r = (k_0 T^m e^{-E/RT}) C_A^2 C_B \quad (0 \leq m \leq 1) \]

where, \(m = 0 \Rightarrow k_0 e^{-E/RT} C_A^2 C_B \) : Arrhenius theory

\[ = \frac{1}{2} \Rightarrow k_0 T^{1/2} e^{-E/RT} C_A^2 C_B \] : Collision theory

\[ = 1 \Rightarrow \text{rate is proportional to } T \] : Transition state theory

Arrhenius theory is the most common

\[ r = k_0 e^{-E/RT} \prod_i C_i^{\nu_i} \text{; } k_0 = \text{frequency factor} \]

\( f^n \) of temperature ; \( E = \text{Activation energy (J/mole)} \)

Below is the energy diagram for the reaction path:

In the energy diagram shown above,


\[ \Delta H = H_2 - H_1 \quad (\text{always} + \text{ve}) \]

\[ (E, \text{overall} = |E_1 - E_{-1}|) \]

\[ = \text{exothermic reaction} \]

\[ (\text{heat content of reactants} > \text{that of product}) \]

\[ , \text{else} - \text{ve for endothermic reaction.} \]

The kinetic rate coefficients or constants can be written as

\[ k_1 = A_1 e^{-E_1/RT} \quad ; \quad k_{-1} = A_2 e^{-E_{-1}/RT} \]

\[ E_1, E_{-1} \text{ are always } +\text{ve} \text{ and are energy barriers for the forward and reversible reactions, respectively; } \]

As are the pre-exponential factors.

⇒ The plot is also known as energy – barrier diagram.

⇒ \( E/RT \) is a dimensionless quantity. Therefore, “RT” can be construed as the “characteristic” energy. \( E \neq f(T) \); it is dependent on the path of the reaction. See the \( X \)-coordinate on the energy barrier diagram.

⇒ The ratio denotes the minimum amount of energy required to overcome the barrier, relative to the energy available at the reaction temperature, \( T \), say, provided thermally via reactor heating. Actual energy supplied at the temperature “\( T \)” requires an energy balance across the reactor, to be discussed much later in the course, and can be expressed as \( m(RT) \), where “\( m \)” is some positive number.

⇒ Considering the exponential nature of the rate coefficient (\( k \)) function, high ‘\( E \)’ means that the rate of reaction is less sensitive to change in temperature (\( \Delta T \)) at high \( T \); low ‘\( E \)’ means the rate of reaction is relatively less sensitive to change in temperature (\( \Delta T \)) at low \( T \). For more, see the table for the rate constants calculated for different cases of low and high activation energies and temperatures, in the Levenspiel’s book (Table 2.1):

\[ E \uparrow \quad T \uparrow \quad T \downarrow \]

\[ E \downarrow \quad T \uparrow \quad T \downarrow \]

e) Development of rate expression for a non- elementary reaction:

(A mechanism is required to develop the rate expressions. In other words, all mechanistic steps must be known a priori)

Example: \( \text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr} \quad (\text{Overall stoichiometric reaction}) \)
(Note: experimental measurements will not be consistent with \( r \) expressed as \( k_1(H_2)(Br_2) - k_{-1}(HBr)^2 \)

1. **Mechanistic steps (Free radical mechanism):**

\[
\begin{align*}
B_r_2 & \xrightleftharpoons[k_{-1}]{k_1} 2Br \cdot \\
\cdot Br + H_2 & \xrightleftharpoons[k_{-2}]{k_2} HBr + H \cdot \\
H \cdot + Br_2 & \xrightleftharpoons[k_{-3}]{k_3} HBr + Br \cdot \\
\end{align*}
\]

These are all elementary reactions; they represent the actual paths of the reactions.

2. **Simplify:** \( H \cdot + Br - Br \gg HBr + Br \cdot \) or \( k_3 \gg k_{-3} \) (negligible)

3. **Write down the rate of reaction:**

\[
r = - \frac{d(Br_2)}{dt} = - \frac{d(H_2)}{dt} = \frac{1}{2} \frac{d(HBr)}{dt}; \text{ concentration in moles/cc and 'w' = volume}
\]

4. Choose a species as per your convenience of calculation or the experimental measurements.

\[
\frac{d(Br_2)}{dt} = -k_1(Br_2) + k_{-1}(Br \cdot)^2 - k_3(Br_2)(H \cdot) \quad (\text{See the book by Carberry})
\]

5. **Quasi-steady state assumption:** \( Br, \cdot H \) are radicals & short-lived species. Therefore,

\[
\frac{d(H \cdot)}{dt} = \frac{d(Br \cdot)}{dt} \approx 0
\]

(At the time scale of change in the concentration of the major species, such species remain 'stationary' or constant (almost zero, very-very small amount)).

Therefore,
\[
\frac{d(H\cdot)}{dt} = k_2(Br\cdot)(H_2) - k_{-2}(HBr)(H \cdot) - k(H \cdot)(Br_2) = 0
\]

\[
\frac{d(Br\cdot)}{dt} = 2k_1(Br_2) - 2k_{-1}(Br \cdot)^2 - k_2(Br \cdot)(H_2) + k_{-2}(HBr)(H \cdot) + k_3(H)(Br_2) = 0
\]

(Note: \(Br_2 \rightarrow 2Br \cdot\); \(r = \frac{1}{2} \frac{d(Br_\cdot)}{dt} = -\frac{1}{2} \frac{d(Br_2)}{dt}\))

6. Substituting (remove all intermediate terms/species and retain major species)

\[
r = \frac{k_3k_2\sqrt{\frac{k_1}{k_{-1}}} (Br_2)^{3/2}(H_2)}{k_{-2}(HBr) + k_3(Br_2)}
\]

(Note that the temperature dependence- and concentration dependence terms cannot be separated)

**Some Special Cases:**

1. \(r = k_2\sqrt{\frac{k_1}{k_{-1}}} (Br_2)^{1/2}(H_2)\) when \((HBr) \ll (Br_2)\) at the beginning of the reaction

2. \(r = \frac{k_3k_2\sqrt{\frac{k_1}{k_{-1}}} (Br_2)^{3/2}(H_2)}{k_{-2}(HBr)}\) when \((Br_2) \ll (HBr)\) towards the end of the reaction.

In either special case, \(r = f(T)\phi(C)\)

But, Note that it must not imply that the reaction is elementary!

Also, note that the order of a non-elementary reaction can be fraction; \(-ve; > 3\)

**Go back to the first case:**

\[r = k, app f(C_i) \Rightarrow k, app = k_2\sqrt{\frac{k_1}{k_{-1}}}
\]

Therefore, \(e^{-E_{app}/RT} = e^{-E_2/RT} \sqrt{\frac{e^{-E_1/RT}}{e^{-E_{-1}/RT}}}\)
\[ E_{app} = \left( E_2 + \frac{E_1 - E_{-1}}{2} \right) \]

E (apparent) does not have physical meaning; can be + ve, −ve no energy barrier or diagram.

However, \( E_2, E_1, E_{-1} \) are always + ve

**Conclusion:** To obtain the rate expression for a non-elementary reaction, rate mechanism must to be known a priori.
Lecture 03

Another example of developing rate expression for a non-elementary reaction:

Ex. Free radical addition polymerization kinetics

⇒ In general, such reactions include
   1) Monomer
   2) Initiator
   3) Catalyst

, and the mechanistic steps are initiation, propagation, and termination.

a) **Initiation**: \(aM_1 + bI \rightarrow k_i P_1\)
   
   \(\text{monomer} \rightarrow \text{initiator} \rightarrow \text{active polymer radical}\)
   
   (eg. ethylene, styrene)

b) **Propagation**: \(\cdot P_1 + M_1 \rightarrow k_{pr} \cdot P_2\)
   
   \(\vdots\)

   \(\cdot P_{n-1} + M_1 \rightarrow k_{pr} \cdot P_n\)

c) **Termination**: \(\cdot P_n + \cdot P_m \rightarrow k_t M_{n+m} \text{ or } M_n + M_m, (inactive/stable molecules)\)

The rates of the reactions are developed as

\[\frac{dM_1}{dt} = -ar_i - k_{pr}M_1 \sum P_n \quad (r_i = \text{rate of initiation reaction for formation of radicals})\]

\[\frac{dP_1}{dt} = r_i - k_{pr}M_1 \cdot P_1 - k_t \cdot P_1 \sum P_n \quad \vdots \quad \text{including itself} (\cdot P_1)\]

\[\frac{dP_n}{dt} = k_{pr}M_1 \cdot P_{n-1} - k_{pr}M_1 \cdot P_n - k_t \cdot P_n \sum P_n \quad (n \geq 2)\]

\[\text{from previous} \quad \text{to form} \quad \text{reaction} \quad \text{to} \quad \text{form} \quad \text{\(P_{n+1}\)}\]
Make use of PSSA (pseudo steady state assumption) or QSSA:

\[
\frac{dP_n}{dt} \approx 0 \quad \text{(true for all reactions involving the short-lived reactive radical species)}
\]

Add \( \sum^n \):

\[
0 = r_i - k_t (\sum P_n)^2
\]

(Thus, under the PSSA, the initiation and termination rates are equal)

Therefore,

\[
\frac{dM_1}{dt} = -ar_i - k_{pr} M_1 \sqrt{\frac{r_i}{k_t}} \quad \text{(substitute } P_n \text{ in the 1st reaction)}
\]

\[
= -k_{pr} M_1 \sqrt{\frac{r_i}{k_t}} \quad \text{(usually, the amounts of monomer is small } a \approx 0) \]

\[
\frac{dM_1}{dt} = -k_{pr} \sqrt{\left(\frac{k_i}{k}\right)} I^{1/2} M_1 \quad \text{(assuming the rate of initiation is 1st order, i.e. } k_i, l) \]

rate at which monomer is consumed or the rate of overall polymerization reaction

See the book by Froment and Bischoff on examples of polyethylene synthesis or thermal cracking of the long-chain hydrocarbons in sunlight.

**Homework (Froment & Bischoff, 2nd ed):** 1.11, 1.12, 1.14 (development of rate expression for the non-elementary reactions)

---

**One more example of developing rate expression for a non-elementary reaction**

(All catalytic reactions are non-elementary!)

\[
e.g. \quad CO + H_2O \xrightarrow{T=450^\circ C} \left(Fe - oxides\right) CO_2 + H_2 \quad \text{(water - gas shift reaction)}
\]

- It is a non-elementary reaction (not exact path of the reaction)

**Some introduction to catalyst:**

'\(X'\) active sites (\(X'\)) (electronically active)
Mechanistic steps (or elementary steps) are as follows:

\[
\begin{align*}
H_2O + X & \xrightarrow{k_1} H_2 + XO \\
XO + CO & \xrightarrow{k_2} CO_2 + X
\end{align*}
\]

\[\text{elementary reactions/steps}\]

\[
1) \quad r = -\frac{d(CO)}{dt} = -\frac{d(H_2O)}{dt} = \frac{d(CO_2)}{dt} = \frac{d(H_2)}{dt}
\]

\[
2) \quad \frac{d(CO)}{dt} = -k_2[XO][CO]
\]

\[
3) \quad \frac{d(XO)}{dt} = k_1[X][H_2O] - k_2[XO][CO]
\]

\[
\frac{d(X)}{dt} = -k_1[X][H_2O] + k_2[XO][CO]
\]

\[
4) \quad \text{PSSA: } \frac{d(XO)}{dt} = \frac{d(X)}{dt} \approx 0
\]

\[
\begin{align*}
[XO] &= \frac{k_1[X][H_2O]}{k_2[CO]} \\
[X] &= \frac{k_2[XO][CO]}{k_1[H_2O]} \quad \text{identical expressions}
\end{align*}
\]

⇒ All it means is that we need one more independent equation.

Site conservation/balance:

\[
[X] + [XO] = [X_0]
\]

\[
\text{free sites} \quad \downarrow \quad \text{occupied sites} \quad \rightarrow \quad \text{total sites (property of the material)}
\]

(At any time, site is either 'X' or 'XO')

\[
r = \frac{[X_0]k_1k_2[CO][H_2O]}{k_1[H_2O]+k_2[CO]} \neq f(T)\phi(C)
\]

(\text{which is the feature of an elementary reaction})

Note:

⇒ order of the reaction cannot be not defined here

\[
\text{(e.g. } \quad r \neq k_1(C_1)^\alpha(C_2)^\beta \ldots )\]
⇒ Activation energy is also not defined here (there is no energy barrier or energy barrier diagram per say)

However if \( k_1 \gg k_2 \) or \( k_2 \gg k_1 \), the order of the reacton or \( E(\text{apparent}) \) can be calculated.

or \( r \approx k_2[X_0][\text{CO}] \) or \( k_1[X_0][\text{H}_2\text{O}] \)

**Possibilities:**

linear with the slope \( -E/R \) (always true for elementary reaction)
\( E \) is always +ve and unique.

non-linear over the entire temperature range

**Be careful:** there are two Es, but these are not true activation energies; these should be termed apparent activation energies.
Lecture 04

Review:

**Ideal reactors**

**Batch**

- Perfectly mixed; intrinsic property is spatially independent ($T, \rho, c, C_p$)

**Plug flow**

- Infinite mixing in $r$-direction
- Zero mixing in axial - director
  \[ v_z \neq v_z(r) \]

**Mixed tank reactor (CSTR)**

- Same as the batch conditions except that there is a flow.

**Design equation of ideal reactors:**

\[ v_A A + v_B B + \ldots \rightarrow \text{Products (} r \equiv \text{rate of the reaction)} \]

**Batch:**

\[
\begin{align*}
  t &= C_{AO} \int_{X_{Ai}}^{X_{Af}} \frac{V_0 \, dX_A}{V \left( -v_A r \right)} \\
  X_A(t) &= \frac{N_{AO} - N_A}{N_{AO}}
\end{align*}
\]

**Plug flow reactor:**

\[
\tau = \frac{v_o}{v_0} = C_{AO} \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{(-v_A r)}; \quad v_o = \text{volumetric flow rate of feed at reference point}
\]

If flow:

\[
X_A = \left( \frac{F_{AO} - F_A}{F_{AO}} \right)
\]

(# of moles/time) $\equiv$ molar flow rate

(Note: space time $\neq$ residence time because of volume-change)
\[ CSTR: \quad \tau = \frac{V}{v_0} = \frac{C_{AO}(X_{Af} - X_{Ai})}{(-v_A R)_f} \]

**Design:**
- \[ \tau(X_A) \]
- or \[ X_A(\tau) \]

If there is no volume change (i.e., no expansion)

\[ t = C_{AO} \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{(-v_A R)} : \text{ batch reactor} \]

\[ \tau = C_{AO} \int_{X_{Ai}}^{X_A} \frac{dX_A}{(-v_A R)} : \text{ plug flow reactor (PFR)} \]

\[ t = \tau ! \]

**Batch time = space time.**

**Notes:**
1. If there is no expansion, differential volume in a PFR moves without mixing with the neighboring elements, i.e., each volume element is like a small ‘batch’ reactor with one concentration. Therefore, batch time is the same as space time of an ideal PFR.

2. \( V \) (plug flow) \( \ll \) \( V \) (CSTR) for the same conversion, if \( \text{order} > + ve \), and vice-versa.

   - gradual decrease in concentration
   - abrupt decrease in concentration

Therefore, \( C_{avg} \gg C_{exit} \),

\[ r_{PFR} \gg r_{CSTR} \]

\[ V_{PFR} \ll V_{CSTR} \]

3. Without expansion:

\[ X_A = \frac{N_{AO} - N_A}{N_{AO}} = \frac{C_{AO} - C_A}{C_{AO}} \quad (V = \text{const}) \]

\[ C_A = C_{AO} (1 - X_A) \]

With expansion:

\[ X_A = \frac{N_{AO} - N_A}{N_{AO}} : V = V_0 (1 + \epsilon X_A) \]

\[ C_A = C_{AO} \left( \frac{1 - X_A}{1 + \epsilon X_A} \right) \]

**Expansion effect**
Multiple reactors:

PFR in series

\[ V_i \rightarrow \sum V_i \rightarrow X_{Af} \]

Two configurations will give the same conversion

CSTR in series

\[ V_i \rightarrow \sum V_i \rightarrow X_{Af} \]

Parallel configurations:

1) PFR:

\[ V_i \rightarrow \sum V_i \rightarrow X_{Af} \]

2) PFR:

\[ V_i \rightarrow \sum V_i \rightarrow X_{Af} \]

Two configurations will give the same conversion

for +ve order

for the same volume.

\[ V > \sum V_i \quad +ve \text{ order} \]

\[ V < \sum V_i \quad -ve \text{ order} \]

for the same conversion

\[ \tau = \frac{V}{v_o} = \frac{V_i}{v_{oi}} \]

adjust '\( \tau_i \)' in each reactor.

\[ V = \sum V_i \quad \text{for the same conversion} \]

\[ \tau = \frac{V}{v_o} = \frac{V_i}{v_{oi}} \]

adjust '\( \tau_i \)' in each reactor.
Non-ideal reactors

Ideal PFR and Ideal CSTR: two extreme situations of ideality, or two model reactors

- Zero (axial) mixing
- Infinite mixing
- Flow direction

Real reactors:

1. Gas flow over packed bed:
   - $v = v(r)$
   - $c = c(r)$
   - Non-uniform concentration (stagnation zones at corners)
   - (Non-ideality arises from a bad design of mixer or stirrer system)

2. Dispersion (mixing) in voids

3. Temperature gradient induces convective flow
   - (non-isothermal)

4. $A \rightarrow R$
   - It causes dispersion/diffusion in axial (flow) direction
   - Local mixing

Zero mixing in an ideal PFR and early/late mixing in a non-ideal/reactor

Inherently present in a tubular reactor.
**Micro – mixing** ⇒ Mixing of fluid (elements) on molecular level.

![Diagram of micro-mixing](image)

there is a finite probability of A & B mixing somewhere in the reactor.

**Macro - mixing** ⇒

![Diagram of macro-mixing](image)

mixing of pocket – zones (little volume)

**Homework (Froment & Bischoff, 2nd ed):** 12.5 (only 1st order)
Lecture 05

- Continue......... (non-ideal reactors)

Concept of “pockets” and criteria for macro-mixing:

1) Contents of individual pockets are well mixed with themselves, but do not mix with second pockets.
2) Pockets should represent chemical reaction conditions. For \( A + B \rightarrow C \), one cannot, therefore, reduce the size of a pocket to one molecule; then the reaction will not occur. Pockets should have a finite volume.
3) Pocket-contents should have same residence time, but different pockets may have different residence times.

⇒ Macro-mixing → macro – fluids (segregated fluids) → macro - reactor

Ideal PFR is a good example of macro – reactors

Fast fluidized bed reactor and liquid-liquid emulsion (LLE) membrane-based reactive continuous separation processes are examples of industrial or practical reactors. In the former reactor, particles do not mix with each other and a spatially constant concentration may be assumed within the micron-sized particles. In the second case, small globules (or droplets) are dispersed and immiscible in a continuous phase without mixing.

⇒ Micro-mixing → micro – fluids (non-segregated fluids) → micro – reactor

1. Ideal CSTR is a good example of micro – reactors.
2. Ideal CSTR cannot be a macro – fluid reactor because residence times are different for different fluid elements. However, for \( A \rightarrow B \) (1st order reaction), an ideal CSTR can be treated as a macro – reactor. In other words, it makes no difference for first-order kinetics whether one assumes non-segregated or segregated flow, or micro- or macromixing in an ideal CSTR. Time of reaction alone and not degree of micromixing determines conversion. This is expected because a first-order process depends upon time of reaction of the reacting species and not on the interaction of molecules (See Carberry).
Design of a non-ideal flow reactor ($\epsilon = 0$)

1. Segregated flow model (a real/non-ideal reactor is modeled as a segregated or macro reactor)

2. Each pocket is a batch reactor (well-mixed) within themselves. $X = X(t)$ is known a priori for all types of reaction.

Each pocket has a residence time (some pockets can exit early and some can exit late).

RTD

(We should be able to determine RTD of each pocket or volume – element of the reactor)

Definition (there are two types of RTDs):

- Volume size $x (\Delta t) = \text{fraction of fluid having residence time between } t \text{ & } (t + \Delta t)$

- Defined in such a way that $\int_0^{\infty} J'(t) \, dt = 1$
or,

\[
J(t) = \int_0^t J'(t)\,dt \\
or \quad J'(t) = \frac{dJ}{dt}
\]

It is clear that

\[
J(t) = \sum_{i=0}^t J'(t)\Delta t
\]

\[
or \quad J'(t) = \frac{\Delta J}{\Delta t}
\]

\[
J(t) = \int_0^t J'(t)\,dt \\
or \quad J'(t) = \frac{dJ(t)}{dt}
\]

Thus, for a non–ideal reactor:

\[
\text{l}ittle \ pocket\ (batch) \ reactors
\]

\[\text{We require the following:}\]

1) \(X(t)\) for a batch reactor
2) \(RTD \ (J \ or \ J')\) of the reactor under consideration

\[
\bar{X} = \int_0^\infty X(t)J'(t)\,dt \quad \text{or} \quad \sum X(t)J'(t)\Delta t
\]

\(\text{Performance/design equation of a segregated/macro reactor}\)

\(\text{(averaged over } RT)\)
Similarly, any intrinsic property, $\bar{r}$ at outlet

$$\bar{r} = \int_0^\infty r(t) J'(t) dt$$

fraction of fluid intrinsic property having RT between $t$ & $t + \Delta t$

The average residence time always holds good as follows:

$$(\tau) \text{ or } \bar{t} = \frac{R}{D} = \int_0^\infty t J'(t) dt$$

**Determining RTD experimentally (two methods)**

*(tracer analysis: no reaction)*

\[ M \text{ (dose/del fn)} \]

output

or $C_{in}$

step - input

output

or $C_{in}$

Area $\equiv M(\text{dose})$

time

\[ M \text{ (dose/del fn)} \]

time

\[ M \text{ (dose/del fn)} \]
Either of the two methods of injecting a tracer will work. It is a question of convenience in the experiment. ‘Q’, flow rate must be the same as that used in the real reactor; however, without reaction (i.e., reaction is switched off!)

**Method 1:**

**Step Tracer Injection**

**Input**

\[ C_{in} \]

\[ v \text{ (flow rate)} \]

**Output**

\[ C_{out}(t) \]

**Calculations:**

By the very definition of \( J(t) \):

\[ J(t) = \frac{C_{out}(t)}{C_{in}} \implies J'(t) = \frac{d(J(t))}{dt} \]

Now, turn on the reaction (no tracer!)

\[ \bar{X} = \int_{0}^{\infty} X(t)J'(t)dt = \int_{0}^{\infty} X(t)d(J(t)) \]

**Method 2:**

**Pulse Injection**

**Input**

\[ 'delta' \text{ function} \]

\[ M = \text{total amount of tracer (dose)} \]

0

**Output**

\[ C_{exit}(t) \]

\[ v \text{ (flow rate)} \]
Species balance (use definition of $J'(t)$)

$$MJ'(t)dt = C_{exit}(t)v dt$$

$$J'(t) = \frac{C_{exit}v}{M} = \frac{C_{exit}(t)}{M/v} = \frac{C_{exit}(t)}{\int_0^\infty vC_{exit}(t)dt/v} = \frac{C_{exit}(t)}{\int_0^\infty C_{exit}dt}$$

$J(t) = \int_0^\infty J'(t)dt$

Again, turn on the reaction (no tracer)

$$\bar{X} = \int_0^\infty X(t)J'(t)dt = \int_0^\infty X(t)d(J(t))$$

Either of the two methods will work: by determining $J(t)$, $J'(t)$ can be determined, or vice-versa.

