Anton Paar

BASICS OF RHEOLOGY
Post Graduate Research Laboratory
IIT kanpur

1 Rheology and Viscous behavior

Drugstore (Apotheken) Museum
in Heidelberg, Germany

Rheology

to describe

deformation and flow behavior of all kinds of materials

rhei or rheo … to flow

Rheometry

measurement of rheological data

Rheology

is used to arrange materials in order.
Let's go through our common household items and line up all that we can find:

on the left - the liquids **on the right - the solids**

and in between - the semi-solid substances

1 Rheology and Viscous behavior

The Rheology Road

viscous — **viscoelastic** — **elastic**

ideal-viscous liquids
water, oils
Viscosity Law

viscoelastic liquids
glues, shampoos

viscoelastic solids
pastes, gels, elastomers

ideal-elastic solids
stone, steel
Elasticity Law

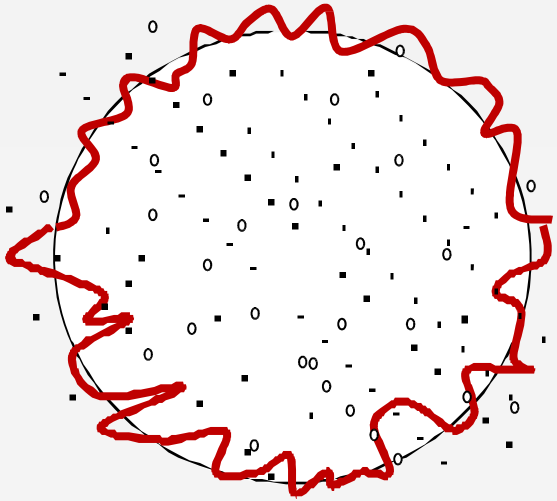
rotational tests

oscillatory tests

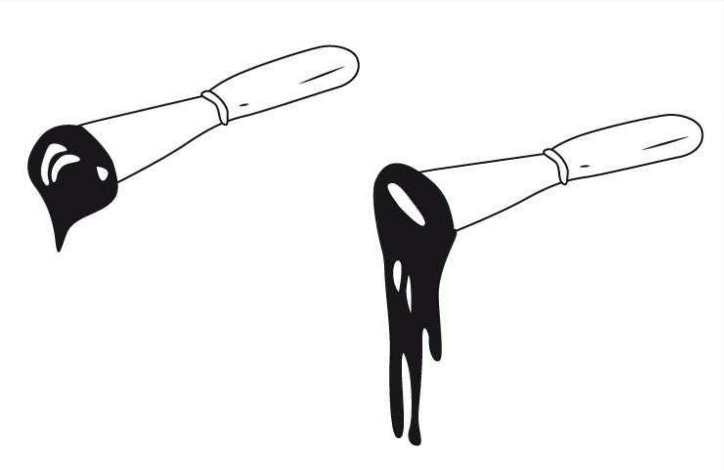
1 Rheology and Viscous behavior

What is viscosity ?

Internal friction or **flow resistance**
between the molecules and particles, when gliding along each other in a flowing state
(Newton in 1687: defectus lubricitatus)