Also, be careful in evaluating or calculating such integrals: $\int_0^\infty X(t)J'(t)dt$, which contain two different functions that may span over different time-domains, thus having different limits of integrations. See the examples and questions in the examinations that follow in the next lectures.
Lecture 06

RTD (…..continued…)

Segregated reactors (let us validate the segregated model with the reactors of known mixing)

Ex. 1. Plug-flow reactor: Performance equation

\[ X_A = 0 \]

\[ X \quad X + dX \]

⇒ 1st order reaction: \( X_A = 1 - e^{-k\tau} \) where, \( \tau \) is the residence time.

\( \text{(Performance equation: } \tau = \frac{V}{v_0} = \int_0^T \frac{dx}{-\tau_A} \)  

Recall previous discussion on RTD:

For a PFR, RTD:

\[ \begin{align*}
  U(t) & \quad \rightarrow \quad f(t) \\
  \delta(t) & \quad \rightarrow \quad f'(t)
\end{align*} \]

Output

\[ \begin{cases}
  0 ; & t < \tau \\
  1 ; & t \geq \tau
\end{cases} \]

Let us apply segregated reactor model to a PFR:

\[ X_{Af}(t) = \int_0^\infty X(t)f'(t)dt = \int_0^\infty (1 - e^{-k\tau})\delta(t-\tau)dt \]

\[ = 1 - e^{-k\tau} \quad (X_{Af}(\tau), \text{same as before}) \]

Ex. 2. CSTR (let us determine RTD first)

\[ X_A = 0 \quad \frac{v}{c(t)} \quad X_{Af} \]
Input:

\[ \frac{C(t)}{C_0} \int_0^\infty \frac{dC}{c(t)} dt \Rightarrow \text{species (tracer) balance at } (t - t + \Delta t) \]

\[ 0 - vC(t)dt = VdC \]

\[ \ln \frac{C}{C_0} = \frac{-v}{V} t = -t/\tau \]

\[ C(t) = C_o e^{-t/\tau}; \quad C_o = \frac{M}{V} \]

\[ C(t) = \frac{M}{V} e^{-t/\tau} \]

\[ J'(t) = \frac{e^{-t/\tau}}{\int_0^\infty e^{-t/\tau} dt} = \frac{e^{-t/\tau}}{\frac{\tau}{(\tau-1)}} = \frac{e^{-t/\tau}}{\tau} \]

\[ J(t) = \int_0^t J'(t) dt = 1 - e^{-t/\tau} \]

else, start from the species balance for the step input case:

\[ (C_o v - C(t) v) dt = VdC \]

\[ \frac{C}{C_o} = 1 - e^{-t/\tau} \quad (\tau = V/v) \]

\[ J(t) = 1 - e^{-t/\tau} \text{ (same as before)} \]

\[ J'(t) = e^{-t/\tau}/\tau \text{ (same as before)} \]
Get back to the performance equation of the segregated reactor:

\[ X_{Af} = \int_{0}^{\infty} X(t)J'(t)dt \]

**Note:** CSTR is a micro (non-segregated) reactor; yet the CSTR reactor can be treated as a macro (segregated) – reactor for the 1st order reaction.

**Ex 2:** Determine conversion for a 1st order reaction in an ideal CSTR.

\[ X_{Af} = \int_{0}^{\infty} \left(1 - e^{-kt}\right) \frac{e^{-t/\tau}}{\tau} dt \]

CSTR: \( \frac{k\tau}{1+k\tau} \equiv \) same as that from the performance equation

(Recall the design/performance equation: \( \tau = \frac{v}{v_o} = \frac{C_{Af}}{(-r_A)f} = \frac{C_{Ao}(X_{Af}-X_{Ai})}{(-v_Ar)f} = \frac{C_{Ao}X_{Af}}{kC_{Ao}(1-X_{Af})} \)

\[ = \frac{X_{Af}}{k(1-X_{Af})} \Rightarrow X_{Af} = \frac{k\tau}{1+k\tau} \]

**Ex 3:** Laminar flow reactor (no diffusion in r direction): It is a segregated or macro reactor.

Determine \( J(t) \) and \( J'(t) \)

\[ v = v_o \left(1 - \frac{r^2}{R^2}\right) \quad \ldots \quad (1) \quad v_o = \text{maximum (center - line) velocity} \]

\[ t_{res} = \frac{L}{v} = \frac{L}{v_o\left(1 - \frac{r^2}{R^2}\right)} \]

\( J'(t)dt \equiv \text{fraction of the fluid having resedne time between (t and t + \Delta t) is the fraction of the fluid between and r and r + \Delta r} \]
\[
\frac{(2\pi r)\Delta rv}{\int_0^R 2\pi r dr} v = \frac{(2\pi r)\Delta rv}{\pi R^2 v_0/2}
\]

and \( v = L/t \)

Differentiating (1)

\[
-2rdr v_o/R^2 = -\frac{L}{t^2} dt
\]

Therefore,

\[
\int_0^t j'(t) dt = 1 - \frac{\tau^2}{4t^2}
\]

The tracer corresponding to the fluid element at the center of the tube will come out first.

Note: \( \tau = \frac{L}{v_o/2} \)

= Avg. residence time

Therefore, \( j(t) = \int_{\tau/2}^{t} j'(t) dt \)

Step Input:

Output:

Note:

\[
\begin{align*}
  t &= 0 \text{ for } CSTR \\
  &= \tau \text{ for } PFR \\
  &= \tau/2 \text{ for } LFR
\end{align*}
\]

when the first tracer comes out/ exits the reactor.
Plot all three together (qualitatively):

For LFR: 
\[ X = \int_{\tau/2}^{\infty} X(t)J'(t)\,dt \]

\[ = \int_{\tau/2}^{\infty} (1 - e^{-kt}) \frac{\tau^2}{2t^3} \,dt \]

Batch

1\textsuperscript{st} order

(no tracer until \(\tau/2\) for LFR) 

Similarly, conversions can be calculated for the other rate orders as well.

Two results (RTD segregated model and traditional species balance/performance equation) will give the same results. See more on this in the book 'Chemical & Catalytic Reaction Engineering' by James Carberry

H.W. (SMITH, 3\textsuperscript{rd} edition) 6.10
Lecture 07

Ex – 4:

Determine $\bar{X}$ and $\bar{\tau}$ ($k = 1 \text{ min}^{-1}$)

Ans: $\bar{X} = \int_0^\infty X(t)J'(t)dt$ : segregated reactor

$\bar{\tau} = \int_0^\infty tJ'(t)dt$ batch kinetics

$k = 1 \text{ min}^{-1} \Rightarrow it is a first order reaction$

$X(t) \equiv batch = 1 - e^{-kt} = 1 - e^{-t}; J'(t)$ to be determined from the table below; work on $t_{avg}$ and $C_{avg}$ for an improved numerical accuracy.

<table>
<thead>
<tr>
<th>$t$</th>
<th>$C$</th>
<th>$C_{avg}$</th>
<th>$t_{avg}$</th>
<th>$(C\Delta t)$</th>
<th>$J'(t)$</th>
<th>$X(t)$</th>
<th>$X(t)J'(t)\Delta t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>calculate</td>
<td>calculate</td>
<td>calculate</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>1.5</td>
<td>2.5</td>
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<td>calculate</td>
<td>calculate</td>
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<td>5</td>
<td>4</td>
<td>7.5</td>
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<td>calculate</td>
<td>calculate</td>
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</tr>
<tr>
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<td>5</td>
<td>5</td>
<td>12.5</td>
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<td>calculate</td>
<td>calculate</td>
<td>calculate</td>
</tr>
<tr>
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<td>4</td>
<td>4.5</td>
<td>17.5</td>
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<td>calculate</td>
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</tr>
<tr>
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<td>2</td>
<td>3</td>
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</tr>
<tr>
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<td>1.5</td>
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<td>calculate</td>
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<tr>
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<td>0</td>
<td>0.5</td>
<td>32.5</td>
<td>calculate</td>
<td>calculate</td>
<td>calculate</td>
<td>calculate</td>
</tr>
</tbody>
</table>

Recall: $\bar{X} = \int_0^\infty X(t)J'(t)dt$ holds good for segregated reactors. However, if the rate of reaction is $1^{st}$ order, the reactor can still be treated as a macro-reactor, and the expression holds good. Correct answers are 99.37% conversion and 15 min of average residence time. For the latter calculation, add one more column for $tJ'(t)\Delta t$ and add the row elements.
Ex 5: A 1st order reaction \( A \xrightarrow{k=2 \text{ min}^{-1}} R \) takes place in a non-ideal mixed reactor. Because of inadequate mixing, only 85% of the reactor volume is well mixed and has the mean residence time of 1 min. The RTD of the remaining 15% (in the corners and close to the walls) can be approximated by the following equation: \( J(\theta) = 1 - e^{-0.5\theta} \) \((0 \leq \theta \leq \infty)\)

**Determine:**
- a) The RTD of the reactor
- b) \( \tau \), and
- c) \( \bar{X} \)

**Ans:**

Note that 15% of CSTR volume also behaves as an ideal CSTR, as seen by the corresponding \( J(\theta) \)

\[
J(\theta) = \frac{Q_1 J_1(\theta) + Q_2 J_2(\theta)}{Q_1 + Q_2}
\]

\[
Q_1 = \frac{0.85V}{\tau_1} = 0.85V \quad ; \quad Q_2 = \frac{0.15V}{\tau_2} = 0.075V
\]

\[
J(\theta) = \frac{0.85(1-e^{-\theta}) + 0.075(1-e^{-0.5\theta})}{0.85 + 0.075} = \frac{0.925 - 0.85e^{-\theta} - 0.075e^{-0.5\theta}}{0.925}
\]

(a) \( J(\theta) = 1 - 0.92e^{-\theta} - 0.08e^{-0.5\theta} \)

(b) \( \tau = \frac{V}{Q} = \frac{V}{(0.85+0.075)V} = 1.08 \text{ min (def)} \)

**Alternatively,**

\[
\tau = \int_0^\infty \theta j(\theta) d\theta
\]

\[
= \int_0^\infty \theta(0.92e^{-\theta} + 0.04e^{-0.5\theta}) d\theta
\]

\[
= \left[ \theta \left( -0.92e^{-\theta} - \frac{0.04e^{-0.5\theta}}{0.5} \right) \right]_0^\infty + \int_0^\infty \left( 0.92e^{-\theta} - \frac{0.04e^{-0.5\theta}}{0.25} \right) d\theta
\]

\[
= 0 + \left[ -0.92e^{-\theta} - \frac{0.04e^{-0.5\theta}}{0.25} \right]_0^\infty = \left[ (0.92e^{-\theta} + 0.16e^{-0.5\theta}) \right]_0^\infty
\]

\[
= 0.92 + 0.16
\]

\[
= 1.08 \text{ min (same as before)}
\]
Ex 6: Coal particles are devolatized in a fast fluidized/moving bed reactor at 450°C, using N₂ gas. The average residence time of the well-mixed particles, \( \tau = 10 \) min. Initial volatile contents are 46% \( (W/W) \). The devolatization rate follows 1st order rate kinetics:

\[
\frac{dx}{dt} = -k(X - 0.2); \quad X \equiv mass fraction of volatiles.
\]

Determine \( \bar{X} \) (the average volatile content of the coal particles) at the reactor exit. Assume \( k = 1 \) min\(^{-1}\).

(Note: 20% of the volatiles never comes out.)
Ans: In such case (g/l + S reaction)/reactors, each particle can be considered to be segregated. There is no concentration distribution within a particle and particles do not mix with each other. The reactor can be considered to be macro or segregated reactor. Therefore,

\[
\bar{X} = \int_0^\infty X(t)f'(t)dt
\]

*(segregated model)*

Ans:

\[
J'(\theta) = \frac{1}{10} e^{-t/10}
\]

(ideal/well-mixed reactor)

\[
\bar{X} = \int_0^\infty (0.2 + 0.26e^{-kt}) x \frac{1}{10} e^{-t/10} dt
\]

\[
= \frac{1}{10} \int_0^\infty (0.2e^{-t/10} + 0.26e^{-1.1t}) dt
\]

\[
= \frac{1}{10} \left[ 0.2 \times 10e^{-t/10} \right]_0^\infty - \frac{0.26}{1.1} \times e^{-1.1t} \bigg|_0^\infty
\]

\[
= \frac{1}{10} \left[ 2 + \frac{0.26}{1.1} \right] = 0.223 \text{ (or 22.3%)}
\]

2) \[
\frac{dX}{dt} = -k (X - 0.2) \text{: batch kinetics}
\]

\[
l_n(X - 0.2)\bigg|_{X_0=0.46}^\bar{X} = -kt|_0^t
\]

\[
l_n\left(\frac{X - 0.2}{0.46 - 0.2}\right) = -kt
\]

\[
X = 0.20 + 0.26e^{-kt}
\]

(batch reactor)

\[
(\text{Note: } t = 0, X = 0.46)
\]

\[
t \to \infty, \ X \to 0.20
\]

HW: (SMITH, 3rd ed) \(\equiv\) 6.1, 6.2
Non-Segregated Model:

If there is mixing, the fluid elements lose their identities; they cannot be tracked.

$\rightarrow$ There are $J$ & $J'$ (RTDs) for a mixed reactor, but they cannot be used to determine conversion:

$$\bar{X} \neq \int X(t)J'(t)dt \quad (\neq \sum X(t)J'(t)\Delta t)$$

Ex:

or

But, they do not yield the same conversion, and one cannot use $\bar{X} \neq \int X(t)J'(t)dt$. \(1^{st}\) order reaction is an exception

⇒ All it means is that ‘RTD’ is not good enough/sufficient to characterize the performance of the non-segregated or mixed reactors, or determine the conversion. One also requires to quantify/determine the extent or rate of mixing, unlike the situation of macro-mixing in which case the segregated model uses only one parameter (RTD) to determine the conversion. Non-segregated model has two parameters: RTD and the extent of mixing (rate of mixing or where & when mixing takes place, or the actual path of mixing). In other words, we need additional details of mixing. Average residence or mixing time alone is not good enough \(1^{st}\) order reaction is an exception.

⇒ Mechanistically, in mixed (non-segregated) reactors the average time a fluid element spends in the reactor is equally important as the actual path and speed of the fluid element to determine the conversion. Two non-segregated or mixed reactors may have the same RTD but different extent (early or late) of mixing and therefore, different conversions \(1^{st}\) order reaction is an exception.

⇒ Re-visit the two configurations consisting of an ideal CSTR and an ideal PFR. In one configuration, there is an early mixing followed by late mixing; in the other late mixing is followed
by early mixing. From the kinetic rate \((order, n > 0)\) viewpoint, the first configuration represents the low-rate reactor followed by the high-rate reactor; the second configuration has the reverse situation. First-order reaction is an exception, discussed earlier. Therefore, an ideal CSTR reactor can still be treated as a segregated reactor for a 1\textsuperscript{st} order reaction and

\[
\bar{X} = \int X(t) f'(t) dt
\]

\(\text{batch reactor}
\)

⇒ There are two commonly used non-segregated models

a) Mixing Cells → two parameters: RTD and ‘n’ (# of ideal CSTRs in series)
b) Dispersion ⇒ two parameters: RTD and ‘\(P_e\)’ (or dispersion number)

In both models, the second parameter characterizes extent (early or late) of mixing or dispersion in the flow – direction. In the extreme situation, \(n = 1\) (ideal CSTR) and \(n \to \infty\) (large) (ideal PFR), or \(P_e \left(\frac{V/L_c}{D}\right) \to 0\) (ideal CSTR) and \(P_e \to \infty\) (large) (ideal PFR). A non-ideal or real reactor assumes an intermediate value for \(n\) or \(P_e\) (in-between ‘infinite’ and ‘zero’ dispersion), i.e. neither an ideal CSTR nor an ideal PFR.

a) **Mixing Cell Model:**

\[
\begin{align*}
V \quad A & \quad \equiv \quad \nu \quad \begin{array}{c}
C_o \\
\vdots \\
0 \\
\end{array} \\
1 & \quad 2 & \quad \ldots & \quad n & \quad \ldots & \quad N \\
\end{align*}
\]

Measure: 1) RTD of A (expt) \((V/N)\) \quad (Note: N = 1 for CSTR and \(\to \infty\) for PFR)

2) RTD of ‘N’ mix-reactors (analytical) \(1 < n < N\)

3) Determine ‘N’ by fitting the model with experimental data of the same RTD.

4) Qualitatively fit the data (an exact or statistical fitting is not required).

Species balance over ‘\(n\textsuperscript{th}\) reactor’

\[
v(C_{n-1} - C_n) = \left(\frac{V}{N}\right) \frac{dC_n}{dt}
\]

i.e. \(t = 0\), \(C_n = 0\) for all \(n_s\) (no tracer)

\(t = 0^+ \quad C_n = C_0 \quad (n = 0)\)

(inlet to the 1\textsuperscript{st} reactor)
Use Laplace transformation \( \mathcal{L}[C_n(t)] = \mathcal{C}(s) \)

\[
v(C_{n-1} - C_n) = \frac{V}{N} s \mathcal{C}_n \quad \text{(at the initial condition functional value is zero)}
\]

or \( \left( 1 + s \frac{\tau}{N} \right) \mathcal{C}_n - \mathcal{C}_{n-1} = 0 \quad \left( \tau = \frac{V}{v} \right) \)

\[
\mathcal{C}_1 = \frac{\mathcal{C}_0}{(1 + s \frac{\tau}{N})}
\]

\[
\mathcal{C}_2 = \frac{\mathcal{C}_1}{(1 + s \frac{\tau}{N})} = \frac{\mathcal{C}_0}{(1 + s \frac{\tau}{N})^2}
\]

\[
\mathcal{C}_n = \frac{\mathcal{C}_0}{(1 + s \frac{\tau}{N})^n}
\]

\[
\mathcal{C}_n(s) = \frac{\mathcal{C}_0}{(1 + s \frac{\tau}{N})^n} \Rightarrow C_n = \mathcal{L}^{-1} \left[ \frac{C_0 \left( \frac{N}{\tau} \right)^n}{s \left( s + \frac{N}{\tau} \right)} \right]
\]

\[
C_n = \mathcal{L}^{-1} \left[ \frac{C_0 \left( \frac{N}{\tau} \right)^n}{s \left( s + \frac{N}{\tau} \right)} \right]
\]

\[
J(t) \equiv \frac{C_n}{C_0} = 1 - e^{-\frac{Nt}{\tau}} \left[ 1 + \frac{Nt}{\tau} + \frac{1}{2!} \left( \frac{Nt}{\tau} \right)^2 + \cdots + \frac{1}{n-1!} \left( \frac{Nt}{\tau} \right)^{n-1} \right]
\]

See the textbooks and draw qualitatively but accurately:

Input:

\[
J(t) = \frac{C_n}{C_0}
\]

\[
Nt/\tau
\]

x \equiv \text{expt tracer data for the real reactor model lines = different values for } n."
(Also note that $J'(t) = d(J(t))/dt \equiv$ same as analytically derived)

**Model:** Non-ideal (mixed) reactor of volume $V \equiv N'$ ideal CSTR of volume $V/N$

Once ‘N’ is known, determine ‘X’ for ‘N’ ideal CSTR reactors (which have been discussed at the UG level).

$$
n, \quad C_0 \quad \rightarrow \quad \rightarrow \quad \rightarrow \quad \rightarrow \quad \rightarrow \quad A \rightarrow \text{Products}
$$

**Species balance (SS):**

$$(C_{n-1} - C_n) v = V / N (-vA')$$

$n = 0, \quad C_A = C_o$

1st order reaction,

$$C_{n-1} - C_n = k \frac{\tau}{N} C_n$$

$$\left[ \left(1 + \frac{k\tau}{N}\right) E - 1 \right] C_n = 0 \quad (E \text{ is the shift operator})$$

$$C_n = C_o \left( \frac{1}{1 + \frac{k\tau}{N}} \right)^n$$

$$\frac{C_o}{C_n} = \left(1 + \frac{k\tau}{N}\right)^n ; \quad C_N = C_o \left(1 - X_A\right)$$

For the 2nd or other order of reaction $\rightarrow$ use numerical technique.

**HW:** (SMITH, 3rd ed) $\equiv$ 6.3, 6.7, 6.15
(b) **Dispersion Model**

Non-ideality arises because of dispersion, implying local mixing along the flow direction, early or late. At high Reynolds numbers, there are turbulent flows and eddies. Also, there is a circulation of fluids in voids between packed bed materials, even at low Reynolds number.

The governing equation or model equation for dispersion is similar to that of molecular diffusion:

\[ J = -D_m \nabla C : \text{molecular diffusion (Fick’s 1\textsuperscript{st} law)} \]

\[ J = -D_L \nabla C : \text{dispersion} \]

axial dispersion coefficient

; no radial dispersion \( \left( \frac{\partial}{\partial r} = 0 \right) \)

\( D_L \) is the model parameter

**How to determine** \( D_L \)?

Species balance for ‘tracer’ (no reaction, transient experiment)

\[ \frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial z^2} - u \frac{\partial c}{\partial z} \quad \left( u \neq u(r) \right) \quad \text{like in PFR} \]

\[ t = 0 \quad C = 0 \quad (z \geq 0) \quad \text{(pure liquid)} \]
\[ t = 0^+, \quad z = 0, \quad uC_o = \left( uC - D_L \frac{\partial c}{\partial z} \right) \bigg|_{z=0^+} = L, \quad \frac{\partial c}{\partial z} = 0 \] (long tube – approximation)

(Note: \( D_L \equiv \) dispersion coefficient of tracer)

**Non-dimensionalize:**

\[ \phi = \frac{C}{C_o}, \quad \eta = \frac{z}{L}, \quad \bar{t} = \frac{t}{\tau}, \text{or} \quad t/L/u \]

\[ \frac{D_L}{uL} \frac{\partial^2 \phi}{\partial \eta^2} - \frac{\partial \phi}{\partial \bar{t}} = \frac{\partial \phi}{\partial \bar{t}} \]

i.e., \( \bar{t} = 0, \quad \phi = 0 \)

**Recall:** \( P_e (axial peclet \#) = \frac{uL}{D_L} \) (convection / dispersion)

\[ 1/P_e \frac{\partial \phi}{\partial \eta} = \phi - 1 \]

\[ \frac{D_L}{uL} \text{ is called dispersion \#) } \]

\[ 2 = 1 \quad \frac{\partial \phi}{\partial \eta} = 0 \]

(\( P_F R \))

In general, \( P_e > 10 : P_F R ; \quad < 1 : CSTR \)

**Solve to get \( C/C_o \) or \( \phi(t) \) or \( J(t) \) numerically:**

![RTD Diagram](image)
**Note:** Determine $P_e$ by fitting the RTD data with the model predictions. For small $D_L$, or large $P_e$ (not very large), analytical solutions are available.

\[
J(t) = \frac{1}{2} \left[ 1 - \text{erf} \left( \frac{1-t}{2\sqrt{P_e}} \right) \sqrt{P_e} \right]
\]

\[
(\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2} dx)
\]

\[
J'(t) = \frac{1}{2} \sqrt{\frac{P_e}{\pi}} \exp \left( -\frac{P_e}{4} (1-t)^2 \right)
\]

If you do a dose-experiment:

![Graph showing J'(t) for different P_e values](image)

**Note that in both cases (J or J'), the responses will be the same as before, i.e., in mixed tanks in series model.**

Once $P_e$ or $D_L$ is known, determine $\bar{X}$

\[
\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial z} = D_L \frac{\partial^2 c}{\partial z^2} + (-v_A r)
\]

**SS**

\[
D_L \frac{\partial^2 c}{\partial z^2} - u \frac{\partial c}{\partial z} + (-v_A r) = 0
\]

**BCs**

\[
z = 0 \quad uC_0 = \left( uC - D_L \frac{\partial c}{\partial z} \right) \bigg|_{z=0^+}
\]

($C = C_0$ if no gradient (mixing) on $z = 0^+$ side)

(A general interfacial boundary condition: \( uC - D_L \frac{\partial c}{\partial z} \bigg|_{z=-} = uC - D_L \frac{\partial c}{\partial z} \bigg|_{z=+} \))

At the exit, continuity in concentration:
\[ C_{L^-} = C_{L^+} \Rightarrow \left. \frac{\partial C}{\partial z} \right|_{L^-} = \left. \frac{\partial C}{\partial z} \right|_{L^+} = 0 \text{ (gradient is flat)} \]

On non-dimensionalization,

\[ \frac{1}{P_e} \frac{\partial^2 \phi}{\partial \eta^2} - \frac{1}{P_e} \frac{\partial \phi}{\partial \eta} = Ra \quad (Ra = \frac{-v_A}{b}) \]

**BCs**
\[ \eta = 0, \quad \frac{\partial \phi}{\partial \eta} \bigg|_{P_e} = \phi - 1 = 1, \quad \frac{\partial \phi}{\partial \eta} = 0 \]

For 1\textsuperscript{st} order reaction,

\[ \frac{C_f}{C_o} = \frac{4a \exp \left( \frac{P_e}{2} \right)}{(1 + a)^2 - (1 - a)^2 \exp \left( \frac{-aP_e}{2} \right)} \]

where, \( a = \sqrt{1 + \frac{4k\tau}{P_e}} \)

For the other reaction orders, numerical technique is required to solve the equation.

**In summary:**

1. Find \( J(t) \) for \( D_L \) or \( P_e \)
2. Determine \( X \left( 1 - \frac{C}{C_o} \right) \) from the performance equation.

**Note:**
1. Numerous empirical equations are available for packed bed reactors to determine \( D_L = D_L(R_e, Sc) \), or under turbulent flow conditions, \( P_{e,L} = P_{e,L}(R_e, Sc) \).
2. In a laminar flow there is no axial dispersion/"eddy".
Explain the 2nd phase in the above-ﬁgure: why does axial dispersion coefficient exceed molecular diffusion coefficient even if Re < 2100?

\[ D_L = D_m + \frac{u^2 d^2}{192 D_m} \] (not because of eddy but because of laminar flow profile)

\[ u_z = u_o \left( 1 - \frac{r^2}{R^2} \right) \]

Species balance:

\[ \frac{\partial c}{\partial t} + 2\overline{u} \left( 1 - \frac{r^2}{R^2} \right) \frac{\partial c}{\partial z} = D_m \frac{\partial^2 c}{\partial z^2} + \frac{D_m}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right); \quad R_e < 2100 \]

\[ t = 0 \quad c = 0 \]

\[ 0^+ \quad C = C_{in} \quad @ \quad z = 0 \]

\[ \frac{\partial c}{\partial z} = 0 \quad @ \quad z = L \]

\[ C(t,r,z) \quad \text{averaged over} \quad r,r' \rightarrow \overline{C}(t,z) \]

From 2D to 1D model:

It can be shown that

\[ \frac{\partial \overline{C}}{\partial t} + \overline{u} \frac{\partial \overline{C}}{\partial z} = D_L \frac{\partial^2 \overline{C}}{\partial z^2}; \quad \overline{C}(t,z) \]

where, \[ D_L = D_m + \frac{u^2 d^2}{192 D_m} \]

extra term arising out of 1D approximation

(See Dean’s book on Transport Phenomena)
RTD Study at a glance: It is an approach or a model to characterize or understand extent of mixing in a non-ideal continuous flow reactor, non-ideality arising out of either less than fully segregation or completely non-segregation. Thus, there are two model ideal reactors as far as the effect of mixing on reaction conversion is concerned: an ideal CSTR or an ideal PFR; all real reactors stand in between. Therefore, “ideal reactors” imply that different fluid elements or pockets or zones are either completely mixed, non-segregated, dispersed, micro-mixed, or earliest mixed like in a well-mixed CSTR, or completely un-mixed, segregated, zero-dispersed, macro-mixed or late mixed like in a PFR without diffusion and dispersion. RTD measurements (either step input or pulse input) can be used to characterize or describe the extent or state of mixing in a real (or non-ideal) reactor, with an objective of predicting or calculating reaction conversion at the exit of the reactor.

If you have enough evidence (experimental or intuition or experience) to judge that a real reactor under consideration is segregated like in an ideal PFR or laminar tubular flow reactor, or fast fluidized gas/liquid-solid reactors or (immiscible) liquid-liquid membrane or extraction systems, the RTD data will suffice to calculate the conversion, and the performance or design or model equation of such non-ideal reactors is based on the RTD data (one parameter only) and the batch kinetics. However, if there is some element or extent of mixing, the RTD measurements alone will not suffice to describe the extent of mixing in such non-ideal reactors, and additional information is required: “where do they (different pockets) mix and at what rate do they mix”. Thus, there are two popular models: “tank-in-series-model” with the number of ideal CSTRs as the model parameter and “Dispersion model” with peclet or dispersion number as the model parameter. Once the RTD and the model parameter are known, reaction conversion can be calculated for such non-ideal (non-segregated) reactors from the first principle (species balance equation). First-order reaction is an exception, and the RTD data (with batch kinetics) alone are enough to calculate or predict the conversion in non-segregated reactors.

H.W. (F&B, 2nd ed) = 12.5
Lecture 10

Catalysts and Catalytic reactions:

- What are catalysts? These are physical entities; show chemical/physical activities of deactivation, degradation, change in morphology, and have life-time.
- What do they do? Enhance (+ve)/retard (-ve) rate of reaction by participating at the molecular or electronic levels, yet preserving/restoring their initial activities.
- How do they do? Direct alternate path (route/step) of reaction that has a lower activation energy barrier:

1. The barrier has come down using catalyst
2. There are two barriers: forward & reverse reactions (E_1 & E_{-1})
3. H_1 & H_2 or ΔH is the same with/without catalyst

⇒ Catalyst enhances reaction rate or kinetics (k) of an elementary reaction without affecting thermodynamic properties including heat of reaction & equilibrium constant (K).

⇒ No reaction is truly irreversible.

⇒ ΔH can be +ve or -ve (endothermic or exothermic)
Note: in both cases |(E₁ − E₋₁)| = |(H₂ − H₁)| with/without catalyst.

- What are the features of a catalyst? large S/V, +ve or −ve, selectivity A → R; may or may not require support; may require promoters (K, Na); there are inhibitors (poisons) (Cs, S, Pb) as well.

- Classification (types) e.g.:
  
  Metal catalyst: \( C_2H_5OH^{Pt} \rightarrow C_2H_4O + H_2 \) (dehydrogenation)
  
  Acid catalyst: \( Si/Al \rightarrow C_2H_4 + H_2O \) (dehydration)

  Bi-functional catalyst

  Zeolites (catalytic reforming)

  Cage-like structure

- History of the catalysts?

  (1) First catalytic reaction (1875)

  \[ SO_2 + \frac{1}{2} O_2^{Pt} \rightarrow SO_3 \] (Contact process)

  \((V_2O_5 + K_2SO_4)\) supported on \( Al_2O_3/\text{SiO}_2 \)

  (2) \( NH_3 + O_2 \rightarrow NO, NO_2 \) (1903)

  \( NO + O_2 \rightarrow NO_2 \) (HNO₃ production)

  (3) \( N_2 + 3H_2 \rightarrow 2NH_3 \) (Haber – Bosch Reaction)

  (4) \( CO + H_2 \rightarrow CH_3OH \) (1923)

  (5) \( CO + H_2 \rightarrow C_2H_4 + H_2O \) (Fischer – Tropsch 1930)

  (synthetic fuels)

(6) Catalytic cracking (1937) in petroleum industry

  \( Al_2O_3/\text{SiO}_2 \): Refractory materials

  Zeolites (molecular sieves)
(7) Reforming: Butane $\rightarrow$ Isobutane (polymer, plastics) (1950)

$$Mo_2O_3/Al_2O_3$$

$$Pt/Al_2O_3$$

(8) Hydrocracking (1960) $\Rightarrow$ Shell
(catalyst mixed with $H_2$ to prevent formation or deposition on catalysts)

(9) Catalytic convertors (60 – 70°) in automobile exhaust
- Very complicated design (unsteady-state conditions of speed, temperature, species, no control)
- $CO + \frac{1}{2}O_2 \rightarrow CO_2$
- $C_XH_Y + \frac{1}{2}O_2 \rightarrow CO_2 + H_2O$  $Pt/Rh$ on $Al_2O_3/SiO_2$
- $2NO + O_2 \rightarrow 2NO_2$  $Bauxite$
- $(NO + CO \rightarrow CO_2 + N_2)$  $O_2$ disproportional reaction
- Modern vehicles have three-ways functional catalysts

**Mechanism (pathway):**

```
all of these involve several electron transfer steps, complex bonds formation
```

Electronic (sites are electronically active); geometrical theory (molecular dimensions/configuration)

Chemical theory (surface complex formation)

↓

underlying solid surface should accommodate $(A \rightarrow A^*)$

- All these different theories & mechanism to help us drive a rate expression for the viewpoint of designing the reactor:

$$r = f(T, C)$$

**Notes:**

1. *Revisit:* $r = \frac{1}{V_1} \frac{dN_i}{dt}$  $S = capacity$  $(A, W, V)$

2. *Collision* on molecular level.

(It is obvious that transport is not a right step)

3. *Unfortunately,* there are transport steps from gas to solid for reactant before reaction, and from solid to gas for products after reaction:

(Intuitively, the transport of $A$ or $P$ retards the overall rate of reaction)
4. Reaction may be isothermal or temp gradient may exist; can be exothermic or endothermic.

\[ A \xrightarrow{B} \text{Product} \]

- **Transport Steps**
  - **a.** Bulk transport of 'A' towards solids (convection, diffusion)
    \[ V \cdot \nabla C + D \nabla^2 C \]
  - **b.** Interphase transport (film transport)
    \[ k_m \]
    \[ B \ (\text{external surface}) \]
    \[ (A \text{ encounters diffusion resistances}) \]
    \[ k_m \Delta C (-D_m \nabla C) \]
  - **c.** Intraphase transport (within pores, pore diffusion)
    \[ (\text{reaction may take place parallel}) \]
    \[ D_{pore} \nabla^2 C \]

- **Surface Reaction**
  - (preceded and followed) by adsorption/desorption

- **First Step**
  - Surface intermediate/complex formation (several possibilities)
Lecture 11

Adsorption (1st step)/Desorption (last step):

(1) Langmuir model (1918)
Assumptions: - Maximum one layer or monolayer
- Uniform surface activity
- No interaction between adsorbing molecules
- Constant activation energy and heat of adsorption, wrt surface coverage, or \( \neq f(\theta) \)

\[
\frac{r_A}{s} = \frac{sp}{(2\pi mK_T)^{1/2}} \quad \text{(adsorption rate)}
\]

\[
s = \alpha(1 - \theta)e^{-E_a/RT}
\]

\[
0 \leq \theta \leq \frac{V}{V_m} \leq 1
\]

\[
p = \text{Partial pressure of adsorbate}
\]

\[
m = (\frac{Mw}{N})
\]

\[
K = \text{Boltzman constant}
\]

\[
\alpha = \text{sticking Coefficient}
\]

\[
\theta = \frac{V}{V_m}
\]

\[
E_a = \text{activation energy of adsorption}
\]

\[
V = \text{present amount, V}_m = \text{full amount to cover the surface}
\]

\[
r_a = k_a p (1 - \theta)
\]

\[
(k_a = k_{ao} e^{-E_a/RT})
\]

\[
r_d = k_d \theta (\text{desorption rate})
\]

\[
\Rightarrow \text{At equilibrium}
\]

\[
r_a = r_d
\]

\[
k_a p (1 - \theta) = k_d (\theta)
\]

\[
\theta = \frac{k_a / k_d p}{1 + k_a / k_d p}
\]

\[
(k_d = k_{do} e^{-E_d/RT})
\]

The model is good for chemisorption (one layer or monolayer)

Linearized form:

\[
\theta = \frac{V}{V_m} = \frac{Kp}{1 + Kp}
\]

\[
p = \frac{1}{V} \frac{1}{K V_m} + \frac{1}{V_m} p
\]

(fully occupied surface: \( \theta = 1 \Rightarrow V = V_m \))
No interactions between adjacent molecules:

\[ E, \Delta H \neq f(\theta) \]

(2) Brunauer, Emmett and Teller (1938)
BET isotherm

Assumptions
- Multilayer adsorption
- Energy of 1\textsuperscript{st} layer \neq \text{that of 2\textsuperscript{nd} layer}; \text{2\textsuperscript{nd} and the other layers have the same energy level.}
- We do not assume that 1\textsuperscript{st} layer is saturated & then 2\textsuperscript{nd} layer is formed
- Finite probability for sitting of one molecule on the vacant or occupied sites.

Isotherm: \[ \theta = \frac{V}{V_m} = \frac{cP}{(p_0-p)[1+(c-1)\frac{p}{p_0}]} \]

\( V = \text{Volume adsorbed}; V_m = \text{Volume adsorbed for one layer} \)
\( c = \text{parameter of model} \)

\[ = \frac{\text{(energy of the first layer)}}{\text{(energy of the other layers)}} = 1 \text{ if the layers have the same energy.} \]

\[ \frac{p}{V(p_o-p)} = \frac{1}{V_m c} + \frac{(c-1)p}{cV_m p_o} \]

If \( c \gg 1 \) \text{(very energetic surface)}
and \( p \ll p_o \)
\[ \theta = \frac{c(p/p_o)}{1 + (p/p_o)} \]
\[ = \frac{Kp}{1 + Kp} \text{ (identical to Langmuir model)} \]

\[ S = \frac{(c-1)}{cV_m} \]
(3) Temkin Model:

\[ r_d = k_a p \]

\[ \begin{cases} 
  r_d = k_d \theta = (k_d \theta \theta) \theta \\
  (E_d = E_{d0} - b \theta ; \ \theta \uparrow E_d \downarrow) \\
  = A \exp(b' \theta) \theta 
\end{cases} \]

At equilibrium, \( k_a p = A \exp(b' \theta) \theta \)

\[ \Rightarrow \theta \propto \ln(p) \]

Similarly, \( \Delta H(E_d - E_a) \propto f(\theta) = -\Delta H_m \ln \theta \) \( (1 > \theta > 0) \)

(Heat of adsorption is dependent on surface coverage)

\[ \theta \uparrow \Delta H \downarrow \]

(4) Freundlich (empirical)

\[ \theta = a p_a^m \]

(For multi-component adsorption \( \Rightarrow \) use Toth, Sips isotherms \( \Rightarrow \) see the book by DO ,1998)

Different types of isotherms:

Physical adsorption (Physisorption)                      Chemical adsorption (Chemisorption)

- No bond formation                                      - Bond formation
- Non-specific                                            - Specific
- Forces between adsorbed & adsorbate molecules are weak
  (Vander Waals forces)
- Heat of adsorption is small                             - Heat of adsorption is large
- Activation energy is low
- Can be low or high
- $T \uparrow$ amount of adsorbed molecules $\downarrow$
- $T \uparrow$ amount $\downarrow$ or $\uparrow$
- Coverage is multilayer
- monolayer
- Characterizes the surface
- Basic component of catalytic effect

**Fundamental mechanism of heterogeneous reaction:**

Rate equations: Langmuir – Hinshelwood model/Eley-Rideal model:

$$A + B \rightleftharpoons C + D$$

(Reaction only in the presence of catalyst; non-elementary reaction)

Elementary steps:

1) Adsorption
2) Surface-reaction
3) Desorption

L-H model assumes that the step (2) or surface reaction is the slowest or rate-determining step. Other possibilities also exist. See the book by Froment - Bischoff for details.

$$
\begin{align*}
A + X & \rightleftharpoons AX \\
B + X & \rightleftharpoons BX \\
AX + BX & \rightleftharpoons CX + DX : \\
CX & \rightleftharpoons C + X \\
DX & \rightleftharpoons D + X
\end{align*}
$$

Surface reaction/re – arrangement
(slowest; other steps are at equilibrium; they are fast enough to reach equilibrium and $r = 0$)
(Note that there is 'X' balance in all steps;
\[O_2 + 2X \rightleftharpoons 2OX\]
or, \[O_2 + X \rightleftharpoons O_2X\])

2) \[r = k_3(AX)(BX) - k_{-3}(CX)(DX)\] (rate determining step)

(Replace all \(AX, BX, \ldots\) etc in terms of major species A, B, C, D)

3) \[K_1 = \frac{(AX)}{(A)(X)}; \quad K_2 = \frac{(BX)}{(B)(X)}; \quad K_4 = \frac{(CX)}{(C)(X)}; \quad K_5 = \frac{(DX)}{(D)(X)}\]

(Note: \(K_4, K_5\) are defined in reverse manner to be consistent with reactions 1 & 2)

Substitute:

4) \[r = k_{-3}[K_1K_2K_3(A)(B) - K_4K_5(C)(D)]X^2\]

\(X\) is still unknown:

5) \[X + AX + BX + CX + DX = X_o\] (property of a catalyst)

\[\text{free} \quad \text{occupied} \quad \text{total}\]

\[X = \frac{X_o}{1 + \sum_i K_iC_i}\]

\[r = \frac{k_{-3}X_o^2[K_1K_2K_3(A)(B) - K_4K_5(C)(D)]}{(1 + \sum_i K_iC_i)^2}\]

**Note:** denominator term appears as the ‘inhibitor’ of the rate. It appears to decrease the rate.

Physically, A & B are adsorbed on the sites, occupying some of the sites, and therefore, inhibiting the reaction. Adsorption is an essential part of the reaction, but at the same time it decreases the rate.

If equilibrium, \(r = 0\)

\[\frac{(C)(D)}{(A)(B)} = K_{eq} = K_3 \frac{K_1K_2}{K_4K_5}\]

\(K_1 \ldots K_5\) are the equilibrium constants of the elementary steps

does not have physical or fundamental significance

(lumped parameter)

(Note: Any elementary reaction, even if it is not at equilibrium has an equilibrium constant. Therefore, \(K_3\) is well defined even if \(r\) in the step 2 is non-zero)

Note “\(r\)” can also be written as
\[ r = \frac{K_f(A)(B) - K_b(C)(D)}{(1 + \sum K_i C_i)^2} \]

Suppose \( \sum K_i C_i \ll 1 \)

\[ r \approx K_f(A)(B) - K_b(C)(D) \]

It appears as an elementary reaction with \( K_f \) & \( K_b \) as the forward & reversible rate constants, respectively! But \( K_f \) & \( K_b \) are lumped parameters, and cannot be written as \( K_f = K_{f_0} \exp(-\Delta H/RT) \), etc.

- These are the features of a catalytic reaction (non-elementary)
**Lecture 12**

**Ex. 1.** \(2CO + O_2 \xrightarrow{\text{catalyst}} 2CO_2\) (non-elementary! All catalytic reactions are non-elementary.)

**Propose a L-H type reaction mechanism**

Elementary steps:

1. \(CO + X \rightleftharpoons COX\) (molecules just sit on the surface; physical adsorption)
   \(O_2 + 2X \rightleftharpoons 2OX\) (chemisorption; \(O_2\) dissociates occupying two sites)
   \((O_2 + X \rightleftharpoons O_2 \cdot X) \leftarrow \text{it can also happen, which is physisorption}\)
   \(OX + COX \rightleftharpoons CO_2X + X\) (surface re-arrangement but ‘\(X\)’ is conserved)
   \(CO_2X \rightleftharpoons CO_2 + X\) (desorption)
   \(CO + \frac{1}{2} O_2 \rightarrow CO_2\) (overall reaction)

How? by multiplying the 2\(^{nd}\) step by ‘\(\frac{1}{2}\)’ and adding to eliminate all intermediates; stoichiometry/mass balance must hold good: \(\frac{1}{2}(O_2 + 2X \rightleftharpoons 2OX)\)

2. Assume that surface-re-arrangement/reaction controls, implying that the other steps are at equilibrium \((r = 0)\)

\[r = k_3(COX)(OX) - k_{-3}(CO_2X)(X)\]

\[\approx k_3(COX)(OX)\] (The reaction under consideration clearly indicates an approximately irreversible reaction/situation)

3. \(K_1 = \frac{(COX)}{(CO)(X)}\); \(K_2 = \frac{(OX)^2}{(O_2)(X)^2}\); \(K_4 = \frac{(CO_2X)}{(CO_2)(X)}\)

(Note \(K_3\) is also defined as \(\frac{k_3}{k_{-3}}\), because the step describes an elementary reaction, even if the step is assumed to be irreversible with a non-zero rate.)
\[(X)_o = (X) + (COX) + (OX) + (CO_2X)\) (sites are either free or occupied)

\[
\begin{align*}
r &= \frac{x_o^2 k_3 k_1 \sqrt{k_2(o_2)^2 CO}}{[1+\sqrt{k_2(o_2)^2 + k_4(CO) + k_4(CO_2)}]^2} \\
\end{align*}
\]

**Special Cases:**

1. \(O_2\) is in excess
2. weak \(CO_2\) adsorption (\(k_4\) is a small quantity; \([CO_2X]\) is small)

\[
\begin{align*}
r &= \frac{aCO}{(\beta + CO)^2} \\
\sqrt{\frac{CO}{r}} &= \sqrt{\frac{1}{\alpha}} (\beta + CO) \\
\end{align*}
\]

**Data:**

\| \(O_2\) | \(CO\) | \(CO_2\) | \(r\) \\
\hline
\(\checkmark\) | \(\checkmark\) | \(\checkmark\) | \(\checkmark\) \\
\(\checkmark\) | \(\checkmark\) | \(\checkmark\) | \(\checkmark\) \\

**Ex. 2.** The following reaction between NO and CO is important in controlling the emission of these air pollutants from IC engines:

\[2NO + 2CO \xrightarrow{Pt/Rh} 2CO_2 + N_2\]

- The reaction takes place on the Pt/Rh supported catalyst and follows the L-H mechanism. NO, CO and \(CO_2\) adsorb on the catalyst non-dissociatively; \(N_2\) adsorbs dissociatively.

- Derive the rate expression for the forward reaction
- What is the rate expression for the reverse reaction?

\[2CO_2 + N_2 \rightarrow 2NO + 2CO\]
Ans: As per the L-H model, the surface re-arrangement or reaction rate is controlling:

\[
\begin{align*}
\text{NO} + X & \rightleftharpoons \text{NOX} \\
\text{CO} + X & \rightleftharpoons \text{COX} \\
\text{NOX} + \text{COX} & \rightleftharpoons \text{CO}_2X + \text{NX} \\
\text{CO}_2X & \rightleftharpoons \text{CO}_2 + X \\
2\text{NX} & \rightleftharpoons \text{N}_2 + 2X
\end{align*}
\]

\[
[\text{NOX}] = K_1[\text{NO}][X] \\
[\text{COX}] = K_2[\text{CO}][X] \\
[\text{CO}_2X] = K_3[\text{CO}_2][X] \\
[\text{NX}]^2 = K_4[\text{N}_2][X]^2
\]

Site conservation equation:

\[
[X_0] = [X] + K_1[\text{NO}][X] + K_2[\text{CO}][X] + K_3[\text{CO}_2][X] + K_4^{1/2}[\text{N}_2]^{1/2}[X]
\]

\[
[X] = \frac{[X_0]}{1 + K_1[\text{NO}]+K_2[\text{CO}]+K_3[\text{CO}_2]+K_4^{1/2}[\text{N}_2]^{1/2}}
\]

Re-read the question “Determine the rate of the forward reaction: \(2\text{NO} + 2\text{CO} \rightarrow \text{CO}_2 + \text{N}_2\). The overall reaction is controlled by the surface arrangement step; the other steps are at equilibrium and do not contribute to the rate of reaction. Therefore,

\[
\dot{r}_{\text{forward}} = k_s[\text{NOX}][\text{COX}] = k_sK_2K_1[\text{NO}][\text{CO}][X]^2
\]

\[
= \frac{K_1K_2k_s[\text{NO}][\text{CO}][X_0]^2}{[1+K_1[\text{NO}]+K_2[\text{CO}]+K_3[\text{CO}_2]+K_4^{1/2}[\text{N}_2]^{1/2}]^2}
\]

\[
\dot{r}_{\text{reverse}} = k_{-s}[\text{CO}_2X][\text{NX}] = k_{-s}K_3K_4^{1/2}[\text{N}_2]^{1/2}[\text{CO}_2][X]^2
\]

\[
= \frac{k_{-s}K_3K_4^{1/2}[\text{N}_2]^{1/2}[\text{CO}_2][X_0]^2}{[1+K_1[\text{NO}]+K_2[\text{CO}]+K_3[\text{CO}_2]+K_4^{1/2}[\text{N}_2]^{1/2}]^2} \quad \text{(Note that the denominator has not changed)}
\]
What are the approximations you can make?