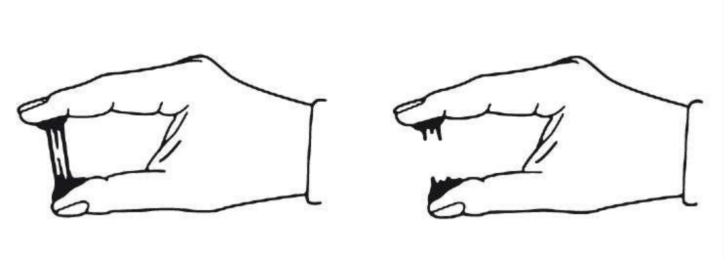


2 Simple Viscosity Tests



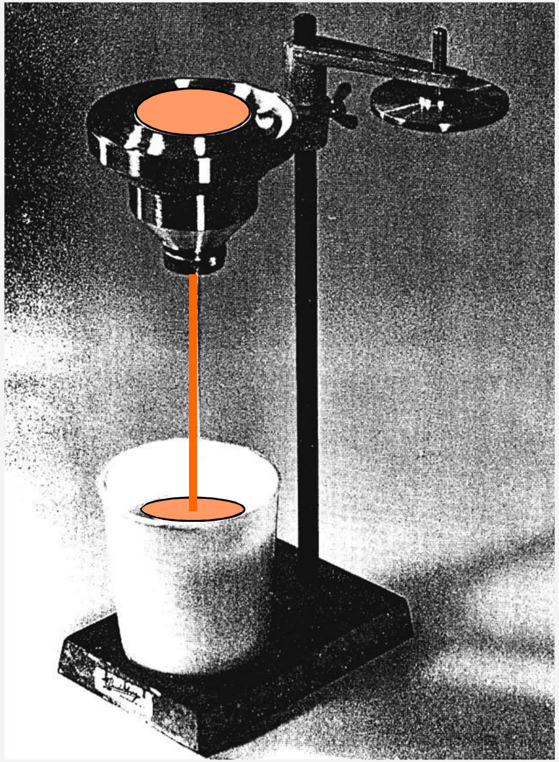
Trowel test

- highly viscous fluids: **thick**
- low-viscosity fluids: **thin**
  e.g. dispersions



Finger test

- tacky: **long**
- less tacky: **short**
  e.g. for adhesives, offset-printing inks, dough



Flow cups

Measurement
flow time
of low-viscosity liquids

Result:
kinematic viscosity
weight-dependent viscosity

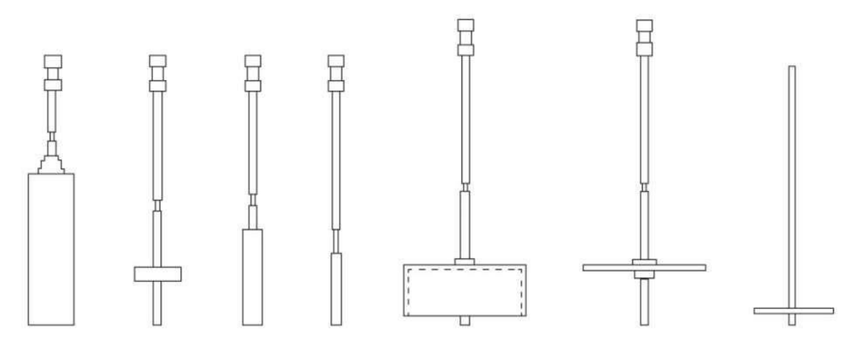
Examples:
oils, solvent-based coatings,
gravure and flexo printing inks

2 Simple Viscosity Tests

Rotational Viscometers

Preset:	rotational speed
Measurement:	torque

Example: **ViscoQC** by Anton Paar

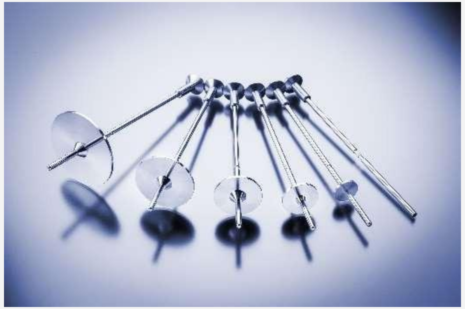


Relative Viscosity Values

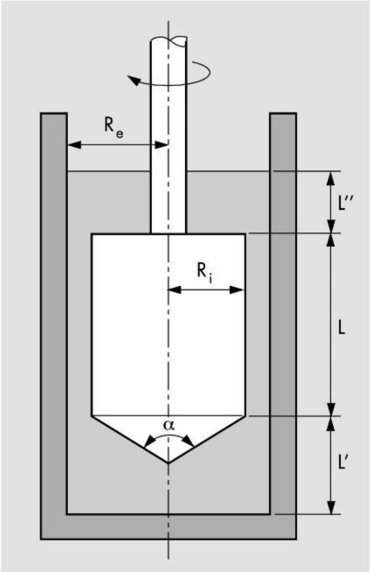
- ISO 2555
- ISO 3219-2

Typical Spindles:

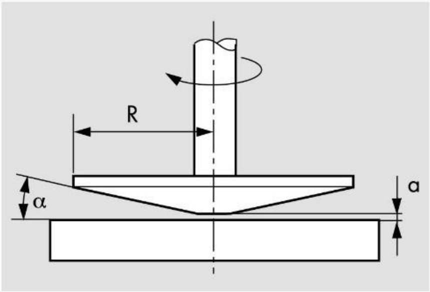
- cylinders
- disks
- T-bars
- pins



Absolute measuring geometries (ISO 3219-2 and DIN 53019)



concentric cylinders, CC
low-viscosity liquids



cone / plate, CP
liquids, dispersions
limited particle size

Example: CP 25-1; **a** = 50 µm,
max. particle size 10 % of **a**

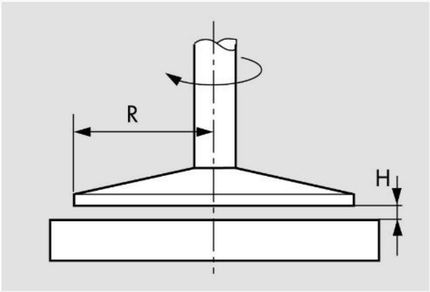
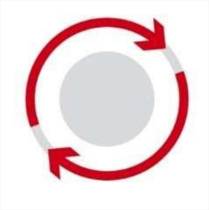


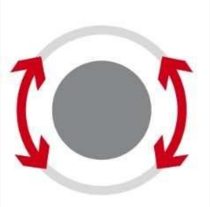
plate / plate, PP
gels, pastes, soft solids,
polymer melts

3 Rheometers and Measuring Geometries



rotation

- shear tests
- tensile tests



oscillation

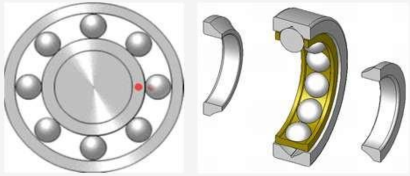
- shear tests
- torsional tests
- tensile tests

3 Rheometers and Measuring Geometries

Rheometers - each drive requires a bearing

Ball Bearing

- inner ring (rotor)
- rolling element (e.g. balls, cylinders, cones)
- outer ring (stator)



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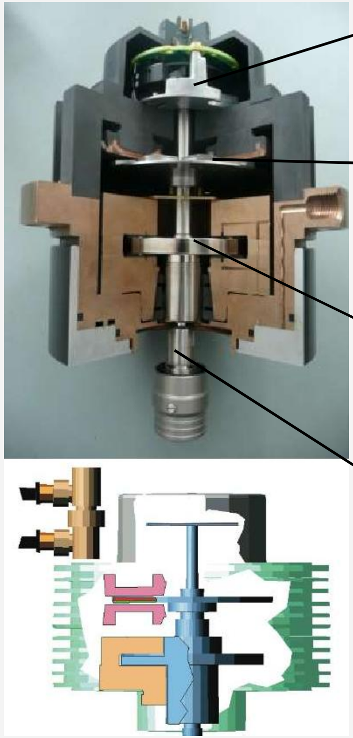

1 Encoder
opto-electronical
detection of deflection angle

2 Measuring drive
electro-motor, torque detection

3 Air Bearing
radial and axial: pressurized air between disc (rotor) and porous graphite (stator)
An air bearing is up to 400 000 times more sensitive than a ball bearing!

4 Motor shaft
coupling for measuring geometries

4 Definitions: Shear Stress, Shear Rate, Viscosity

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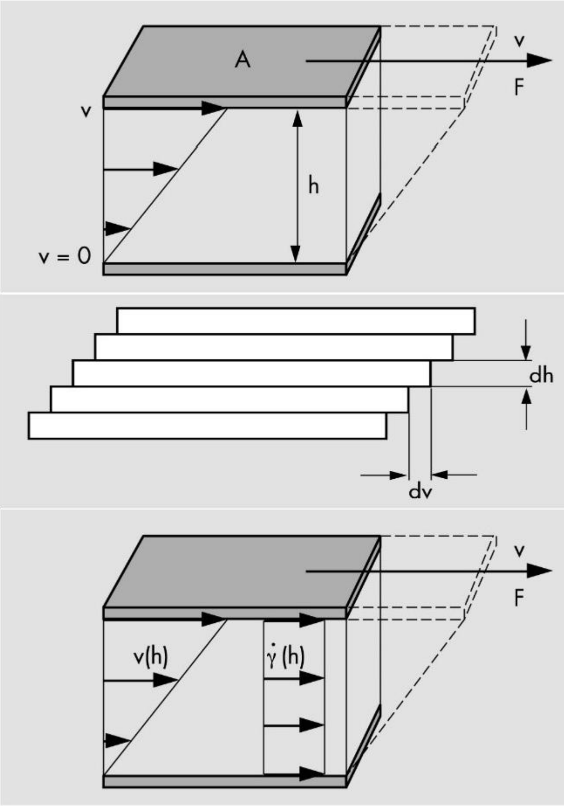