⇒ $CO_2$ adsorbs weakly: $K_3 \ll K_1, K_2, K_4$

$$r_{\text{forward}} = \frac{K_1 K_2 k_s [NO][CO][X_0]^2}{[1 + K_1 [NO] + K_2 [CO] + K_4^{1/2}[N_2]^{1/2}]^2} \quad \text{(Similarly for } r_{\text{reverse}})$$

⇒ $N_2$ adsorbs weakly? No. This may not be a good approximation.

⇒ $N_2$ adsorbs physically without dissociation. This is a possibility. Therefore,

$$N_2 X \rightleftharpoons N_2 + X \quad K_4 = \frac{[N_2 X]}{[N_2][X]}$$

In this case, re-do the calculation for $[X_0] = \cdots$

substitute to get $[X] = \frac{[X_0]}{1+\cdots}$

Thus, obtain a new rate expression for the reaction

⇒ Initial rates? These are often useful. Product concentrations, $(N_2), (CO_2) \ll (CO), (O_2)$. In such case, $r_{\text{forward or reverse}}$ can be approximated by neglecting the product terms in the denominator.

H.W. (F-B 2nd ed.): 2.1, 2.2(a), 2.3(a), 2.4, 2.7(a-b)
Characterization of a catalyst

(a) BET area, $m^2/g$

⇒ Measurement using a gas ($N_2$) ⇒ It gives the non-selective surface area.

e.g. Adsorbate on adsorbent

$N_2$ carbon, zeolites, Pt, Si/Al$_2$O$_3$

First determine the isotherm:

(1) **Static method**: The material is brought in contact with $N_2$ at different pressures but at a constant temperature. Determine the amounts of $N_2$ (moles or volume at STP) adsorbed at equilibrium at different pressures.

\[
T = \text{fixed}
\]

\[
P: \ P_{e_1} \rightarrow P_{e_2} \rightarrow \ldots
\]

\[
V: \ V_1 \rightarrow V_2 \rightarrow \ldots
\]

(2) **Dynamic Method**: (Shell development)

- A mixture of $N_2$ (adsorbing) and $He$ (non-adsorbing) gases of known composition is used. $P$ and $T$ are maintained constant. The gaseous mixture is allowed to flow or pass over/through the solid and reach an equilibrium. Difference between the thermal conductivity ($K$) of the exit (equilibrated) stream (mixture) and that of the inlet stream is measured. The compositions of the mixture are changed, keeping the total $P$ & $T$ constant. The experiment is repeated at the new partial pressures of $N_2$. Thermal conductivity of the mixture ($N_2 + He$) is calibrated wrt. its composition.
BET model (linearize):

\[ S = \frac{c-1}{cV_m} \; ; \; \quad I = \frac{1}{cV_m} \Rightarrow V_m = \frac{1}{I+S} \quad (STP) \]

\[ S_g \rightarrow \frac{V_m (cc,STP/gm)}{22400 (cc,STP/mole)} = \# \ of \ moles \ of \ N_2 \ required \ to \ saturate \]

\[ \rightarrow \frac{V_m \times N}{22400} \Rightarrow \left( \frac{V_m \times N}{22400} \right) \times \alpha \ (surface \ area \ occupied \ per \ molecule) \]

where, \( \alpha = 1.09 \left( \frac{M}{N\rho} \right)^{2/3} \rightarrow V = \frac{4}{3} \pi r^3 \}

\[ S = \pi r^2 \]

density of the condensed (liquid \( N_2 \)) phase

For \( N_2 \) at \(-195.8^\circ C, M = 28, \rho = 0.808 \text{ g/cc}, \alpha = 16.2 \text{ A}^2, N = 6.023 \times 10^{23} \]

\( \text{cm}^2 / g : \quad S_g (N_2) = 4.35 \times 10^4 \ V_m (cc/gm \ at \ STP) \)

Some examples (\( m^2 / g \)):

Activated clay: 150 - 220; SiO\(_2\)/Al\(_2\)O\(_3\) : 200 - 500; Silica gel: 200 - 600;

Activated Carbon: 500 - 1500; molecular sieves > 1000

Note: There are porous as well as non-porous silica gels.

(b) Porosity, density

( void fraction )

\[ \rho_g = \rho_s (1 - \varepsilon_g) \left\{ \begin{array}{l} \text{skeletal density, } \rho_s \text{ grain/particle density, } \rho_g \end{array} \right\} \]

\( \downarrow \)

grain (micro) porosity

\[ \rho_p = \rho_g (1 - \varepsilon_m) \left\{ \begin{array}{l} \text{powder/pellet density, } \rho_p \end{array} \right\} \]

\( \downarrow \)

powder/pellet/ macro – porosity

\[ \rho_b = \rho_p (1 - \varepsilon_b) \left\{ \begin{array}{l} \text{packed bed, } \rho_b \text{ density} \end{array} \right\} \]

\( \downarrow \)

packed bed porosity

(Note: grain is "one" powder; powder is plural!)
<table>
<thead>
<tr>
<th>Volume</th>
<th>Density</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_s$</td>
<td>$\rho_s$</td>
<td>$\epsilon_g$ or $\epsilon_{\mu}$</td>
</tr>
<tr>
<td>$V_g$</td>
<td>$\rho_g$</td>
<td>$\epsilon_m$</td>
</tr>
<tr>
<td>$V_p$</td>
<td>$\rho_p$</td>
<td>$\epsilon_b$</td>
</tr>
<tr>
<td>$V_b$</td>
<td>$\rho_b$</td>
<td></td>
</tr>
</tbody>
</table>

**Terminologies:**

- Non-porous (no porosity)
- Intra-particle
- Inter – particle
- Macro pores
- Micro pores
- Bed, powder
- Grain, Sub-grain
- Pores

**Note:** A pellet/powder may have both micro and macro porosities.

2. There is a hierarchical structure in the materials and packed bed reactors.
Measurements:

**Displacement method:** Mercury – Helium displacement

will not penetrate micro – pores

will penetrate all pores without adsorbing

Two extremer situations

measure displacement

‘one’ grain

\[ V_{Hg} - V_{He} = \text{pore volume} \]

\[ \epsilon_g = \frac{V_{Hg} - V_{He}}{V_{Hg}} \]

(c) **Pore size distribution (PSD)**

1. **Mercury-penetration method (Mercury porosimetry)**

   Non-wetting liquid

   - used for large pores (generally micron-size > 0.1 - 1 \( \mu \)m or 100 – 1000 nm)

   \( P \times \pi a^2 = -(2\pi a) l \cos \theta \)  

   pore – size \((a) = -\frac{2l \cos \theta}{P} \)  

   \[ a = \frac{8.75 \times 10^5}{P(\text{psi})} \text{ for Hg (} \theta = 140^\circ \text{ for Hg)} \]

   One ‘particle’ \(ightarrow\) otherwise Hg will penetrate the pores or voids between the grains (pores in powder), rather than ‘grain’ pores.
### Some calculations:

\[
a = 100\, \text{A}^\circ \text{ or } 10 \, \text{nm} \rightarrow \, P = 8750 \, \text{Psi/} \sim 500 \, \text{atm)  \\
= 1000\, \text{A}^\circ \text{ or } 100 \, \text{nm} \rightarrow P = 875 \, \text{Psi/} \sim 50 \, \text{atm)  \\
= 1 \, \mu\text{m} \quad \rightarrow \, P = 87.5 \, \text{Psi/} \sim 5 \, \text{atm}
\]

(The material of construction is a concern in such high pressure systems)
There is an IUPAC classification:

<table>
<thead>
<tr>
<th></th>
<th>micro</th>
<th>meso</th>
<th>macro</th>
</tr>
</thead>
<tbody>
<tr>
<td>size</td>
<td>50 Å</td>
<td>450 Å</td>
<td></td>
</tr>
<tr>
<td>(nm)</td>
<td>(5 nm)</td>
<td>(45 nm)</td>
<td></td>
</tr>
</tbody>
</table>

nanopores: < 2-3 nm

2. **Capillary condensation** (very small pores)  
   
   (micro – meso pores)

**Kelvin Effects:**

\[ P_{ads} = P_0 \exp \left( -\frac{\sigma V_1 \cos \theta}{RT(a-\delta)} \right) : \text{Kelvin equation (1)} \]

\[ P_{des} = P_0 \exp \left( -\frac{2\sigma V \cos \theta}{RT(a-\delta)} \right) : \text{Kelvin equation (2)} \]

\[ \delta(A^0) = 9.52 \left( \log \left( \frac{P_o}{P} \right) \right)^{-1/n} \]

\[ n = 1 \text{ for } N_2 \]

Pores already filled (wet); evaporation occurs from the top surface (desorption is axial)
Therefore, routes are different for filling & emptying, and there is a hysteresis

1. $P_{\text{des}} < P_{\text{ads}}$ for the same $V_{\text{ads/des}}$.
2. Also, 2 ways of doing experiment to determine $V(P): \text{ads/des}$.
   lower is ‘a’, lower is $P_{\text{ads}}$; first small sized pores will be filled in the low pressure to high pressure experiment. On the other hand, big size pores will desorb first in the high pressure to low pressure experiment.

Expt:

(d) $\text{Avg pore – size } (\bar{a})$

$$\bar{a} = \frac{2V_{\text{eg}}}{S}$$

$$S = 2\pi r L$$

$$V = \pi r^2 L$$

$$r = \frac{2V}{S}$$

(assuming cylindrical pores)
**Lecture 14**

**Material Characterization** (......continued)

**Example:** Al₂O₃ pellets: Mass = 3.15 g (per pellet)

Data: macro – pore volume = 0.205 cc/g  
*These data come from PSD analysis.*

- **a)** Density of the pellet = ?
  \[
  \rho_p = \frac{M}{V} = \frac{3.15}{\left(\frac{\pi d_p^2}{4} \times t\right) / 3.22} = \frac{3.15}{0.978} \text{ g/cc}
  \]
  
  - macro – volume

- **b)** Determine \( \epsilon_m \) (macro – porosity) = \( \frac{0.205 \text{ cc/g}}{1/\rho_p \text{ (cc/g)}} = 0.205 \times 0.978 = 0.2005 \)
  
  \( \text{total volume of pellet} \)

- **c)** Determine skeletal volume fraction = (Total volume – all pore volumes)/Total volume
  
  \( \epsilon_s = \frac{1/\rho_p - 0.205 - 0.4}{1/\rho_p} = \left(1 - \frac{0.205}{1/0.978} - \frac{0.4}{1/0.978}\right) - \epsilon_m - \epsilon_\mu \)

- **d)** Particle/grain density
  
  **Basis:** 1 cc of pellet:
  
  \( \rho_p \text{ (g/cc)} = \frac{\text{weight of pellet}}{\text{inclusion of grain (\mu) porosity or void}} \)

  \( \frac{0.978}{1-0.2005} \text{ g/cc} \)

(Note: Assume that there is no binder, and pellet is prepared by press-fitting)
Or, it can also be calculated: 

\[
\frac{3.15}{(3.22 - 0.2005 \times 3.22)}
\]

e) skeleton (solid) density = \[
\frac{0.978}{(1 - \varepsilon_m - \varepsilon_\mu)} = 2.39 \text{ g/cc}
\]

or

\[
\left(\frac{3.15}{3.22 - 3.22 \times (\varepsilon_m + \varepsilon_\mu)}\right) \text{ or } \frac{\text{mass of pellet}}{(\text{volume of pellet}) \times \varepsilon_s} = \frac{0.978}{0.4083}
\]

(c) Diffusion coefficient in pores

Mechanism of diffusion:

1. Bulk-phase diffusion (resistance is because of collision between the molecules) (molecules will experience intermolecular forces)

\[
D_{AB} = \frac{1}{3} \bar{V} \lambda
\]

(mean – free path)

linear velocity of molecules

\[
= \frac{\alpha T^{3/2}}{P(M_{avg})^{1/2}} : \text{ Chapman – Enskog equation}
\]

\[
\left(\frac{1}{M_{avg}} = \frac{1}{M_A} + \frac{1}{M_B}\right)
\]

2. Knudsen diffusion (porous media)

(Resistance is only from walls)

\[
D_K = \frac{2}{3} a \bar{V}
\]

\[
\text{cm}^2/\text{s} = 9700 a \sqrt{\frac{T(K)}{M_a}}
\]

\[(\text{cm})\]
If pore size $<<$ mean free path
or $a << \lambda$ particles will collide with walls before they colloid with themselves

$$D_K \ll D_{AB}$$

$$K_n (Knudsen \#) = \frac{\lambda}{a}$$

If $a \gg \lambda \Rightarrow D_{AB} \ll D_K$ (intermolecular collision is more prominent)

For gases at room temperature (?) and 1 atm

$$\lambda = 1000 A^0 \text{ or } 100 \text{ nm} \quad \text{and} \quad D_{AB} = \begin{cases} 0.11 & \text{to } 1 \text{ cm}^2/\text{s (gas)} \\ 10^{-5} & \text{in liquid} \\ 10^{-8} & \text{in solid} \end{cases}$$

(3) Surface diffusion ($\sim 10^{-10} \text{ cm}^2/\text{s}$)

$$D_S = A e^{-E_s/RT}$$

creeping/hopping mechanism

(4) Intra-lattice or intraege diffusion (solid may not have pores but cracks)

eg. $H_2$ purification by $Pd$ membrane.

- very slow and highly activated process

$$\approx 10^{-10} \text{ to } 10^{-15} \text{ cm}^2/\text{s}$$

(5) Combination of bulk and Knudsen diffusion

$$a \approx \lambda \left( \frac{1}{D_{comb}} = \frac{1}{D_K} + \frac{1}{D_{AB}} \right)$$

(both are important)

(a) Micro-dispersed pores: Use $D(\text{effective})$ or $D_e$

$$J_A = -D_{AB} \nabla C \quad \text{analogous} \Rightarrow J = -D_e \nabla C$$

$$D_e = \epsilon D_{\text{Comb}}$$

fraction (porosity) parallel pores

Pores may be tortuous

$$D_e = \frac{\epsilon D_{\text{Comb}}}{\tau}$$
tortuosity factor
\[ \tau \approx 1/\varepsilon \text{ (expt data)} \]

\[ D_e = \varepsilon^2 D_{comb} \]

(b) Bimodel pore size

\[ D_e = \overline{D}_m \varepsilon_m^2 + \frac{\varepsilon_{\mu}^2(1+3\varepsilon_m)}{1-\varepsilon_m} \overline{D}_{\mu} \]

\[ \frac{1}{\overline{D}_m} = \frac{1}{D_{AB}} + \frac{1}{(D_K)_m} \]

\[ \frac{1}{\overline{D}_{\mu}} = \frac{1}{D_{AB}} + \frac{1}{(D_K)_{\mu}} \]

(c) Random pore model:
- Peterson, AIChE (Vol 3.4(1957))

**Experimental:**

- **steady - state:**
  - \( \nu_A \) gas \( A \)
  - \( \Delta z \)
  - \( y_{A_1} \) porous solid
  - \( y_{A_2} \) detector
  - \( \nu_{N_2} \) (carrier gas)
  - (no reaction)
  - (measure \( A \) in \( N_2 \))

**Model pore – diffusion equation is similar to that of bulk - phase diffusion equation:**

\[ J = -D_{AB} \nabla C = -D_e \left( \frac{C_1 - C_2}{\Delta z} \right) \]

\[ N_A = -D_e \frac{dC}{dz} = -D_e \frac{P}{RT} \left( \frac{y_{A_2} - y_{A_1}}{\Delta z} \right) \text{ (flux)} \]

\[ = \nu_{N_2} C_A = \nu_{N_2} \frac{P}{RT} y_{A_2} \text{ (flux)} \]
Determine $D_e$ from the above-measurement/calculation

Determine $D_e$ from the above-measurement/calculation

Pulse:

![Diagram of pulse experiment]

$$D_e = \frac{(\Delta z)^2}{6} \varepsilon \int_0^\infty \frac{c_A}{C} t \, dt \quad (\text{cm}^2/\text{s})$$

Porosity in solids

\[ \Delta z \]

Unsteady-state experiment

$N_2$ → $gas$ → detection

\[ \frac{dC}{dt} = (\text{cm}^2/\text{s}) \]

\[ \text{If porous} \]

\[ C_A \]

\[ t \]

\[ \text{If no pores} \]

\[ C_A \]

\[ t \]

d. Effective thermal conductivity:

$$q = -\lambda \nabla T \quad q_e = -\lambda_e \nabla T$$

$$\lambda_e = \lambda_s \left( \frac{\lambda_f}{\lambda_s} \right)^\varepsilon$$

\( (10^{-4} - 10^{-5} \text{ cal/cm} - \text{s o c}) \)

Ref: Masamune & Smith

Ind Chem Eng Date 8, 54 (1963)

HW (Smith, 3rd ed): 8.1, 8.6, 8.7, 8.8

HW (F&B, 2nd ed): 3.2, 3.4
Example (1):

<table>
<thead>
<tr>
<th>liq. N₂:</th>
<th>P(kPa)</th>
<th>V (adsorbed amount, cc @ STP/g of sample)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.6</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>6.6</td>
<td>127</td>
</tr>
<tr>
<td></td>
<td>37.4</td>
<td>170</td>
</tr>
</tbody>
</table>

(a) Find Sg (m²/g) using Langmuir model
(b) Calculate $D_{eff}$ of N₂ in this sample at 100 °C.

Assume uniform pore size & $\epsilon = 0.5$. $D_k$ is dominant; $\rho_p = 1$ g/cc

Plot:

$\theta = \frac{V}{V_m} = \frac{KP}{1+KP}$

$P = \frac{1}{KV_m} + \frac{P}{V_m}$

(a) Use $S_g = (4.35 \times 10^4)V_m = 8050000$ cm²/g or 805 m²/g
(b) $\frac{1}{D_{comb}} = \frac{1}{D_{AB}} + \frac{1}{D_k} \Rightarrow D_{comb} \approx D_k$ (D_k dominates)

$D_k \left( \text{cm}^2/\text{s} \right) = 9700 \bar{a} \left( \text{cm} \right) \sqrt{\frac{T}{m_A}}$ ; $\bar{a} = \frac{2V_{pore}}{S_g} = \frac{2}{S_g} \times \frac{\epsilon_g}{\rho_g}$ (assuming cylindrical pores)

$\epsilon_g$ or $\epsilon_p$

$= 12.4 \, \text{Å} \, or \, 1.24 \, \text{nm}$

$\epsilon_g$ or $\epsilon_p$ particle or grain

$= 9700 \times 1.24 \times 10^{-7} \sqrt{\frac{373}{28}}$
\[ = 4.39 \times 10^{-3} \text{ cm}^2/\text{s} \]

\[ D_{eff} = \frac{\varepsilon D_{comb}}{\tau} = \varepsilon^2 D_{comb} = \varepsilon^2 D_k = 0.5^2 \times 4.39 \times 10^{-3} = 1.1 \times 10^{-3} \text{ cm}^2/\text{s} \]

**Example 2**

<table>
<thead>
<tr>
<th>( P(kP) )</th>
<th>0.8</th>
<th>3.3</th>
<th>18.7</th>
<th>30.7</th>
<th>38.0</th>
<th>42.7</th>
<th>57.3</th>
<th>67.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V(\text{cc at STP/gm}) )</td>
<td>6.1</td>
<td>12.7</td>
<td>17.0</td>
<td>19.7</td>
<td>21.5</td>
<td>23.0</td>
<td>27.7</td>
<td>33.5</td>
</tr>
</tbody>
</table>

(a) Plot BET isotherm (2) Find \( S_g \) using BET equation.

\[ \frac{P}{V(P_0-P)} = \frac{1}{V_mC} + \frac{(C-1)}{CV_m} \frac{P}{P_0} \]

\[ V_m = \frac{1}{I+S} = 13.69 \text{ cm}^3/\text{g} \]

\[ S_g = (4.35 \times 10^4) V_m = 600000 \text{ cm}^2/\text{g} \text{ or } 60 \text{ m}^2/\text{g} \]

(3) CO adsorption on Pt surface at 0\(^\circ\)C: How plots will change if you raise the temperature to 50\(^\circ\)C?
Non-porous catalyst (single particle analysis)

(Effect of interphase transport on reaction)

(intraphase transport is fast)

So far, 1. We developed the intrinsic rate expression, \( r = f(C,T) \) based on the (L-H) mechanism

2. Characterized the catalyst/material: \( d_p, \varepsilon: (\varepsilon_{\mu}, \varepsilon_{m}) \), BET area, \( \overline{a}, \rho: (\rho_{g}, \rho_{p}, \rho_b) \), \( D_K \)

(once again, be careful with the different nomenclatures or subscripts used in different books and manuscripts)

Next let us discuss (interphase transport + kinetics) under isothermal condition (one temperature in the reaction-system):

\[

\begin{align*}
\text{Step 1:} & \quad \text{bulk transport} \\
\text{isothermal} & \quad \text{A} \rightarrow \text{R} \\
\text{(moles/m}^3\text{)} & \quad (\vec{V}.\nabla C + D_{\text{disp}} \nabla^2 C) \\
\text{Step 2:} & \quad \text{Diffusion flux from bulk to the external surface} \\
& \quad J = k_m(C_b - C_s) \\
& \quad = -D \frac{dC}{dr} \bigg|_{r = r_p} \\
& \quad \text{(definition for } k_m) \\
& \quad \text{(non - dimensionalize to define Sherwood No)}
\end{align*}
\]

\[

\begin{align*}
\text{concentration of A near or at the surface, moles/m}^3\text{)} & \quad \neq C_s.X \text{ (adsorbed species, moles/m}^3\text{)}
\end{align*}
\]
R (heterogeneous rate, moles/s - m$^2$) = $k_m(C_b - C_s)$ (no local accumulation of reactant in the film)

= $R(C_s)$

= $k C_s$ (if 1$^{st}$ order)

$k_m = f(R_e, p, Sc)$

$\Rightarrow Sh = f(R_e, p, Sc)$

\[
\frac{k_m d_p}{D_m} = f \left( \frac{\nu_0 d_p \rho_f}{\mu_f} \right)
\]

Correlations for calculating $k_m$ are available for various scenarios (types of fluids, $R_e$, $Sc$, etc)

\[
J_D = \frac{k_m \rho}{G} (Sc)^{2/3} = f/2 \quad \text{(Colburn's analogy)}
\]

<table>
<thead>
<tr>
<th>$Re, p$</th>
<th>$\varepsilon$</th>
<th>$J_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt; 190$</td>
<td>0.37</td>
<td>$1.66(R_e, p)^{-0.51}$</td>
</tr>
<tr>
<td>$&gt; 190$</td>
<td></td>
<td>$0.983(R_e, p)^{-0.4}$</td>
</tr>
</tbody>
</table>

In general, $J_D(R_e, d_p, Sc, types of fluids, T)$

Non-isothermal:

\[
\text{moles/s - m}^2: \quad J_m = k_m(C_b - C_s) = R(C_s, T_s)
\]

\[
\text{cal/s - m}^2: \quad J_h = h(T_b - T_s) = R(C_s, T_s) \times \Delta H(T_s) / [k(T_s)]
\]

References are available to determine $h$ and $k_m$. 

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Isothermal $n^{th}$ order reaction with interphase transport

$A \rightarrow R:$

\[ r \equiv kC^n \left( \text{moles} / \text{s} - m^3 \text{ of cat} \right) \]

Note:
\[ r = k_s a C^n \quad \text{effect of 'a' (} \frac{a}{dp} \text{)} \]

or moles/s - $m^2$ of cat

or moles/s - g of cat

\[ = k_m a (C_b - C_s) \quad (1) \]

$m^2/m^3$ of catalyst volume

$C_s$ is unknown & must be substituted to determine rate of reaction. Reaction takes place at or near the surface-concentration level.

Define:

a) $R_b = \text{maximum rate} = kC_b^n (\text{No } \Delta C \text{ across the film})$  
\text{observed/apparent /global/true}

b) $\eta = \text{effectiveness factor} = \frac{R}{R_b}$  
\text{or rate at bulk conditions i.e. rate w/o external diffusion resistance}

c) $D_a = \text{Damkohler number} = \frac{(kC_b^{n-1})}{k_m a}$

(Definition of $D_a$ originates from the non-dimensionalization of equation (1) on substitution of $C_s$ (intermediate variable) using definition of $\eta$ in (b) above)

Let us revert to eq (1)

\[ k_m a \left( C_b - C_b \eta^{1/n} \right) = (kC_b^n) \eta \]

Non-dimensionalize/re-arrange:

\[ 1 - \eta^{1/n} = \left( \frac{kC_b^{n-1}}{k_m a} \right) \eta \]

\[ 1 - \eta^{1/n} = D_a \eta \quad \text{where, } D_a = \frac{kC_b^{n-1}}{k_m a} \]
Note: $D_a$ is large, $>>1$; transport or diffusion step controls (slow) and kinetics is fast.

$D_a \ll 1 \Rightarrow$ kinetic controlled (slow) or diffusion rate is fast.

Or $D_a \eta + \eta^{1/n} - 1 = 0$; $0 \leq D_a \leq \infty$

Plot:

One can also write:

$$\eta = (1 - \eta D_a)^n$$

Concentration profiles:

$$(r = kC^n; \ A \rightarrow R)$$

Note: If $R_e \uparrow k_m a \uparrow \Delta C \downarrow C_s \rightarrow C_b$ $r \uparrow$ and $r \rightarrow kC_b^n$} $D_a \downarrow \eta \rightarrow 1 C_s \rightarrow C_b$ or $r \rightarrow kC_b^n$.}
Lecture 16

Special Cases (continued...)

1st order \( R' = k_m a(C_b - C_s) = kC_s \) (moles/s – m³)

\[ \quad = K_p C_b \] (Definition of overall mass transfer coefficient)

Therefore,

\[ \frac{1}{K_p} = \frac{1}{k_m a} + \frac{1}{k_m} \]

\[ K_p = \frac{ak_m}{ak_m + k} = \frac{ak_m A e^{-E/RT}}{ak_m + A e^{-E/RT}} = A' e^{-E'/RT} \]

(Note: \( k_m \) has a weak dependence on \( T \))

If \( k_m a > k \), \( K_p = k \); \( R \equiv \) kinetic controlled (interphase diffusion is fast) = \( \overline{kC_b} \)

In other words, \( C_b - C_s \approx 0 \) (No \( \Delta C' \) or concentration drop)

\[ C_s \rightarrow C_b \]

If \( k_m a < k \), \( K_p = k_m a \); \( R \equiv \) diffusion controlled (kinetic is fast) = \( \overline{k_m a C_b} \)

\[ C_s \rightarrow 0 \quad \text{or} \quad C_b - C_s \approx C_b \]

Thus, the effects (mass transfer vis a vis kinetics) earlier explained through \( D_o \) have now been explained using or defining \( K_p \).
Temp - dependence:

\[ \ln(K_p) \quad (\text{expt}) \]

\[ \text{High } T \quad (\text{diff. controlled}) \]
\[ E_{\text{app}} \sim 0 \]
\[ (\text{weak dependence}) \]

\[ \text{Low } T \quad (\text{kinetic controlled}) \]

\[ \text{linear (slope } = -\frac{E}{R}) \]
\[ \sim \text{true activation energy} \]

\[ \frac{1}{T} \]

**Non-isothermal + interphase transport**

\[ (\delta_m, \delta_h) \equiv \text{different } (\delta_m = \delta_m(R_e, Sc), \delta_h = \delta_h(R_e, Pr)) \]

Mass – transfer always hurts the rate

\[ C_s < C_b \]

Heat – transfer may or may not hurt the rate

\[ T_s > T_b \quad (\text{exothermic}): \text{heat transfer helps rate} \]

\[ T_s < T_b \quad (\text{endothermic}): \text{heat transfer hurts rate} \]

**n^{th} order reaction rate**

\[ R = k_m\alpha(C_b - C_s) = k_sC_s^n \quad (\text{moles}/s - m^3 \text{of catalyst}) \]

\[ \eta \quad (\text{definition}) = \frac{R_{\text{obs}}/R_{\text{global}}}{R_b} = \frac{k_sC_s^n}{k_bC_b^n} = \left( \frac{k_s}{k_b} \right) \left( \frac{C_s}{C_b} \right)^n \]

\[ \text{based on bulk condition (without diffusion)} \]
On substitution,

\[ k_m a C_b \left[ 1 - \left( \frac{k_b \eta}{k_s} \right)^{1/n} \right] = \eta k_b C_b^n \quad (C_s \text{ is substituted in terms of } C_b) \]

\[ \Rightarrow 1 - \left( \frac{k_b}{k_s} \eta \right)^{1/n} = \eta \left( \frac{k_b C_b^{n-1}}{k_m a} \right) \]

\[ \eta = \frac{k_s}{k_b} (1 - \eta D_a)^n = (1 - \eta D_a)^n \exp \left( -\frac{E}{RT_b} \frac{T_b}{T_s} - 1 \right) \]

**Note:** If isothermal, \( T_s = T_b \), the equation is reduced to the isothermal case.

To determine \( \left( \frac{k_s}{k_b} \right) \) \( (k_s(T_s) \text{ is unknown}), \) energy balance equation:

\[ R (+\Delta H) = h a (T_b - T_s): \quad \text{energy balance} \left( \frac{\text{cal}}{\text{S} - \text{m}^3 \text{ of catalyst}} \right) \]

\[ \text{moles/} \text{S} - \text{m}^3 \quad \text{cal/moles} \quad \text{m}^2/\text{m}^3 \quad \text{cal/} \text{m}^2 - \text{S} - K \]

\[ R = k_m a (C_b - C_s) \]

substitute, \( \frac{T_s - T_b}{T_b} = \frac{C_b - C_s}{C_b} \times \frac{k_m (-\Delta H) C_b}{hT_b} \]

\[ \quad \rightarrow \text{heat production rate} \]

\[ \quad \rightarrow \text{heat dissipation rate} \]

Define \( \beta \) (*Prater #; measurement of isothermality*)

Therefore, \( \left( \frac{T_s}{T_b} - 1 \right) = \left( 1 - \frac{C_s}{C_b} \right) \beta \)

or, \( \frac{T_b}{T_s} = \frac{1}{\frac{1}{1 + \left(1 - \frac{C_s}{C_b} \right) \beta}} \)

It can be shown that \( \frac{T_b}{T_s} = \frac{1}{\frac{1}{1 + \beta D \eta}} \) (try yourself as a homework)
\[
\eta = (1 - \eta D_a)^n \exp \left( -\frac{E}{RT_b} \left( \frac{1}{1 + \beta D_a \eta} - 1 \right) \right)
\]

Note: \( \eta = \eta(n, D_a, \beta, \frac{E}{RT_b}) \)  

Arrhenius #

Compare to \( \eta_{isothermal} = \eta(n, D_a) \) (\( \beta = 0 \))

In either case (isothermal or non-isothermal), you are interested in calculating \( R_{obs} \) by determining rate based on bulk conditions and then correcting or modifying it with the effectiveness factor as \( R_{obs} = \eta R_b \)

**Catalyst Operation**

\[ \Delta H - ve \]
\[ \beta > 0 \text{ (exothermic)} \]

Both mass & heat transport help reaction rate

\[ \eta < 0 \]

Process is kinetic controlled (mass transfer coefficient is large)

\[ n < 0 \]

Reaction rate is hurt by drop in \( C_s \) at high \( D_a \)

\[ n = 1/2 \]

\[ n = 1 \]

\[ n = 2 \]

\[ T_s > T_b \]

\[ C_b \]

\[ C_s < C_b \]

\[ n > 0 \]

Best Operation: maximum rate  
(Some diffusion is preferred or desirable!)

\[ \eta_a D_a \]

- \( \eta \) indicates how effective the catalyst is relative to the bulk conditions
- For isothermal operation \( D_a < < 1 \) to get \( \eta = 1 \) (\( n > 0 \))
- For non-isothermal condition, operate at same intermediate \( D_a \) (bring some diffusion resistance!) to get \( \eta > 1 \).
How about endothermic reaction? $\beta < 0$ ($\Delta H; +ve$): Not interesting (results are straightforward);

Some more analysis:

$$\eta = \eta(D_a, n, \beta, \epsilon)$$

$$\frac{-\Delta T}{T_b} = \frac{\Delta C}{C_b} \beta$$  \text{(Recall)}

How to find $\beta$?

$$\beta = \frac{k_m(-\Delta H)C_b}{hT_b} \quad (C_b, T_b \text{ are known, } \Delta H \text{ is a thermodynamic property, }$$

$$k_m, h \Rightarrow k_m(Sh), h(Nu): \text{easy to calculate}$$

$$= \frac{-\Delta H C_b}{\rho C_p T_b} \frac{k_m}{h/\rho C_p}$$

$$J_D = \frac{k_m P}{G \left(\frac{\nu}{D}\right)^{2/3}} \quad ; \quad J_H = \frac{h}{G C_p \left(\frac{\nu}{\alpha}\right)^{2/3}}$$  \text{(Refer BSL for analogy between heat & mass transport)}

Take the ratio:

$$\frac{k_m}{h/\rho C_p} = \frac{J_D}{J_H} \left(\frac{\nu}{D}\right)^{2/3} \left(\frac{L_e}{\alpha} = \frac{\alpha}{D} = \text{Lewis #}\right)$$

Therefore, $\beta = \frac{(-\Delta H)C_b}{\rho C_p T_b} \left(\frac{J_D}{J_H}\right)^{-2/3} \quad : \text{Damkohler equation}$

$(J_D, J_H \equiv \text{there are correlations reported in the literature})$

For many practical cases ($\text{high } R_e$): $J_D = J_H = \frac{f}{2}$

Therefore, $\beta = \frac{(-\Delta H)C_b}{\rho C_p T_b}$ \quad \text{($Pr \sim 1 - 1000$)}

and $\left(\frac{T_s-T_b}{C_b-C_s}\right) = -\frac{\Delta H}{\rho C_p}$ (thus simplified)

**HW (SMITH, 3rd ed): 10.3, 10.5**
Lecture 17

Non-porous catalyst (interphase + reaction)

-----continued

Different cases (non-isothermal):

\[ \eta = \left( \frac{k_s}{k_b} \right) \left( \frac{C_s}{C_b} \right)^n \]

(1) \( \beta > 0 \) and \( n < 0 \) \( \Rightarrow \) \( \eta > 1 \) : \( R_{\text{heat}} \uparrow \) \( R_{\text{mass}} \uparrow \)

(2) \( \beta > 0 \) and \( n > 0 \) \( \Rightarrow \) \( \eta > 1 \) or \( \eta < 1 \) depending upon \( D_a : R_H \uparrow R_m \downarrow \)

(3) \( \beta < 0 \) and \( n > 0 \) \( \Rightarrow \) \( \eta < 1 \) : \( R_H \downarrow R_m \downarrow \)

(4) \( \beta < 0 \) and \( n < 0 \) \( \Rightarrow \) \( \eta > 1 \) or \( \eta < 1 \) : \( R_H \downarrow R_m \uparrow \)

**Special Cases:** Non-isothermal (1st order)

**Mass Flux:** \( \frac{\text{moles}}{s \cdot m^2} \) \( r = k_m (C_b - C_s) = k_s C_s \)

\( \frac{\text{moles}}{s \cdot m^3} \) \( R = k_m a(C_b - C_s) = a k_s C_s = k_s' C_s \)

Therefore,

\[ C_s = \left( \frac{k_m}{k_m + k_s} \right) C_b \]

\[ R = \left( \frac{a k_s k_m}{k_m + k_s} \right) C_b \] (same as before, i.e. isothermal condition)
Heat Transport:

\[
\begin{align*}
Q_{\text{reaction/generation}} &= R (-\Delta H) \quad \text{mole/s} - \text{m}^3 \text{cal/s/mole} \\
Q_{\text{transferred/removed}} &= ah(T_s - T_b) \quad \text{cal/s} - k - m^2
\end{align*}
\]

or, \( Q_{\text{reaction}} = \left( \frac{-\Delta H a k_m k_s}{k_m + k_s} \right) C_b \equiv \left[ \frac{(-\Delta H)a C_b}{1 + \frac{1}{k_m} \exp\left(\frac{-E}{RT_s}\right)} \right] \text{cal/s/m}^3
\]

**SS solution**

Investigate under SS:
- Multiplicity (3 solutions)
  - cold/hot/unstable solutions
- Mass transport:
  - weak/linear dependence on \( T \)
- Heat transport (reaction):
  - Exponential dependence

**Recall:** Similar situation in the exothermic CSTR operation: instability is an issue
Example 1: A well-mixed basket type reactor is used for carrying out the reaction $A \rightarrow P$ over a non-porous catalyst under constant flow-condition. The following data are available:

<table>
<thead>
<tr>
<th>$d_p$</th>
<th>W</th>
<th>$X_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2</td>
<td>0.6</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>0.2</td>
</tr>
</tbody>
</table>

What controls the reaction? Interphase transport or kinetic rate?

Ans: Write down the species balance equation across the reactor.

$$
\frac{moles}{s}: \quad (-r)_{obs} W = v_o C_{Ao} X_A \quad C_A = C_{Ao}(1 - X_A)
$$

$$
\frac{moles}{S - gm} \quad (v_o C_{Ao} - v_o C_A)
$$

$$
(-r)_{obs} = \frac{v_o C_{Ao} X_A}{W}
$$

$$
\frac{(-r)_{obs,1}}{(-r)_{obs,2}} = \left( \frac{X_A}{W} \right)_1 \times \left( \frac{W}{X_A} \right)_2 = \frac{0.6}{2} \times \frac{1}{0.2} = \frac{3}{2} \quad \text{(from the measurements)}
$$

Recall: If external mass transfer/interphase rate controls or kinetics is fast

$$
r_{obs} = k_m a C_b \quad (C_S \rightarrow 0)
$$

$$
\frac{(r_{obs})_1}{(r_{obs})_2} = \frac{a_1 (1-X_A)_1}{a_2 (1-X_A)_2} = \frac{dp_2 (1-X_A)_1}{dp_1 (1-X_A)_2} = \frac{6}{2} \times \frac{0.4}{0.8} = \frac{3}{2} \quad \left( a = \frac{\sigma}{dp} \right)
$$

(Assume $k_{m1} = k_{m2}$ under two conditions) $m^2/m^3$

Ans: Interphase mass transfer controls
Alternatively, recall definition of overall mass transfer coefficient
\[
\begin{align*}
\left( \frac{r_{\text{obs}}_1}{r_{\text{obs}}_2} \right) & = \frac{K_p_1}{K_p_2} \left( \frac{C_b_1}{C_b_2} \right) = \frac{K_p_1 C_A_0 (1-X_1)}{K_p_2 C_A_0 (1-X_2)} = 3 \times \frac{0.4}{0.8} = \frac{3}{2} \\
\end{align*}
\]
Ans: (Interphase mass transfer controls)

**Example 2:**  
*Reaction:* \( \text{SO}_2 + \frac{1}{2} \text{O}_2 \stackrel{\text{cat}}{\rightarrow} \text{SO}_3 \)  
*Smith 10.1*  

\[
\begin{align*}
\text{SO}_2 & = 6.42\% \\
\text{Air} & = 93.50\% \\
G & = 0.199 \text{ kg/m}^2 \cdot \text{s} \\
\end{align*}
\]

\[
\text{Conditions} \\
\begin{align*}
P & = 790 \text{ mm Hg} \\
T & = 480^\circ \text{C} \\
\text{nonporous Al}_2\text{O}_3 \text{ catalyst} \\
& \left( \frac{1}{8}'' \times \frac{1}{8}'' \right \text{ cylindrical} \\
& \text{pellets, } \rho = 950 \text{ kg/m}^3 \\
& \epsilon_b = 0.43 \\
& \text{Assume } Sc = 1.2 \\
& \rho(\text{air}) = 0.487 \text{ kg/m}^3 \\
& \mu(\text{air}) = 3.72 \times 10^{-5} \text{ Pa s} \\
\end{align*}
\]

**Data:**

<table>
<thead>
<tr>
<th>( X_{\text{SO}_2} )</th>
<th>( r \left( \frac{\text{g moles } \text{SO}_2}{\text{h-g of cat}} \right) )</th>
<th>( p_b, \text{ atm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.0956</td>
<td>\text{SO}_2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0603</td>
</tr>
<tr>
<td></td>
<td></td>
<td>\text{SO}_3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0067</td>
</tr>
<tr>
<td></td>
<td></td>
<td>\text{O}_2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.201</td>
</tr>
</tbody>
</table>

Determine \((C_b - C_s) \text{ or } (p_b - p_s) \text{ or } \frac{(p_b - p_s)}{p_b}\)

Ans: \( r_{\text{obs}} = k_m a (C_b - C_s) \text{ moles/s m}^3 \)

\[
(= k C_s^n )
\]
Determine \( dp \) first for the pellet: \[
\pi dp^2 = \pi dL + \frac{2\pi d^2}{4} (sphere) + \frac{2\pi d^2}{4} (cylinder)
\]

\( dp = 0.0039 \text{ m} \rightarrow Re = \frac{dp G}{\mu} = 21, \ Sc = 1.2, \ a = \frac{6}{dp} = 1538 \text{ m}^{-1} \)

Recall: Definition for \( J_D = St \ Sc^{2/3} = \frac{k_m \rho}{G} \left( \frac{\mu}{\rho D} \right)^{2/3} \)

\[
= \frac{0.458}{e_b} \ Re_p^{-0.407} \text{ (from correlation)} = 0.31
\]

Calculate \( k_m \) from here: \[0.31 \times \frac{0.199}{1.2^{2/3} \times 0.487} = 0.112 \text{ m/s}\]

Therefore,

\[
(C_b - C_s) = \frac{r_{obs}}{k_m a} = \frac{0.956/3600 \times 950}{0.112 \times 1538} = 1.46 \times 10^{-4} \text{ kg mol/m}^3
\]

\[
(p_b - p_s)_{SO_2} = RT(C_b - C_s) = 0.009 \text{ atm}
\]

\[
(p_b - p_s)_{SO_2}/p_{b,SO_2} = 15\% \text{ (large interphase diffusion resistance)}
\]

Example 3: A liquid phase oxidation reaction is carried out over non-porous spherical catalyst particles (\( W = 500 \text{ g} \)) in a well-mixed basket type of reactor. Some oxidation also takes place over the inner walls (\( A = 0.1 \text{ m}^2 \)) of the reactor. The following kinetic and transport conditions are known:

<table>
<thead>
<tr>
<th>Intrinsic rate</th>
<th>Da</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst particles: 1.0C moles/min-kg</td>
<td>1</td>
</tr>
<tr>
<td>Inner walls of reactor: 1.0C moles/min-m²</td>
<td>2</td>
</tr>
</tbody>
</table>

Determine the exit conversion of the reactant if the volumetric flowrate of the reacting mixture is 0.5 m³/min.

Try this example yourself. The answer is 36%. First, write down the species balance equation for the reactor. Then, you can use either of “two methods/approaches” to solve this problem. One is to use effectiveness factor, and the other is to use \( C_s \). You should get the same result, i.e., 36%.
**Lecture 18**

**Porous Catalyst (intraphase transport + kinetics)**

\( A \rightarrow R \)

- **Interphase transport is fast**

(Assume \( n^{\text{th}} \) order) \( C_s \rightarrow C_b \) \((k_m \alpha \uparrow)\) (the surface sees the bulk phase concentration)

- Reaction occurs within the material as the reacting species ‘A’ diffuses inside the pores.

\[
\begin{align*}
\text{Isothermal case} \\
\text{Take a CV (}4\pi r^2 \Delta r\text{) between } r \text{ and } r + \Delta r : \\
\text{Species balance:} \\
\frac{\partial C_A}{\partial t} + \nabla \cdot \nabla C_A \equiv D_{\text{eff}} \nabla^2 C_A - k C_A^n
\end{align*}
\]

\[

\Rightarrow \quad D_{\text{eff}} \nabla^2 C_A = k C_A^n \quad \text{(moles/s \text{- m}^3)} \\
\quad (0 \leq r \leq r_o)
\]

\[
\frac{D_{\text{eff}}}{r^2} \frac{d}{dr} \left( r^2 \frac{dC_A}{dr} \right) = k C_A^n
\]

\[
\text{Bc 1} \quad r = 0, \quad \frac{dC_A}{dr} = 0 \quad (\text{symmetric BC})
\]

\[
2 \quad r = r_o, \quad C_A = C_{A,b} \quad (C_A |_{r=r_o} = C_b)
\]
Non-dimensionalize:

\[ z = \frac{r}{L} \quad \text{&} \quad f = \frac{C_A}{C_A b} \]

\[ L = \text{characteristic length} \]
\[ = \frac{1}{a} = \frac{r_o}{3} \quad \text{(sphere)} \]

(m²/m³)

Substitute,

\[ \frac{D_{eff} C_{A b}}{L^2} \nabla^2 f = kf^n C_{A b}^n \]

\[ \nabla^2 f = \frac{L^2 k}{D_e} C_{A b}^{n-1} f^n \]

\[ \nabla^2 f = \phi^2 f^n \quad \text{;} \quad \phi \equiv \text{Thiele modulus} = L \sqrt{\frac{k C_{A b}^{n-1}}{D_e}} \]

**BCs.**

\[ z = 0 \quad \nabla f = 0 \quad \text{(symmetry)} \]

\[ z = 3 \quad f = 1 \quad \text{(surface)} \]

1. \[ \phi \equiv \frac{\text{kinetic rate}}{\text{mass transfer rate}} = \frac{R_{obs/global/apparent}}{R_b} \leq 1 \text{ for } + \text{ve order} \]

2. \[ \eta = \text{effectiveness factor} = \frac{R_{obs}}{R_b} \]

where, \( R_b = \text{rate w/o diffusion (max at the surface)} \)

\[ R_{obs} = \eta (k C_{A b}^n) \Rightarrow \eta_{\text{intra}} = \eta (\phi, n) \quad \text{compare to } \eta_{\text{inter}} = \eta (D_a, n) \]

- First solve the equation (numerically) ⇒ \( f(z) \text{ or } C_A(r) \)
- Calculate ‘\( R_{obs}’
  
  Alternatively, calculate \( \phi, \eta_{\text{intra}} \) and then \( R_{obs} \)
**Special Case:** 1\textsuperscript{st} order reaction (analytical solution is available)

\[
D_e \nabla^2 f = kf
\]

\[
D_e \left( \frac{d^2 f}{dz^2} + \frac{2 df}{z dz} \right) = k L^2 f
\]

\[
\frac{d^2 f}{dz^2} + \frac{2 df}{z dz} = \phi^2 f; \quad \phi = L \sqrt{\frac{k}{D_e}} \quad (L = \frac{r_o}{3} \text{ for sphere})
\]