The two-plates model

shear stress $\tau = F / A$

unit: $1\ N / m^2 = $ **1 Pa**

shear rate $\dot{\gamma} = v / h$

unit: $1\ m / (s \cdot m) = $ **$1 / s = 1\ s^{-1}$**

Requirement: **Laminar flow**
in contrast to **Turbulent flow**

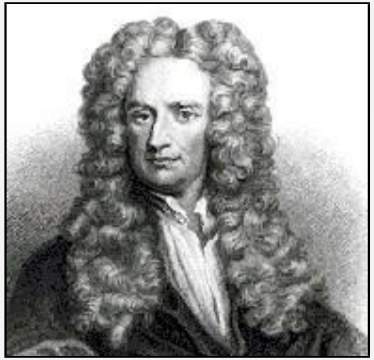
$\dot{\gamma} = dv / dh = const / const = const$

→ *e-learning (laminar, 2-P-M)*

→ *movie (peas)*

→ *movie (turbulence)*

4 Definitions:
Shear Stress, Shear Rate, Viscosity



Isaac Newton
(1643 to 1727)
wrote about the
flow resistance
of fluids
(e.g. of air and water).

This was later known as:
Viscosity Law "of Newton"
was formulated in the 19. century
(e.g. by G.G. Stokes in 1845).

(shear) viscosity

$$\eta = \tau / \dot{\gamma}$$

unit: 1 Pa / (1/s) = **1 Pas = 1000 mPas**

Previously used unit (not SI):
1 cP (centi-poise) = 1 mPas

5 Rotational Tests

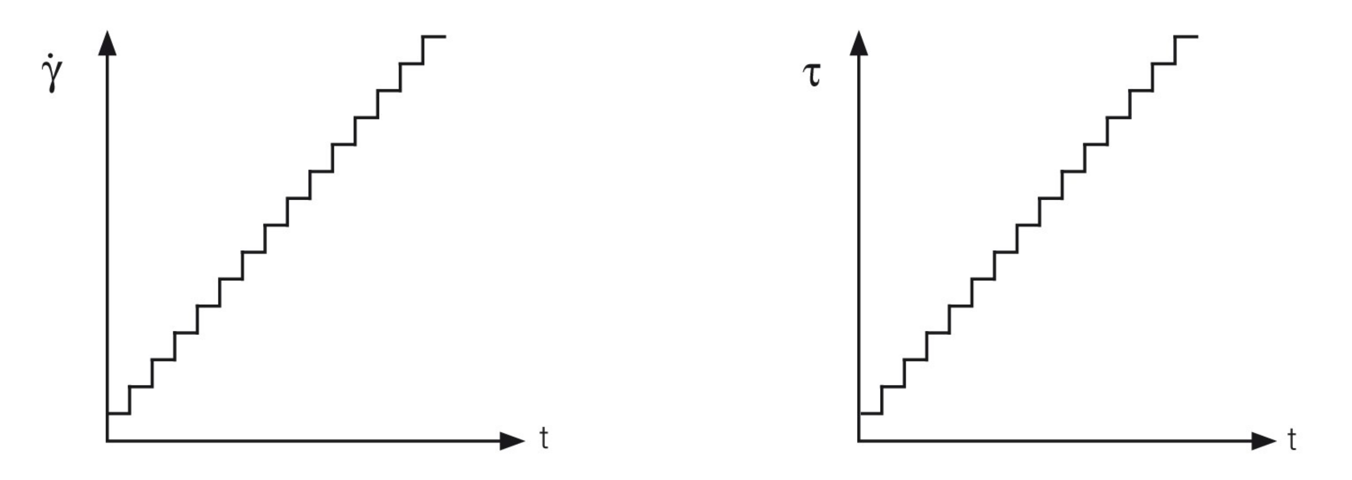
rotation CSR controlled shear rate	test preset		result	
raw data	**rotational speed n**	[min^{-1}]	**torque M**	[Nm]
rheological parameters	shear rate $\dot{\gamma}$	[s^{-1}]	shear stress τ	[Pa]

rotation CSS controlled shear stress	test preset		result	
raw data	**torque M**	[Nm]	**rotational speed n**	[min^{-1})
rheological parameters	shear stress τ	[Pa]	shear rate $\dot{\gamma}$	[s^{-1}]

torque M: 1 Nm = 1000 mNm = 1,000,000 µNm = 1,000,000,000 nNm

For each measuring geometry there are **two conversion factors**: $M \rightarrow \tau$ and $n \rightarrow \dot{\gamma}$