BCs \quad z = 0, \quad \nabla f = 0
\quad \quad z = 3 \quad f = 1 \quad (z = \frac{r}{L} = \frac{r_o}{\frac{r_o}{3}} = 3)

Let \( g = f z \); \( f = \frac{g}{z} \)

Differentiate \( f \) twice wrt \( z \), simplify and substitute in the equation above to show the following transformation:

\[
\frac{d^2 g}{dz^2} - \phi^2 g = 0 \quad \text{BCs:} \quad z = 0 \quad , \quad g = 0 \quad \quad z = 3 \quad , \quad g = 3
\]

\[
g = C_1 \sinh \phi z + C_2 \cosh \phi z
\]

\[
C_2 = 0, \quad C_1 = \frac{3}{\sinh 3 \phi} \quad \text{(apply BCs)}
\]

\[
g = \frac{3 \sinh(\phi z)}{\sinh(3 \phi)}
\]

\[
f = \frac{3 \sinh(\phi z)}{z \sinh(3 \phi)} \quad \text{: (dimensionless solution)}
\]

\[
\frac{C_{A}}{C_{A,b}} = \frac{3 \sinh(\phi' r/L)}{r/L \sinh(3 \phi)} = \frac{r_o \sinh(\phi'^3 r/r_o)}{r \sinh(3 \phi)} \quad \Rightarrow \text{Thus, } C_A(r) \text{ is determined.}
\]

Calculate the reaction rate by equating the rate of species arriving at the surface of the catalyst to that of species consumed/reacted in the catalyst volume under SS conditions.
\[ R \left( \frac{\text{moles}}{s} \right) = \int_0^{r_o} kC_A(r) \, 4\pi r^2 dr \quad \text{("A" is consumed in the catalyst pores)} \]

\[ = -D_e \frac{dC_A}{dr} \, \bigg|_{r=r_o} 4\pi r_o^2 ; \quad \text{(flux of A arriving at the surface)} \]

(Note that one can also write:
\[ R_{\text{global}} = kC_A(r) \], based on the volume average concentration inside the catalyst)

It is easier to differentiate than to integrate (use the second expression)

\[ \eta_{\text{intra}} = \frac{R_{\text{global}}}{R_b} = \frac{-D_e \frac{dC_A}{dr} \, \bigg|_{r=r_o} 4\pi r_o^2}{(kC_{A,b}) \frac{4}{3}\pi r_o^3} \]

\[ = D_e \frac{d(C_A/C_{A,b})}{d(r/L)} \bigg|_{r=r_o} \times \frac{1}{L^2 k} \quad \left( L = r_o/3 \right) \]

\[ = \frac{1}{\phi^2} \frac{df}{dz} \bigg|_{z=3} \]

Already we have the solution \( f(z) \) from the previous exercise; substitute to obtain:

\[ \eta_{\text{intra}} = \frac{1}{\phi} \left[ \frac{1}{\tanh 3\phi} - \frac{1}{3\phi} \right] , \quad \phi = L \sqrt{\frac{k}{D_e}} \left( \frac{1}{s} \text{ (1st order)} \right) \]

\[ \text{Once we know } \eta_{\text{intra}} \Rightarrow \text{calculate } R_{\text{global}} = \eta_{\text{intra}} \times (kC_{A,b}) \frac{\text{mole}}{s - m^3} \]
**Plot:**

(The curve is hand-drawn. See the textbook for an accurate representation of the data)

\[
\eta \sim \frac{1}{\phi} \quad (\phi \text{ is high})
\]

- **When** \( \phi \downarrow \) or \( D_e \uparrow \) or \( L \downarrow \) (relative to 'k')
  - (large pore diffusion) small particle size
  - diffusion is fast
  - \( \eta \to 1 \)
  - \( R_{obs} \to R_b (kC_{A,b}) \)
  - kinetic controlled

- **Alternatively,**
  - \( \phi \uparrow \) or \( D_e \downarrow \) or \( L \uparrow \) (relative to 'k')
  - or \( k \) is large or \( \eta \) is narrow
  - \( \eta \to \text{small} \) or \( \eta \ll 1 \)
  - \( R_{obs} \ll R_b \)
  - diffusion controlled

\( \nabla C_A(r) \to 0 \)

\( \nabla C_A(r) \text{ increases with increasing '}\phi' \)
Note:

Graphical solutions are available for different shapes of the materials and different orders of reaction.

Again, calculate $\phi$ first and then $\eta_{\text{intra}} \Rightarrow calculate R_{\text{global}} = \eta_{\text{intra}} \times (C_{A,b}^n) \text{ mole/s} - m^3$

We will close the discussion on intraphase transport + kinetics in this lecture before taking up the examples in the next few lectures.

Smith has devoted two-three pages (507-510) on the effect of internal transport on selectivity in chapter 11. It is not difficult for you to go through this section yourself. Briefly, Smith categorizes the effects through Type 1, 2 and 3 series or parallel reactions.

**Type 1:** $A \rightarrow B$ (desired) and $R \rightarrow S$ (undesired)

**Type 2:** $A \rightarrow B$ (desired) and $A \rightarrow C$ (undesired)

**Type 3:** $A \rightarrow B \rightarrow D$, where $B$ is the desired product.

Examples are from hydrogenation, dehydrogenation, dehydration, and oxidation of some hydrocarbons.

Type 1 and 2 are easy to handle and quantify. Type 3 requires some thinking and calculations. For Type 1 reactions, internal transport or diffusion decreases the selectivity. For Type 2 (both first order irreversible reactions), selectivity is unaffected by diffusion. Type 3 is slightly trickier to understand because the product $B$ is the reactant for the second consecutive/series reaction. Therefore, pore-diffusion coefficient for $B$ becomes as important as the pore-diffusion coefficient of the reactant $A$! May be there are two Thiele modulus? And, there may be so many different situations which you should be able to recognize......
Lecture 19-20

**Example 1:** Explain \( n = 0 \), mathematically

Two situations:

\( \phi \leq 1, \ \phi > 1 \)

\[ \eta = \frac{1}{\phi} \]

\( \eta = 1 \)

\( n < 1 \)

**Hint:** For a zero-order reaction, analytically integrate the non-dimensional species conservation differential equation to derive a general expression for concentration in the pellet. Note that concentration is minimum at the center; however it cannot be zero. With this constraint you should be able to derive an expression for concentration profiles inside the pellet with a limit for \( \phi < \phi^* \). In this case, the process is kinetic controlled and \( \eta = 1 \) (observed rate = intrinsic rate for zero-order reaction). For sphere \( \phi^* = 1 \) and for slab \( \phi^* = \sqrt{2} \). For \( \phi > \phi^* \), concentration, however, decreases to zero at some distance \( (r^*) \) away from the center inside the pellet, beyond which region \( \eta = 1/\phi \) and the process is diffusion controlled. Below that distance, there is no gas (reactant) and no reaction. See Rodrigues and Orfao (1984) in Chem. Eng. Commun. 27, pp. 327-33.

**Ex 2.** For reversible, \( A \rightleftharpoons B \): calculate \( \eta(\phi) \).

\[ r = -\frac{dC_A}{dt} = k_1C_A - k_{-1}C_B \]

Ans:

\[ \eta = \frac{R_{obs}}{R_b} = \frac{R_{obs}}{(k_1+k_{-1})(C_{A,b}-C_{Ae})} \]

(based on bulk phase)
, and $R_{obs} = -D_e \frac{dc_a}{dr} \bigg|_{r=r_o}$ (moles/s – m$^3$ of catalyst volume)

Equation (species balance):

$$D_e \nabla^2 C_A - (k_1 + k_{-1})(C_A - C_{Ae}) = 0 \quad \text{(moles/s – m$^3$)}$$

Or,

$$D_e \left( \frac{d^2 C_A}{dr^2} + \frac{2}{r} \frac{dC_A}{dr} \right) - (k_1 + k_{-1})(C_A - C_{Ae}) = 0$$

BCs. $r = 0, \frac{dC_A}{dr} = 0; \quad r = r_o, \quad C_A = C_{A,b}$

Modify the species balance equation:

$$D_e \left( \frac{d^2 (C_A - C_{Ae})}{dr^2} + \frac{2}{r} \frac{d(C_A - C_{Ae})}{dr} \right) - (k_1 + k_{-1})(C_A - C_{Ae}) = 0$$

BCs $r = 0 \quad \frac{d(C_A - C_{Ae})}{dr} = 0; \quad r = r_o \quad (C_A - C_{Ae}) = (C_{A,b} - C_{Ae})$

Compare the equation and BCs to the previous situation (irreversible reaction):

$$A \xrightarrow{k_1} B$$

Solution is: $\eta = \frac{1}{\phi} \left[ \frac{1}{\tanh 3\phi} - \frac{1}{3\phi} \right], \quad \phi = L \sqrt{\frac{k_1 + k_{-1}}{D_e}}$

(No need to solve again)

Ex 3. Determine the effect of temperature on $\phi, \eta$ and $R_{obs}$ for the catalytic reaction $A \rightarrow B, \quad r = kC_A$ (Intrinsic rate)

Ans:
\[
\phi = L \sqrt{\frac{k}{D_e}} \quad k \propto \exp\left(-\frac{1}{T}\right) \quad D_e \propto \sqrt{T}
\]

Therefore, if \( T \uparrow \) \((k/D_e) \uparrow \) \( \phi \uparrow \) \( \eta \downarrow \) (moves towards diffusion control)

\[
R_{obs} = \eta \times R_{in} = \eta k_o \exp\left(-\frac{E}{RT}\right) C_A = \eta \left(\frac{1}{\phi}\right) k_o \exp\left(-\frac{E}{RT}\right) C_A
\]

\[
R_{obs} = \eta \left(\frac{1}{\sqrt{\exp\left(-\frac{E}{RT}\right)}}\right) k_o \exp\left(-\frac{E}{RT}\right) C_A
\]

4. Determine observed activation energy

If (a) the reaction is kinetic controlled (b) diffusion controlled

(a) \( \eta = 1, \quad E_{obs} = E_{int} \quad (E_{app} = E_{int}) \)

\[
\left[R_{obs} = \eta k_o \exp\left(-\frac{E}{RT}\right) C_A = k_o \exp\left(-\frac{E}{RT}\right) C_A = k_{app} C_A \right]
\]

\[
k_{app} = k_{int}
\]

(b) \( \eta = \frac{1}{\phi} \)

\[
R_{obs} = \frac{1}{\phi} (k C_A) = \frac{1}{L} \sqrt{\frac{D_e}{k}} (k C_A) = \frac{1}{L} \sqrt{D_e k} C_A = k_{obs} C_A
\]

\[
k_{obs} \text{ or } k_{app} = \frac{1}{L} \sqrt{D_e k} \Rightarrow E_{app} = \frac{E_{int}}{2}
\]

\[
E_{obs} = \{E/2, E\} \text{ compare this to } E_{obs} = \{0, E\} \text{ for interphase + kinetics}
\]

(diffusion controlled) \rightarrow (kinetic controlled)

We should perform expt at low \( T \) to determine true activation energy

\[
\ln(k_{app}) \quad \frac{-E}{2R} \\
1/T \quad \frac{-E}{R}
\]

(high \( T \): diffusion controlled) \quad \quad \quad \quad \text{Low} \( T \) \quad \quad \quad \quad \text{(kinetic controlled)}
5. Determine the pellet size effects on $\phi$ and $\eta$

\[
\phi = L \sqrt[\frac{k}{D_e}] \quad ; \quad \eta = \eta \left( \frac{1}{\phi} \right)
\]

If $L \downarrow$, $\phi \downarrow$, $\eta \uparrow$

Also, large pore size, $D_e \uparrow$, $\phi \downarrow$, $\eta \uparrow$ \( \text{kinetic controlled} \)

(diffusion is fast)

\( (R_{obs} \rightarrow R_{int}) \)

If a catalyst is given to you to find intrinsic rate (or true ‘E’), make it powder, and also, conduct reaction at low temperature (see the finding in Q4).

\[
A \rightarrow R \ (1^{st} \ \text{order, irreversible}) \over \text{over porous catalyst}
\]

\[
\left\{ \begin{array}{l}
d_p = 0.4 \ \text{cm} \\
D_{eff} = 0.015 \ \text{cm}^2/s \\
k_{int} (100^\circ C) = 0.93 \ s^{-1} \\
E = 20,000 \ \text{cal/mole}
\end{array} \right.
\]

interphase diffusion rate is fast

\textbf{Q1: Determine } R_a \text{ or } R_{obs} \text{ at } 100^\circ C, \text{ if } C_{A_0} = 3.25 \times 10^{-2} \text{ moles/L}

\[
R_{obs} = \eta \ (R_b) = \eta (kC_{A_0})
\]

\[
\phi = L \sqrt[\frac{k}{D_e}] = \frac{d_p}{6} \sqrt[\frac{k}{D_e}] = \frac{0.4}{6} \sqrt[\frac{0.93}{0.015}] = 0.525
\]

\[
\eta = \frac{1}{\phi} \left[ \frac{1}{\tanh 3\phi} - \frac{1}{3\phi} \right] \Rightarrow \eta = 0.866
\]
\[ R_{obs} = 0.866 \times 0.93 \times 3.25 \times 10^{-2} = 2.61 \times 10^{-2} \text{ moles/L - s} \]

**Q2:** For \( C_A^0 = 3.25 \times 10^{-2} \text{ moles/L} \), what is \( R_{obs} \) at 150\(^\circ\)C?

\[
k_{150} = k_{100} \exp \left( -\frac{E}{R} \left( \frac{1}{(150+273)} - \frac{1}{(100+273)} \right) \right)
\]

\[
= 0.93 \exp \left( -\frac{20,000}{1.98} \left( \frac{1}{423} - \frac{1}{373} \right) \right)
\]

\[
= 22.83 \text{ s}^{-1}
\]

\[
D_{eff} = 0.015 \times \left( \frac{150+273}{100+273} \right)^{1/2} = 0.016
\]

Therefore, \( \phi = \frac{0.4}{6} \sqrt{\frac{22.83}{0.016}} = 2.51 \)

\[
\eta = \frac{1}{\phi} \left[ \frac{1}{\tanh 3\phi} - \frac{1}{3\phi} \right] = 0.345
\]

\[ R_{obs} = \eta (kC_A) = 0.345 (22.83 \times 3.25 \times 10^{-2}) \]

\[ = 2.52 \times 10^{-1} \text{ moles/L - s} \]

**Q3:** Why \( \eta (150^\circ C) < \eta (100^\circ C) \)

- Temperature effects (kinetics is faster at 150\(^\circ\)C; pore-diffusion controls)

(catalyst is less effective if there is a pore-diffusion) \( (\eta = 0.45) \); catalyst will be more effective at relatively lower temperatures.

To make the catalyst relatively more effective at a fixed high temperature, you can make smaller pellets; see if the material pore size distribution can be tailored to increase pore diffusion coefficient \( (D_{eff}) \), although the latter is not trivial.
Q4: Determine $E_{obs}$ (you have two data points)

$$\left(\frac{k_{150}}{k_{100}}\right)_{app\ or\ obs} = \left(\frac{R_{150}}{R_{100}}\right)_{app\ or\ obs} \quad (C_{A,b} = const)$$

bulk concentration is the same in two cases

$$= \frac{2.52 \times 10^{-1}}{2.61 \times 10^{-2}} = \exp\left(-\frac{E_{obs}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right)$$

or, $9.655 = \exp\left(-\frac{E_{obs}}{1.98}\left(\frac{1}{423} - \frac{1}{373}\right)\right) \rightarrow E_{obs} = \frac{2.267 \times 1.98}{3.17 \times 10^{-4}} = 14.16\ kcal/mole.$
Example continued...

Q5: Consider a catalytic reaction over a porous catalyst. The data for the catalyst grain (particle) are given as follows:

\[
\begin{align*}
T &= 803 \text{ K}, \quad d_p = 0.32 \text{ cm}, \quad k_{obs} = 0.94 \text{ cm}^3/\text{s} - \text{gm of cat} \\
a &= 110^o \text{ A}, \quad \tau = 3.0, \quad v_{pore} = 0.35 \text{ cm}^3/\text{gm}, \quad M (\text{reacting species}) = 58
\end{align*}
\]

Determine/Calculate \(\eta\). Assume \(D_k\) is dominant.

Ans:

\[
D_{eff} = \rho \frac{D_c}{\tau} \quad ; \quad D_c = D_k
\]

\[
D_k = 9700 \times a (\text{cm}) \sqrt{\frac{T(K)}{M}}
\]

\[
v_{pore} = 9700 \times 110 \times 10^{-8} \sqrt{\frac{803}{58}} = 3.97 \times 10^{-2} \text{ cm}^2/\text{s}
\]

\[
\epsilon = 0.35 \times \rho_p \text{ (particle density is not provided)}
\]

\[
\frac{\text{cm}^3}{\text{gm}} \quad \frac{\text{gm}}{\text{cm}^3} \quad \text{(total)}
\]

\[
D_{eff} = \frac{0.35 \times \rho_p \times 3.97 \times 10^{-2}}{3} = 4.6 \times 10^{-3} \rho_p \text{ cm}^2/\text{s}
\]

1. Check \(k_{obs}\) \(\Rightarrow R_{obs} = k_{obs} C_{A,b} = \eta(R_b) = \eta(k_{int} C_{A,b})\)

2. Check the unit of \(k_{obs}\) \(\Rightarrow \text{cm}^3/\text{s} - \text{gm of cat} (1^{st} \text{ order})\)

\[
R = \text{ moles/s - gm of cat} \quad \left\{ \begin{align*}
&= k C_A \rightarrow \text{ moles/cm}^3 \\
&= \frac{\text{cm}^3/\text{s} - \text{gm of cat}}{k}
\end{align*} \right.
\]
The equation \( \phi = L \sqrt{\frac{k_{int}}{D_{eff}}} = \frac{d_p}{6} \sqrt{\frac{k_{int}}{D_{eff}}} \) was derived for \( R = \text{moles/s} - \text{cm}^3 \) of cat volume.

Therefore,

\[
k_{obs} \xrightarrow{\text{modified/converted}} k_{obs} \times \rho_p \rightarrow (k_{obs} \times \rho): \frac{1}{S}
\]

CM\(^3\)/gm \rightarrow \frac{gm}{cm\(^3\)}

Therefore,

\[
\phi = \frac{d_p}{6} \sqrt{\left(\frac{k_{obs} \times \rho_p}{\eta}\right) \times \left(\frac{1}{D_{eff} \times \rho_p}\right)}
\]

\[
\phi = \frac{d_p}{6} \sqrt{\frac{k_{obs}}{\eta D_{eff}}} = \frac{0.32}{6} \sqrt{\frac{0.94}{4.6 \times 10^{-3} \times \eta}}
\]

\[
\eta = \frac{1}{\phi} \left[ \frac{1}{\tanh 3\phi} - \frac{1}{3\phi} \right]
\]

Solve to get \( \eta \) or \( \phi \) (requires iteration)

In the exam, just do one or two iterations.

**Q6:** Oxidation of \( CO \) occurs over the porous \( Pt/Al_2O_3 \) catalyst at \( T = 400 \, ^\circ C, \, P_{CO} = 0.15 \, \text{atm} \)

(film transport is negligible or \( k_m \) is very high):

Intrinsic rate: \( \eta_i = 10^{-6} \, C_A \, (\text{moles/cm}^2 - \text{s}) \)

Data for the catalyst: \( S = 20 \, m^2/gm, \quad \epsilon = 0.5 \, \text{cm}^3/cm^3 \)

\[
\rho_p = 5.3 \, g/cm^3, \quad d_p = 8 \, \text{mm}
\]

Grain (particle) density

\( Dm \) at \( 0^\circ C = 0.04 \, \text{cm}^2/s \)

**Determine** \( \dot{r} \), the rate of reaction in one particle, i.e., or \( R_{obs} \) in

\( \text{moles/s} - \text{one particle} \)

**Ans:** First modify \( \eta_i = 10^{-6} \, C_A \times S \times \rho_p \, (\text{moles/cm}^3 - s) \)
\[ D_{400} = 0.04 \left( \frac{T_1}{T_2} \right)^{\frac{3}{2}} = 0.04 \left( \frac{673}{273} \right)^{1.5} \]
\[ D_{400} = 0.155 \text{ cm}^2/s \]

2. \( D_k = 9700 \overline{a} \text{ (cm)} \sqrt{\frac{T}{M}} = 9700 \overline{a} \sqrt{\frac{673}{28}} \)
\[ \overline{a} = \frac{s V_p \epsilon}{s} \text{ (Recall)} \]

Assume cylindrical pores:

\[ \begin{align*}
S &= 2\pi rL \\
V_p &= \pi r^2L
\end{align*} \]

\[ r = \frac{2V_p}{S} = \frac{2V_p \epsilon_p}{S} \]
\[ \overline{a} = \frac{2\epsilon_p}{s} \]

\[ \epsilon_p = \epsilon_g(\epsilon) \]
\[ S = \text{pore (surface) area} \]
\[ V_p = \text{grain/particle volume per unit volume of particle or grain} \]

Therefore,
\[ \overline{a} = \frac{2 \times 0.5}{s \times \rho_p} = \frac{2 \times 0.5}{20 \times 10^4 \times 5.3} = 9.4 \times 10^{-7} \text{ cm} \]
\[ D_k = 9700 \times 9.4 \times 10^{-7} \sqrt{\frac{673}{28}} = 0.045 \text{ cm}^2/s \]

\[ D_{eff} = \frac{\epsilon D_{comb}}{\tau} = \epsilon^2 D_{comb} = \epsilon^2 \left( \frac{1}{1 + \frac{1}{D_k}} \right) \]
\[
= 0.5^2 \left/ \left( \frac{1}{0.045} + \frac{1}{0.155} \right) \right. = 0.0087 \ \text{cm}^2/\text{s}
\]

---

both are important

3. \( \phi = L \sqrt{\frac{k (1/s)}{D_{\text{eff}} (cm^2/s)}} = \frac{0.8}{6} \sqrt{\frac{1.06}{0.0087}} = 1.471 \)

Therefore, \( \eta = \frac{1}{\phi} \left[ \frac{1}{\tanh 3\phi} - \frac{1}{3\phi} \right] = 0.526 \)

4. \( C_A = \frac{p_A}{RT} = \frac{0.15}{82 \times 673} = 2.7 \times 10^{-6} \ \text{moles/cm}^3 \)

\( R_{\text{obs}}: \)

\[
\frac{\text{Rate}}{\text{particle}} = 0.526 \times 1.06 \ C_A \left( \frac{\text{moles}}{\text{s-cm}^3} \right) \times \left( \frac{\pi d_p^3}{6} \right) \text{cm}^3 \text{ of particle volume}
\]

\[
= (0.526 \times 1.06 \times 2.7 \times 10^{-6} \times 0.268) = 0.4 \times 10^{-6} \ \text{moles/s} - \text{particle}
\]

H.W.: 3.8, 3.9 (FB)
Lecture 22

n\textsuperscript{th} order reaction, intraphase transport + reaction, non-isothermal (interphase is fast)

Write down transport equations:

Species balance: \( D_e \nabla^2 C_p = k C_p^n \)

\[ r = 0 \quad \nabla C_p = 0 \text{ (symmetric boundary condition)} \]

\[ r = r_0 \quad C_p = C_b \text{ (surface condition)} \]

Energy balance: \( \lambda_e \nabla^2 T = (k C_p^n)(-\Delta H) \)

\[ \lambda_e = \text{thermal conductivity} \]

\[ r = 0 \quad \nabla T = 0 \text{ (symmetric boundary condition)} \]

\[ r = r_0 \quad T = T_b \text{ (surface condition)} \]

or \( \lambda_e \nabla^2 T = D_e \nabla^2 C_p (-\Delta H) \) (substitute kinetics from the previous eqn)

or \( \nabla^2 T = \left( \frac{-\Delta H D_e}{\lambda_e} \right) \nabla^2 C_p \)

To solve: non-dimensionalize

\[ f = C_p/C_b, \quad \theta = \frac{T}{T_b}, \quad z = \frac{r}{L} \]

On substitution in the species balance equation

\[ \nabla^2 f = \phi^2 f^n \left( \frac{k}{k_b} \right) \]

Note: \( k \neq k_b \) and \( T(r) \neq T_b \) (non-isothermal condition)

\[ \phi = L \sqrt{\frac{k_b C_b^{n-1}}{D_e}} \]

(See the text for the generalized Theile modulus for \( n = 0 \) and –ve order reactions; term within the square root contains \( (n+1)/2 \) )
Similarly,

\[
\nabla^2 \theta = \frac{D_e}{\lambda_e} \cdot \frac{C_b(-\Delta H)}{T_b} \nabla^2 f
\]

Define prater number \( \beta' = \frac{D_e}{\lambda_e} \cdot \frac{C_b(-\Delta H)}{T_b} = \left( \frac{\text{generation}}{\text{transport}} \right)_{\text{bulk condition}} = 0.00001 - 0.01 \) (lit\rature)

should be solved numerically,

\[
\eta_{\text{intra}} = \eta_{\text{intra}}(n, \phi, \beta', \epsilon) \xrightarrow{\text{Arrhenius}} \eta_{\text{intra}}(n, \phi)
\]

Compare to isothermal case \( \eta_{\text{intra}} = \eta_{\text{intra}}(n, D_a) \)

Compare to isothermal case (interphase) \( \eta_{\text{inter}} = \eta_{\text{inter}}(n, D_a) \)

Compare to non-isothermal case (interphase) \( \eta_{\text{inter}} = \eta_{\text{inter}}(n, D_a, \beta, \epsilon) \)

\( (\beta = \beta' \approx 0, \text{ if isothermal}) \)

Approximation can be made to calculate \( (\Delta T)_{\text{max}} \)

\[
(T_s - T_c) \approx (C_s - C_c) \left( \frac{-\Delta H D_e}{\lambda_e} \right)
\]

\( (\Delta T)_{\text{max}} = \Delta C_{\text{max}} \left( \frac{-\Delta H D_e}{\lambda_e} \right) \)

Therefore,

\[
\beta' = \frac{(-\Delta H D_e C_b)}{\lambda_e T_b} \quad \text{If } C_{\text{center}} \ll C_b
\]

\[\beta' = \frac{\Delta T_{\text{max}}}{T_b} \quad \text{diffusion - conrol}\]

\[
\eta = \frac{R_{\text{obs}}}{R_b} = \frac{k C_p}{k_b C_b} = \left( \frac{k}{k_b} \right) \left( \frac{C_p}{C_b} \right)^n \quad \text{Note: } k = k(T) \text{ and } T = T(r)
\]

\( R_{\text{obs}} = -D_e \left. \frac{d C_p}{d r} \right|_{r=r_o} \times \alpha \) \quad \text{where, } C(r) \text{ is solved numerically together with } T(r);

\( \bar{C}_p \) is the volume-average quantity for pore concentrations or within the solid.
For $\beta' > 0$ $\eta$ can be greater than 1, because $R_H \uparrow \ R_m \downarrow$

(Not all $\beta' > 0$ show $\eta > 1$, but all $\beta' < 0$ show $\eta < 1$ or curves monotonically decreases with increasing $\phi$)

Simple Case (1st Order):

There is a hysteresis/multiplicity occurs
Q: 1. What conditions will lead $\eta > 1$ always

a) $n < 0$   b) exothermic

2. Is it practical to operate catalytic reaction with $\eta > 1$

- Yes ($\eta > 1$ is genuine)

Exothermic (real situations)

**Interphase plus intraphase + reaction (isothermal):**

Intrinsic rate

$r = kC^n$

$R_{obs} \left( \frac{\text{moles}}{s-m^3} \right) = a \, k_m \, (C_b - C_s)$

eq. (1)

$= -D_e \frac{dC_p}{dr} \bigg|_{r=r_p}$  (Note that $C_p @ r = R$ is $C_s$)

$= (kC_s^n)\eta_{intra}$  $\left( \eta_{intra} = \frac{R_{obs}}{R_s} \right)$

Surface conditions

$$R_{obs} = a \, k_m \left[ C_b - \left( \frac{R_{obs}}{k \eta_{intra}} \right)^{\frac{1}{n}} \right]$$ substitute intermediate $Cs$ in the previous eqn

where, $\eta_{intra} = \eta_{intra} (n, \phi)$ and

$\phi = L \sqrt{\frac{kC_s^{n-1}}{D_e}}$  eq. (2)

One can also define,

$\eta_{total} = \frac{R_{obs}}{R_{max}} = \frac{(kC_s^n)\eta_{intra}}{(kC_b^n)} = \eta_{intra} \left( \frac{C_s}{C_b} \right)^n$  eq. (3)

(based on bulk phase concentration)
\[ \eta_{\text{total}} = \eta_{\text{total}}(n, \phi, D_a) \]

Recall \( \frac{c_s}{c_b} = \frac{c_s}{c_b}(\eta) = \frac{c_s}{c_b}(D_a) \)

Therefore, \( R_{\text{obs}} = \eta_{\text{total}} \times kC_b^n \)  \hspace{1cm} \text{eq. (4)}

You should note that the calculation for \( R_{\text{obs}} \) is not straightforward if \( C_s \neq C_b \) or film transfer (interphase) resistance is significant or \( Da >> 1 \). In an iterative procedure, assume a value of \( C_s < C_b \) (depending on the value of \( Da \)), calculate \( \phi \) and \( \eta_{\text{intra}} \). Then, calculate \( R_{\text{obs}} \) from eq. (2). Check the calculated value of \( R_{\text{obs}} \) from eq. (1). Alternatively, calculate \( \eta_{\text{total}} \) from eq. (3) and \( R_{\text{obs}} \) from eq. (4). Check the calculated value of \( R_{\text{obs}} \) from eq. (1). The calculations for 1\(^{st}\) order reaction are straightforward without requiring iterations because \( \phi \) becomes independent of \( C_s \), and so does \( \eta_{\text{intra}} \).

**1\(^{st}\) order reaction:**

\[ R = a \ k_m \ (C_b - C_s) \ \left( \frac{\text{moles}}{s - m^3} \right) \text{ of cat. vol.} \]

\[ = (kC_s)\eta_{\text{intra}} \]

\[ = K_p C_b \ \text{(overall mass transfer coefficient)} \]

\[ \frac{1}{K_p} = \frac{1}{ak_m} + \frac{1}{k \eta_{\text{intra}}} \]

**External or interphase mass transfer resistance is in series with the other two (kinetics and intraphase diffusion resistances) but these are simultaneous. Reaction and pore-diffusion occur simultaneously.**
Lecture 23-24

There are some design criteria/rule for interphase or intraphase transport to be considered or neglected.

**Intraphase transport** (1\(^{\text{st}}\) order)

a) Weisz-Prater rule (criterion)

\[
\phi \leq \frac{1}{3} \quad \text{and} \quad \eta \geq 0.9 \quad (90\% \text{ kinetic controlled})
\]

\[
\eta \approx 1 \quad (\text{kinetic controlled})
\]

\[
\phi = \frac{k}{D_e} \quad \eta = \frac{k}{a D_e}
\]

or

\[
\frac{r_0}{C_b D_e} \leq 1 \quad \text{and} \quad R_{\text{obs(app)}} = \eta (kC_b) = kC_p \quad (\eta = 1)
\]

\[
\frac{r_0^2 R_{\text{obs}}}{C_b D_e} \leq 1 \rightarrow \text{kinetic controlled}
\]

In general, for the \(n\)\(^{\text{th}}\) order reaction

\[
\frac{r_0^2}{C_b} \times \frac{R_{\text{obs}}}{D_e} \ll \frac{1}{|n|} : \text{Hudgin's criterion}
\]

rate per catalyst
volume \((R_p)\)

b) Heat transfer \((\text{isothermal: no } \Delta T \text{ within particle}):\)

\[
|\beta| \left( \frac{E}{RT_b} \right) \ll 0.13 : \text{Peterson criterion}
\]

\[
\frac{\Delta H (r_0 R_p)}{\lambda_e T_b} \left( \frac{E}{RT_b} \right) < 0.3 : \text{Anderson criterion}
\]

**Interphase:**

\[
\frac{r_0 R_p}{C_b k_m} < \frac{0.15}{n} \quad (\text{kinetic controlled})
\]

\[
\frac{r_0 R_p (-\Delta H)}{T_b h} < \frac{0.15 R T_b}{E} : \text{isothermal (no } \Delta T \text{ across film)}
\]

- Mears Criterion.
Example:

\[ A \rightarrow R \]

\[ r = kC_A \]

**What controls?**

\[
d_p = 2.4 \text{ mm} \\
D_e = 5 \times 10^{-5} \text{ m}^2/\text{h} \\
C_b = 20 \text{ moles/m}^3 \\
k_m = 300 \text{ m/h} \\
R_p = 10^5 \text{ moles/h - m}^3 \text{ of catalyst volume.}
\]

Interphase:

\[
\frac{r_0R_p}{C_b k_m} = \frac{1.2 \times 10^{-3} \times 10^5}{20 \times 300} = 0.02 < \frac{0.15}{n} \quad (n = 1)
\]

Therefore, no interphase resistance.

\[(k_m \uparrow \uparrow; \text{is very high})\]

Intraphase:

\[
\frac{r_0^2R_p}{C_b D_e} = \frac{(1.44 \times 10^{-6}) \times 10^5}{20 \times 5 \times 10^{-5}} = 144 > > 1
\]

(heavily intraphase resistance)

\[ \text{diffusion controlled.} \]

\[ \nabla C \approx 0 \quad (film) \]

\[ \text{in pores} \]
Ex 2: \[
R(\text{intrinsic}) = kC^n \text{ (rate/unit volume of cat)}
\]

Fill up the table: **How do the conditions effect the rate (through which variable)?**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Controlling Step</th>
<th>Rate expression (rate/unit-volume of catalyst)</th>
<th>Effect of concentration (reaction order)</th>
<th>Effect of Temp</th>
<th>Effect of particle size</th>
<th>Effect of fluid velocity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>kinetics {non- porous }</td>
<td>[kC^n = ks_1C^n]</td>
<td>[n]</td>
<td>[E]</td>
<td>[a]</td>
<td>[-]</td>
</tr>
<tr>
<td>2.</td>
<td>kinetics {porous}</td>
<td>[kC^n = ks_2C^n]</td>
<td>[n]</td>
<td>[E]</td>
<td>[-]</td>
<td>[-]</td>
</tr>
<tr>
<td>3.</td>
<td>Interphase *</td>
<td>[ak_mC_b]</td>
<td>1</td>
<td>[\approx 0]</td>
<td>[ak_m(a)]</td>
<td>[k_m]</td>
</tr>
<tr>
<td>4.</td>
<td>Intraphase *</td>
<td>[a\sqrt{kD_eC^n}^{n+1}]</td>
<td>[\frac{n+1}{2}]</td>
<td>[E/2]</td>
<td>[a]</td>
<td>[-]</td>
</tr>
<tr>
<td>5.</td>
<td>Interphase + Intraphase (both control)</td>
<td>[ak_mC_b]</td>
<td>1</td>
<td>[\approx 0]</td>
<td>[ak_m(a)]</td>
<td>[k_m]</td>
</tr>
</tbody>
</table>

Ans:

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Controlling Step</th>
<th>Rate expression (rate/unit-volume of catalyst)</th>
<th>Effect of conc (reaction order)</th>
<th>Effect of Temp</th>
<th>Effect of particle size</th>
<th>Effect of fluid velocity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>kinetics {non- porous }</td>
<td>[kC^n = ks_1C^n]</td>
<td>[n]</td>
<td>[E]</td>
<td>[a]</td>
<td>[-]</td>
</tr>
<tr>
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<td>[kC^n = ks_2C^n]</td>
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<td>[\approx 0]</td>
<td>[ak_m(a)]</td>
<td>[k_m]</td>
</tr>
</tbody>
</table>

\[* R_{obs} = (R_{int}) \eta \]
\[= (kC^n) \frac{1}{\phi} \quad ; \quad \phi = \frac{1}{a} \sqrt{\frac{kC^n}{D_e}} \]
\[= ak \sqrt{\frac{D_e}{kC^n}} \cdot C^n \]
\[= a\sqrt{kD_eC^n}^{n+1} \]
Notes 1. \( a \equiv \text{external surface area} = \frac{A}{V} = \frac{1}{L} \) (particle size effect)

\[ a_s = \text{internal surface area} \left( \frac{m^2}{m^3 \text{ of catalyst}} \right) \left( m^{-1} \right) \left( \text{no effect of particle size} \right) \]

- whether small or large particle size \( \Rightarrow \) BET area is constant \( \Rightarrow a_s \) is constant (it is an intrinsic material property). On the other hand,

\[ a \equiv (\text{particle size})^{-1} = (\text{characteristic length})^{-1} \]

2. Interphase: \( R_{obs} = a k_mC_b - C_s = kC_s^n \)

kinetics is fast \( \Rightarrow C_s \rightarrow 0 \) or \( C_s \ll C_b \). Therefore,

\[ R_{obs} = a k_mC_b \] (order of the reaction is ‘1’ even if the intrinsic order of reaction is \( n \))

3. \( k_m \Rightarrow \) Recall \( Sh = f(Re, Sc) \)

\[ \frac{k_md_p}{D} = f(Re, Sc) \]

\[ d_p \downarrow \quad k_m \uparrow \quad \text{or} \quad d_p \uparrow \quad k_m \downarrow \]

\[ k_m \propto \frac{1}{d_p} \quad \text{or} \quad k_m \propto a \]

Also, \( Re \uparrow \quad k_m \uparrow \) Therefore, both fluid velocity and particle size affect \( k_m \)

4. \( \sqrt{k} = \sqrt{k_o e^{-E/RT}} \Rightarrow E_{obs} = \frac{E_{int}}{2} \)

Plot concentration profiles for all 5 controlling steps/cases:

1. Kinetics (non-porous)

\[ C_b \]

\( (C_s \approx C_b) \)

2. Kinetics (porous)

\[ C_b \]

\[ C_p \]

\( C_p \approx C_b \)
3. Interphase

\[ C_s \ll C_b \]

4. Intraphase

\[ C_p \ll C_b \]

5. Interphase + Intraphase  (same as that in 3 above):

Two are in series, and interphase comes ahead of intraphase resistance. Therefore, if the reaction is interphase controlled, catalyst surface will starve of concentrations, and the reaction will remain interphase controlled irrespective of conditions in the catalyst particle or in its pores.
Example 1: Cracking of cumene ($C_9H_{12}$) over a catalyst: Data:

\[ P = 1 \text{ atm}, T = 510^\circ \text{ C}, \ E_{\text{true/intrinsic}} = 60 \text{ kcal/mole}; \ k_{\text{int}} = 0.04 \text{ s}^{-1}, S_g = 342 \text{ m}^2/\text{g}, \ \epsilon = 0.6, \ \rho = 1.14 \text{ g/cm}^3, \ D_m = 0.15 \text{ cm}^2/\text{s}. \]

a) \[ D_{\text{eff}} = ? \]
\[
\bar{a} = \frac{2\epsilon}{S_{g} \rho} = \frac{2 \times 0.6}{342 \times 10^4 \times 1.14} = 30.8^\circ \text{A} \text{ (assuming cylindrical pores)}
\]
\[ cm^2/g \quad g/cm^3 \]
\[
D_k = 9700 \bar{a} \sqrt{\frac{T}{m}} = 9700 \times 3.08 \times 10^{-7} \sqrt{\frac{783}{120}} = 0.00763 \text{ cm}^2/\text{s}
\]
\[ D_{\text{comb}} = 1/(\frac{1}{D_k} + \frac{1}{D_m}) = 0.00726 \text{ cm}^2/\text{s} \]
\[ D_{\text{eff}} = \frac{\epsilon D_{\text{comb}}}{\tau} = \epsilon^2 D_{\text{comb}} = 0.00726 \times 0.6^2 = 0.0026 \text{ cm}^2/\text{s} \]

b) What is maximum particle size before intraphase diffusion becomes important?

Apply Weisz – Prater criteria:

\[
r_o^2 \leq \frac{C_b D_{\text{eff}}}{r_p}; \quad C_b = \frac{p}{RT} = \frac{1.0}{783 \times 82} = 1.557 \times 10^{-5} \text{ moles/cc}
\]
\[
\text{particle size} \quad \text{moles/s} - \text{cm}^3
\]
\[
\text{cat - volume} \quad \text{moles/s} - \text{cm}^3
\]
\[
= \frac{C_b \times 0.0026}{(0.04 \times C_b)}
\]
\[ r_0 = 0.26 \text{ cm} \]

\[ r_{\text{obs}} = k_i C_b \]

\textbf{Note:} \( r_p \) is the observed rate. At the incipient condition when the intraphase diffusion just starts to become important, \( r_{\text{obs}} = k_i C_b \)

\( \text{surface condition} \)

(it is kinetic controlled)

(re – read the problem statement)

(c) What \( k_{\text{obs}} \) or \( k_{\text{app}} \) will be measured at 510\(^\circ\)C for the particles of 5 mm diameter?

\[ r_{\text{obs}} = \eta \left( r_{\text{int}} \right) = \eta(k_{\text{int}} C_b) : \text{definition for } \eta \]

\[ r_{\text{obs}} = k_{\text{obs}} C_b = \eta k_{\text{int}} C_b: \text{definition for } k_{\text{obs}} \Rightarrow k_{\text{obs}} = k_{\text{obs}} = \eta k_{\text{int}} = \eta \times 0.04 \]

(what if it is not a 1\(^{st}\) order reaction or some complex reaction rate? Then, it is a pseudo first order reaction?)

\[ \phi = \frac{d_p}{6} \sqrt{\frac{k'''}{D_e}} \quad \rightarrow \quad \text{\( r_{\text{in}} \) is measured in moles/s – cm\(^3\) of cat – volume} \]

\[ = \frac{0.5}{6} \sqrt{\frac{0.04}{0.0026}} = 0.33; \quad k''' \text{ must be in } 1/\text{s} \]

\[ \eta = \frac{1}{\phi} \left[ \frac{1}{\tanh 3\phi} - \frac{1}{3\phi} \right] = 0.94 \]

\[ k_{\text{obs}} = 0.04 \times 0.94 = 0.0376 \text{ s}^{-1} \]
Example 2: Isothermal, 1st order reaction, reaction in a porous catalyst, pore diffusion control; How does $\phi$, $\eta$, $R_{obs}(T) = ?$

a) $\phi = \frac{r_o}{3} \sqrt{\frac{k}{D}} = L \sqrt{\frac{k_o \exp(-E/RT)}{D}}$

or $\ln \phi = \ln \left( \frac{Lk_o^{1/2}}{D^{1/2}} \right) - \frac{E}{2RT} \Rightarrow \ln \phi$

$T \uparrow \phi \uparrow$

b) $\eta = \frac{1}{\phi} \Rightarrow \frac{1}{\phi} = \frac{1}{L} \left( \frac{D}{k} \right)^{1/2}$

$\ln(\eta) = \ln \left( \frac{D^{1/2}}{Lk_o^{1/2}} \right) + \frac{E}{2RT}$

$T \uparrow \eta \downarrow$

(There may be some effects of 'T' on 'D': some non-linearity in plots)

c) $R_{obs} = \eta (kC_A)_{surface}$ condition/intrinsic

$\frac{R_{obs}}{C_b} = \eta k = \eta(T)k(T) \quad \left( k_{obs} = \eta k_{in} \right)$

(There is a dependence of $R_{obs}$ on 'T' through both $\eta$ & $k$)

$\ln \left( \frac{R_{obs}}{C_b} \right) = \ln \eta + \ln k = \ln(const) - \frac{E}{2RT}$

($\ln k = \ln k_o - \frac{E}{RT}$)

$\ln \left( \frac{R_{obs}}{C_b} \right) \downarrow -\frac{E}{2R}$

(diffusion control)
Recall previous lectures: overall (reactive) mass transfer coefficient

![Graph showing ln(Kp) vs 1/T with diffusion and reaction control regions](image)

or

![Graph showing ln(Kp) vs 1/T with E/2R and E/R lines](image)

**Example 3: Basket reactor** (continuous operation)

<table>
<thead>
<tr>
<th>case No.</th>
<th>pellet dia</th>
<th>rpm</th>
<th>Cout</th>
<th>R_{obs}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>↑ (high)</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>Low</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>↑</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

**What controls?**

⇒ Case 2 & 3 (choose two conditions in which one variable is varied at a time)
Interphase transport or diffusion does not have influence. $k_m$ is high; interphase resistance is negligible at high or low stirring speed over that range; No $\Delta C$ across film; $C_s \rightarrow C_b$.

Case 1 & 3: $R_{obs} \downarrow$ with $d_p \uparrow$: indicates the influence of intraphase. Do some calculations.

If pore-diffusion controls, $\eta = \frac{1}{\phi}$

$$\frac{\phi_1}{\phi_3} = \frac{d_{p1}}{d_{p3}} = \frac{1}{3}$$

$$\frac{\frac{R_{obs,1}}{R_{obs,3}}} = \frac{\eta_1(kC_b)_1}{\eta_3(kC_b)_3} = \frac{\eta_1}{\eta_3} = \frac{3}{1} \text{ (Note it is a well–mixed reactor)}$$

- Pore-diffusion controls $\eta = \frac{1}{\phi}$

Example 4:

$C_{A,in} = 1 \text{ mole/L}$
$v_o = \text{fixed}$
(negligible film resistances, const. temperature)

$X_A, C_{A,exit}$

\[ \begin{array}{|c|c|c|}
\hline
 d_o & W & X_A \\
\hline
 2 & 2 & 0.6 \\
 6 & 1 & 0.2 \\
\hline
\end{array} \]

$\Rightarrow 1^{st}$ order

$\Rightarrow$ porous catalyst

What controls?
Ans: \( C_A = C_{Ao}(1 - X_A) \Rightarrow C_{A,1} = 0.4, \ C_{A,2} = 0.8 \)

Species balances equation across the reactor (design equation/performance equation):

\[
F_{Ao}X_A = (-r_A)_{obs} W \quad \text{or,} \quad v_o(C_{Ao} - C_A) = (-r_{obs}) \times W
\]

\[
(-r_A)_{obs} = \frac{F_{Ao}X_A}{W}
\]

\[
\left( \frac{r_{A,1}}{r_{A,2}} \right)_{obs} = \frac{x_{A,1}}{x_{A,2}} \times \frac{W_2}{W_1} = \frac{0.6}{0.2} \times \frac{1}{2} = \frac{3}{2}
\]

(Note \( C_{A,bulk} = C_{A,exit} \) in a well-mixed reactor)

Theory:

\[
\left( \frac{r_{A,1}}{r_{A,2}} \right)_{obs} = \frac{\eta_1}{\eta_2} \times \left( \frac{C_{A,1}}{C_{A,2}} \right)_{bulk} \quad \text{(isothermal)}
\]

\[
= \frac{\phi_2}{\phi_1} \times \frac{0.4}{0.8} = \frac{3}{2}
\]

(if diffusion control, \( \eta \propto \frac{1}{\phi} \))

\[
\left( \frac{\phi_2}{\phi_1} = \frac{L_2}{L_1} = \frac{d_{p,2}}{d_{p,1}} = \frac{6}{2} = \frac{3}{1} \right)
\]

- Diffusion controls
Example 5: $A \xrightarrow{1st\ order} R$ (porous catalyst)

<table>
<thead>
<tr>
<th>$T (^\circ C)$</th>
<th>$d_p (\text{mm})$</th>
<th>$R_{obs} (g/L - s)$</th>
<th>$C_A (g/L)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>6</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>40</td>
<td>6</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>30</td>
<td>3</td>
<td>0.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

a) What controls?
b) True activation energy?

**Ans:** Choose 1-3 (constant temperature)

\[
\frac{\phi_1}{\phi_3} = \frac{d_{p1}}{d_{p3}} = \frac{6}{3} = \frac{2}{1}
\]

\[
\frac{\eta_1}{\eta_3} = \left(\frac{r_1}{r_3}\right)_{obs} \times \left(\frac{C_{A,3}}{C_{A,1}}\right)_b = \left(\frac{0.3}{0.2} \times \frac{1}{0.3}\right) = \frac{1}{2}
\]

\[
\eta \propto \frac{1}{\phi} \Rightarrow \text{pore – diffusion controls}
\]

Choose 1-2 (constant particle size): Increasing temperature at the same catalyst (particle) size – reaction will remain diffusion controlled (**it is an important statement**)

\[
R_{obs} = K_p C_{A,b} \ (or \ k_{obs} C_{A,b})
\]

\[
\frac{k_1}{k_2}_{obs} = \left(\frac{r_1}{r_2}\right)_{obs} \times \left(\frac{C_{A,2}}{C_{A,1}}\right)_b = \left(\frac{0.3}{0.3} \times \frac{0.1}{0.3}\right) = \frac{1}{3}
\]

\[
ln \left(\frac{k_1}{k_2}\right)_{obs} = -\frac{E_{obs}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)
\]

\[
E_{obs} = (1.098 \times 1.98)/\left(\frac{1}{303} - \frac{1}{313}\right) = 20.47 \ kcal/mol
\]

\[
E_{int} = 2E_{obs} = 40.94 \ kcal/mol
\]
\[ \ln\left(\frac{R_{\text{obs}}}{C_A}\right) \]

or

\[ \ln(K_p) \]

\[ \frac{1}{T} \]

\[ -\frac{E}{2R} \]

\[ -\frac{E}{R} \]

\( (\text{diffusion controls}) \)

\( (\text{kinetic controls}) \)

Lecture 26-27

Tubular packed bed reactor

So far, we did a single-particle analysis:

\[ \eta_{total} = \eta_{total}(n, D_a, \phi) : \text{isothermal} \]
\[ = \eta_{total}(n, D_a, \phi, \beta, \beta', Ar) : \text{non-isothermal} \]

\[ R_{obs} = \eta_{total} R_b (C_b, T_b) \]

Now, let us consider a packed bed reactor of catalyst particles, and determine the performance or design equation.

Rate expression: \( r_{intrinsic}(T, C) \). Let us assume isothermal condition.

Particles: \( d_p, \epsilon_\mu, \epsilon_m, \rho_p \ldots \) all physical properties are determined a priori.

Reactor: \( L, ID, \epsilon_b \) or catalyst amount = \( (1 - \epsilon_b)V \), where \( V \) is the reactor volume

Let us focus on the 1D species conservation balance equation over CV

\[ \Rightarrow v_z \text{ is determined from momentum balance equation} \ (v_z = \bar{v}_z \text{ in packed bed}) \]

\[ \rho_z \neq \rho_z(Z) \]

1D species balance on \( C_A \):

\[ v_z \neq v_z(r) : \text{a good assumption at high Reynolds number} \]
\begin{align*}
&\epsilon_b \frac{\partial C_A}{\partial t} + v_z \cdot \nabla C_A = D_z \nabla^2 C_A - (1 - \epsilon_b) (R_{\text{obs}}) \\
&\text{moles/s} - m^3 \\
&\text{of void} - m^3 \text{of total CV}
\end{align*}

Or, \( \epsilon_b \frac{\partial C_A}{\partial t} + \bar{v}_z \frac{dC_A}{dz} = D_z \frac{d^2 C_A}{dz^2} - (1 - \epsilon_b) (k C_A \eta_{\text{total}}) \)

\text{disposition coefficient}

\( C_A \neq C_A(r) \): narrow tube; \( +r_{A,i} = k C_A; \ R_{\text{obs}} = \eta_{\text{total}}(k C_A(z)) \)

Note that the traditional 1D species conservation equation written for a homogenous reaction system is modified by just one term, i.e. \( (1 - \epsilon_b) \eta_{\text{total}}! \) There is no other modification required!!

If you assume \( Re_p \) is large and there is no film resistance,

\( \eta_{\text{total}} = \eta_{\text{intra}} = \eta_{\text{intra}}(n, \phi) \)

In general: \( \eta_{\text{total}} = \eta_{\text{intra}} \left( \frac{c_s}{c_b} \right)^n \)

and \( \frac{c_s}{c_b} = \frac{c_s}{c_b}(D_a) \)

Alternatively, recall from previous lecture:

\[ R_{\text{obs}} = a \ k_m \left[ C_b - \left( \frac{R_{\text{obs}}}{k \eta_{\text{intra}}} \right)^{\frac{1}{n}} \right] \] 

\( \text{substitute intermediate } C_s \text{ in the previous eqn} \)

\( \eta_{\text{intra}} = \eta_{\text{intra}}(n, \phi) \)

\( \phi = L \frac{k C_s^{n-1}}{D_e} \)

Therefore, at this stage with the single-particle analysis already done \textit{a priori}, the conservation equation can be integrated with the necessary boundary conditions.

\[ \bar{v}_z \frac{dC_A}{dz} = D_z \frac{d^2 C_A}{dz^2} - (1 - \epsilon_b) (k C_A) \eta_{\text{total}} \]

\( z = 0, \ vC_A_0 = vC_A - D_z \left. \frac{\partial C_A}{\partial z} \right|_0^+ \) \( (C_A \neq C_A_0 \text{ because of the reaction}) \)

\( = L, \ \frac{\partial C_A}{\partial z} = 0 \) \( \text{(long-tube approximation)} \)
or \( vC_A - D_z \frac{\partial C_A}{\partial z} \bigg|_{L^-} = vC_{A,L} \) (interfacial flux balance)

Solve to get \( C_A(z) \) or \( C_A(z = L) \) or \( X_{AF} \): This is what a performance or design equation yields.

At this stage, you should have realized that the RTD study has taught us how to calculate or determine \( D_z \).

**Some discussion on 1-D vs 2-D:**

\[
D \nabla^2 C_A + \frac{D_r}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_A}{\partial r} \right) = 0 \quad \text{2 BCs}
\]

\[
r = 0 \quad \frac{\partial C_A}{\partial r} = 0; \quad \text{symmetric BC}
\]

\[
r = R - D_r \frac{\partial C_A}{\partial r} = 0; \quad \text{non-reactive/impervious walls}
\]

radial dispersion coefficient.

How about if the reaction is non-isothermal? Let us say that it is exothermic and heat is removed from the walls of the tube by convection or some cooling jacket provided on the reactor.

In such case a thermal energy balance equation is required:

\[
r_A = r_A(C_A, k(T)) \quad \text{and } T(z) \text{ depends on } r_A(-\Delta H)
\]

exothermic heat of reaction

Therefore, both species and energy balance equations are required, which must be solved simultaneously.

\[
v_z \nabla T = \alpha \nabla^2 T + \frac{(1-\epsilon_b)}{\rho C_p} (R_{obs})(-\Delta H)
\]

cal/\( S - m^3 \):

**1-D:**

\[
\frac{\partial T}{\partial z} = \alpha \frac{d^2 T}{dz^2} + \frac{(1-\epsilon_b)}{\rho C_p} (kC_A) \eta_{total}(-\Delta H)
\]

\[
\eta_{total}(n, C_A, T, \beta, \beta', Ar)
\]

axial thermal diffusion/dispersion coefficient

**BCs**

\[
z = 0 \quad T = T_o \quad \text{or} \quad \rho \overline{C_p \overline{v} T_o} = \left( \rho \overline{C_p \overline{v} T} - k \frac{\partial T}{\partial z} \right) \bigg|_{0^+}
\]

\[
z = L \quad \frac{\partial T}{\partial z} = 0 \quad \text{or} \quad \left( \rho \overline{C_p \overline{v} T} - k \frac{\partial T}{\partial z} \right) \bigg|_{L^-} = \rho \overline{C_p \overline{v} T_{exit}} \quad : \text{Flux balance}
\]

(long-tube approximation)
Here also, if $2-D$ 
\[ \alpha \quad \xrightarrow{\alpha_z \text{ and } 2 \text{ BCs are required}} \] 

Bc 1: 
\[ r = 0 \quad \frac{\partial \tau}{\partial r} = 0 \quad \text{(symmetric condition)} \]
\[ r = R - k \frac{\partial \tau}{\partial r} \left( \text{cal/s} - m^2 \right) = h(T - T_a) \]
\[ = q_{\text{cooling}} \]

or 
\[ T = T_w \quad \text{(specified)} \]

(Recall the constant wall temperature and constant heat flux cases in Transport Phenomena)

It is clear that you require the knowledge of transport conservation equation, in conjunction with kinetics to design a tubular reactor or $X(z = L) = ?$

**How about the empty tubular reactors whose walls are coated with a non-porous catalyst?**

Assume that $Re$ is large $\gg 2100$,
\[ \text{moles/s} - m^2: \quad r = kC_a \quad \text{(1st order)} \]
(at the walls)
\[ C_A \neq C_A(r): 1D \]

\[ \nu = \nu_z(r) \]

\[ C_A(z) \quad \text{(isothermal)} \]

\[ \text{moles/s} - m^3: \quad \nu_z \nabla C_A = D \nabla^2 C_A - (R_{obs}) \times a \quad \text{moles/s} - m^2 \quad \text{of tubular reactor} \]

\[ \frac{\partial C_A}{\partial z} = D_z \frac{\partial^2 C_A}{\partial z^2} - (kC_A) \frac{4}{D} \times \eta_{\text{inter}} \quad \text{eq. (1)} \]

\[ \eta_{\text{inter}} = \eta_{\text{inter}}(D_a) \]

(No intra – diffusional resistance; there is a thin coating of catalyst)

Alternatively,
\[ \frac{\partial C_A}{\partial z} = D_z \frac{\partial^2 C_A}{\partial z^2} + \frac{\partial r}{\partial z} \left( r \frac{\partial C_A}{\partial r} \right) \quad \text{(no reaction/source term because the reaction occurs at the walls)} \]
BCs: on z: same as before

\[ r = 0 \quad \frac{\partial C_A}{\partial r} = 0 \quad \text{(symmetry)} \]

\[ = R - D_r \frac{\partial C_A}{\partial r} = k_m (C_A - C_S) \quad \text{(interphase/film)} \]

\[
\text{moles} / S - m^2: = k C_S \quad \text{@ or near surface}
\]

\[ = \frac{kk_m}{k+k_m} C_A \]

If you consider \( C_A \neq C_A(r) \), the governing equation is to be modified as a 1D model:

\[
\bar{v}_z \frac{dC_A}{dz} = D_z \frac{d^2 C_A}{dz^2} - \left( \frac{kk_m}{k+k_m} \right) C_A \times a \quad \text{(m^2/m^3 of tubular reactor)}
\]

\[
\text{moles} / S - m^2 \quad \text{(same term appears in the main equation)}
\]

\[
\bar{v}_z \frac{dC_A}{dz} = D_z \frac{d^2 C_A}{dz^2} - \frac{4}{D} \left( \frac{kk_m}{k+k_m} \right) C_A \quad - \text{eq. (2)}
\]

You must realize equations (1) & (2) are the same!

What about installing a pre-heater and/or post-cooler?

Species balance in the segment \( l_2 \) will be the same as before?

One can also assume

\[
C_A(z = l_1) = C_{A_0} \quad \text{no reaction in pre – heater \& post – cooler.}
\]

\[
C_A |_{z=(l_1+1, l_2)} = C_A |_{z=(l_1+1, l_2)} \]

Energy balance over \( l_1 \):

\[
\rho_C v_z \nabla T = k \nabla^2 T \quad \text{(no source term)}
\]

\[
1-D: \bar{v}_z \frac{dT}{dz} = \alpha \frac{d^2 T}{dz^2} + q_{w,1} \times a/(\rho C_p)
\]

\[
T \neq T(r) \quad \text{heat flux} \quad m^2/m^3 \text{ of tube}
\]

\[
(\text{cal}/S - m^2)
\]
BCs: \( z = l_1 \) \( T = T_{\text{inlet}} \) to reactor

(known; to be specified/calculated)

In case of 2D, \(-k \frac{\partial T}{\partial r} = -q_w(\text{heat is supplied}): \text{cal/s} - m^2\)

↑

↑

\(note\ the\ sign\)

Energy balance over \( l_3 \):

\[
\overline{v}_z \frac{dT}{dz} = \alpha \frac{d^2T}{dz^2} - q_{w,3} \times a/(\rho C_p)
\]

BCs 1: \( T^+ (z = l_1 + l_2) = T^- (z = l_1 + l_2) \)

2: \( \nabla T = 0 \) @ \( z = (l_1 + l_2 + l_3) \)

In such problems interfacial boundary conditions are important @\( z = l_1, l_1 + l_2 \).

The general BC at interface:

\[
\begin{aligned}
&\left. \left( v_c - D \frac{dC}{dz} \right) \right|_{z^-} = \left. \left( v_c - D \frac{dC}{dz} \right) \right|_{z^+} \\
&\left. \left( \overline{\rho C_p v_T} - k \frac{dT}{dz} \right) \right|_{z^-} = \left. \left( \overline{\rho C_p v_T} - k \frac{dT}{dz} \right) \right|_{z^+}
\end{aligned}
\]

Flux (mass or thermal)

(Considering a broad applicability of such physical models, it is difficult to suggest any assignment or homework on this topic, yet you may try 11.2 of F&B....it is the simplest of all to solve!)
Many situations and BCs at the interfaces for $C_A$ and $T$:

1. **Most general**
   \[
   \begin{align*}
   \left( vc - D \frac{dC}{dz} \right)_{z^-} & = \left( vc - D \frac{dC}{dz} \right)_{z^+} \\
   \left( \bar{p} \bar{C}_p \nu T - k \frac{dT}{dz} \right)_{z^-} & = \left( \bar{p} \bar{C}_p \nu T - k \frac{dT}{dz} \right)_{z^+}
   \end{align*}
   \]

2. **Most simple**
   \[
   \nabla T = \nabla C = 0 \\
   T^+ = T^- \\
   C^+ = C^-
   \]

3. Mixed boundary condition with the gradient at the left of the interface set to 0

4. Mixed boundary condition with the gradient at the right of the interface set to 0

To this end, this lecture should teach you how to write transport equations in conjunction with kinetics, with the latter role limited to the calculations for $D_z$ (from RTD study) and Robs (or $\eta_{total}$) only!
Lecture 28

Deactivation (catalyst)

(1) Poisoning (impurities in the feedstock; they sit on the active sites & do not leave (chemical process), e.g. Li, S, Pb, Cd, P; trace amounts.

(2) Coking or fouling (deposit over the surface, cover the surface, pores): common in petroleum or hydrocarbon processing industries.

(3) Sintering – at high temperature (Pt/Al₂O₃) – catalyst particles migrate, and distribution is altered; crystallinity may also be changed.

Case 1: Uniform poisoning:

\[
\begin{align*}
A & \xrightarrow{k} R \quad (desired) \\
S & \xrightarrow{kp} S \quad (poisoned)
\end{align*}
\]

Over a long time

Case 1.1: Uniform poisoning:

How is rate impacted?

\[
C_{p,x} = C_{p,b} \times \sigma_p
\]

Note that if \(k\) has a unit of 1/s or 1/h, \(k_p\) have the unit of 1/month or 1/year; the time scale of poisoning is much longer than that of the primary reaction.

It is clear that if \(P \rightarrow S\) is slow or the rate of mass transfer to the catalyst surface is fast, deposition of poison on catalyst will be uniform.

\[
k = k_o(1 - \alpha) ; \quad \alpha = extent \ of \ poisoning
\]

\[
\eta = n(\phi) \Rightarrow \phi = L \sqrt{\frac{k_o(1 - \alpha)}{D_e}} \quad \alpha \equiv \frac{\text{# of sites poisoned}}{\text{# of original active sites}}
\]
\[ \alpha = \alpha(t), \text{ but rate of poisoning is much smaller over the characteristic reaction time.} \] 

Therefore, \( P \rightarrow S \) (slow; kinetic controlled; diffusion is fast)

**Two cases:**

a) \( A \rightarrow R \) **kinetic controlled** (reaction time-scale)

\[ \eta_{\text{total}} = \frac{R_{\text{obs}}}{(R)_{\text{w/o diffusion, poison}}} = \frac{\eta(k_o(1-\alpha)C_{A,b})}{k_oC_{A,b}}; \quad \eta = 1 \]

\[ = (1 - \alpha) \]

(b) \( \eta_{\text{total}} = \frac{R_{\text{obs}}}{(R)_{\text{w/o diffusion, poison}}} = \frac{\eta(k_o(1-\alpha)C_{A,b})}{k_oC_{A,b}} \]

considering \( \eta = \frac{1}{\phi} = \frac{1}{L} \sqrt{\frac{D_e}{k_o(1-\alpha)}} \), \( \eta_{\text{total}} \sim \sqrt{(1 - \alpha)} \)

\[ \sqrt{(1 - \alpha)} \quad \text{(diffusion – control; } \phi \text{ very large; } \eta = \frac{1}{\phi}) \]

\[ \frac{R_{\text{obs}}}{(R_{\text{obs}})_0} \]

\[ \alpha (\text{poison level}) \]

\[ \eta_{\text{total}} = (1 - \alpha) \]

In general, \( R_{\text{obs}} = R_{\text{obs}}(\alpha) \) (\( \alpha \) impacts 'k' over long period)

new parameter

\[ \frac{d\alpha}{dt} = k_pC_{p,b}(1 - \alpha) \] (Langmuir type of kinetics)

\( P \rightarrow S \) (kinetic rate constant)

sites unoccupied

bulk phase poison concentration

\( \{C_{p,b} \} \)
Case 2: **Shell-progressive poisoning** (shrinking core model)

\[ \alpha = 1 - \left( \frac{r_c}{r_o} \right)^3 \]

'\(t\)'is relatively longer time.

\[ \rightarrow a(t) \text{ or } r_c(t) \]

should be independently determined a priori before addressing the rate of the reaction \(A \rightarrow R\). For either reaction, \(A \rightarrow R\) or \(P \rightarrow S\), 'Shrinking – Core' type model is applied. You should revisit where it was discussed (@ UG level). Recall the reaction:

\[ CaO \text{ (core layer)} + SO_2 \rightarrow CaSO_3 \text{ (ash layer)} \]
\[
\frac{d}{dt} \left( \frac{4}{3} \pi (r_o^3 - r_c^3)C_{p,\infty} \right) \rho_s = 4\pi r_o^2 k_{m,p} (C_{p,b} - C_{p,s}^s) \\
\text{Avg. concentration of poison in shell (mole/m}^3) \\
= \frac{4\pi D_{e,p}}{\left( \frac{1}{r_c} - \frac{1}{r_o} \right)} (C_{p,s}^s - C_{p,s}^c) = 4\pi r_c^2 k_p C_{p,s}^c \\
\text{at the outer core} \quad \text{eq. (1)}
\]

(Note: You have made quasi-steady-state assumption in deriving the above equation)

Also, the 3\textsuperscript{rd} term (shell-diffusion equation) of eq. (1) originates from the general species balance equation:

\[
\begin{align*}
\begin{cases}
D_e \nabla^2 C_{p,s} = 0 & (r_o > r \geq r_c(t)) \\
BCs: r = r_o & -D_e \nabla C_{p,s} = k_{m,p} \left( C_{p,b} - C_{p,s}^s \right) \\
& = r_c & -D_e \nabla C_{p,s} = k_p C_{p,s}^c
\end{cases}
\end{align*}
\]

\[r_c(t) = ? \quad \text{Solve from eq. (1).}\]

There are three independent equations and three unknowns (variables): \(r_c, C_{p,s}^s, C_{p,s}^c\)

Superimpose \(r_c(t)\) on \(A \rightarrow R\) (reaction takes place in core)

There are two regions:

\textbf{A: Shell (poisoned layer):}

\[
D_e \nabla^2 C_{A,s} = 0 \quad (r_c \leq r \leq r_o) \\
r = r_o: -D_e \nabla C_A = -k_m (C_{A,b} - C_{A,s}^s)
\]

check the sign \quad \text{at the outer shell}
\[ r = r_c(t): -D_e \nabla C_A|_{r^+} = -D_e \nabla C_A|_{r^-} \quad \text{(if } D_e \text{ in shell } \equiv \text{ } D_e \text{ in cat, otherwise)} \]

**B: Core:**

\[ D_e \nabla^2 C_A = kC_A \quad (0 \leq r \leq r_c) \]

\[ r = r_c \quad -D_e \nabla C_A|_{r^+} = -D_e \nabla C_A|_{r^-} \]

(same as before or \( C_A^+ = C_A^- \))

\[ r = 0 \quad \nabla C_A = 0 \quad \text{(symmetry)} \]

**Solve:** \( C_A \equiv C_A(r_c(t)) \) and calculate \( \eta_{\text{total}} \) (at what level of poison concentration or \( r_c \) (poisoned layer))

\[
\eta = -4\pi r_o^2 \frac{D_e \frac{dC_A}{dr}|_{r=r_o}}{4/3 \pi r_o^3} \frac{kC_{A,b}}{R_{\text{obs}}} \]

[In a regular semester, these course materials are usually covered in 28 lectures of 1 h 15 min duration each, or 42 lectures of 50 min duration each. For record and due acknowledgement, most of these materials were part of my graduate level lectures delivered by my Ph.D. thesis supervisor (Prof. Farhang Shadman) way back in 1995 at the University of Arizona, Tucson, USA. At Kanpur, I offer this course to graduate students only. To this end, you are welcome to send me any comments, or mistakes or errors you notice in the lectures, to my email id: vermanishith@gmail.com.]
About the Author

Nishith Verma is currently the Chevron Corporation Chair Professor of chemical engineering at IIT Kanpur (India). Having pursued B. Tech in chemical engineering (1982-86) from IIT Kharagpur (India) and Ph.D. in chemical engineering (1991-95) from the University of Arizona, Tuscon, USA, Prof. Verma worked as a process engineer (1995-97) at BOC Gases (now Linde Engineering), NJ, USA, before joining IIT Kanpur as an assistant professor. His research interests are environmental remediation techniques, nanomaterials, catalysts, sensors, and lattice Boltzmann methods-based modelling. Prof. Verma is the recipient of Alexander von Humboldt Research Fellowship and Fulbright-Nehru Academic and Professional Excellence Fellowship. He was Head, Chemical Engineering Department, 2011 – 13 and Coordinator, Center for Environmental Science and Engineering, 2011 – 14, both at IIT Kanpur.

From the Author

ChE TRIAD e-Lecture Series materials were prepared during the pandemic when faculty were quarantined at home, and classes were held in online mode. It was a unique and first-hand experience for me to deliver online lectures. The online lectures ran for almost three academic years or six semesters. During that period, we also uploaded lecture materials at the Institute’s e-server, which students accessed. As an instructor, I taught Transport Phenomena, Finite Difference-based Numerical Methods, and Heterogeneous Chemical Reaction Engineering at the graduate level. The lecture materials that I prepared during the online classes have culminated in ChE TRIAD e-Lecture Series. Most of the Indian as well as foreign universities consider these three courses to be compulsory for graduate students. I hope that this e-lecture series are useful to readers, but I must caution students that they should not wholly depend on the materials covered in the series. Rather, they should refer the standard text books prescribed by their course instructors in regular offline classes. I have my opinion that a comprehensive understanding of the topics is possible only through the offline lectures. Thus, I have a plan to develop audio lectures in the near future, which will be instructive and recorded in sync with the present e-lectures. To this end, this effort is painfully dedicated to all the Covid warriors who risked their health and life in serving the people during the pandemic, while we enjoyed delivering online lectures at home.

December 2022, IIT Kanpur