5 Rotational Tests



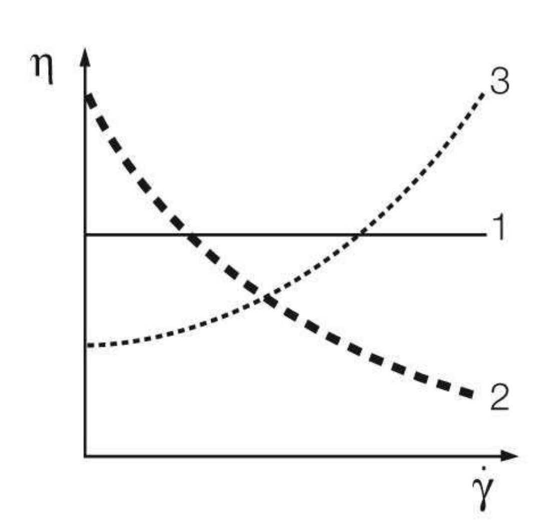
rotational speed preset

shear rate ramp
step-like upwards or downwards
CSR: controlled shear rate

torque preset

shear stress ramp
step-like upwards or downwards
CSS: controlled shear stress

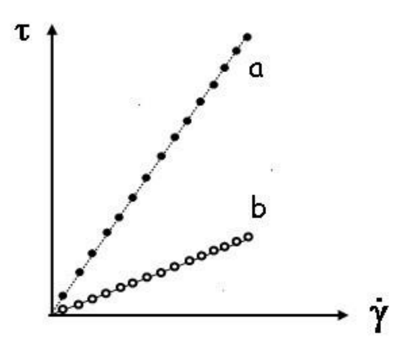
6 Flow Behavior

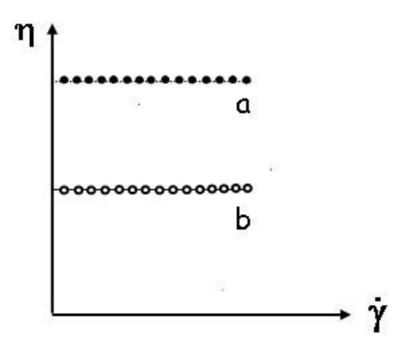


Viscosity curves

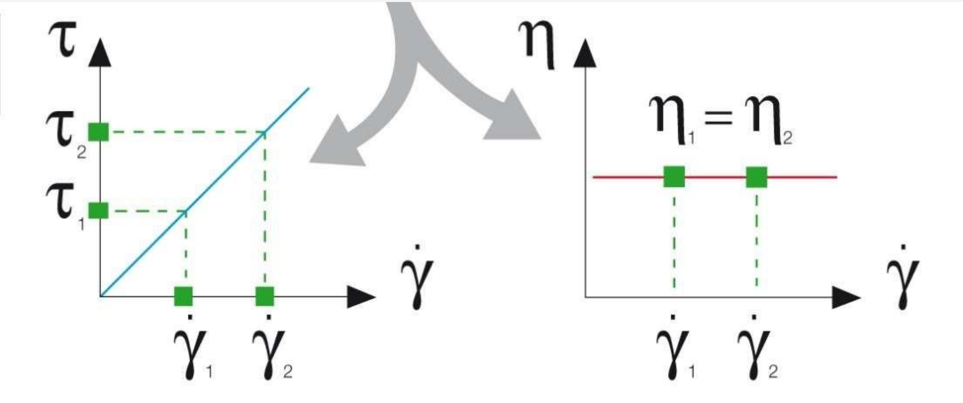
1	ideal-viscous	(Newtonian)
2	shear-thinning	(pseudoplastic)
3	shear-thickening	(dilatant)

ideal-viscous / Newtonian flow behavior



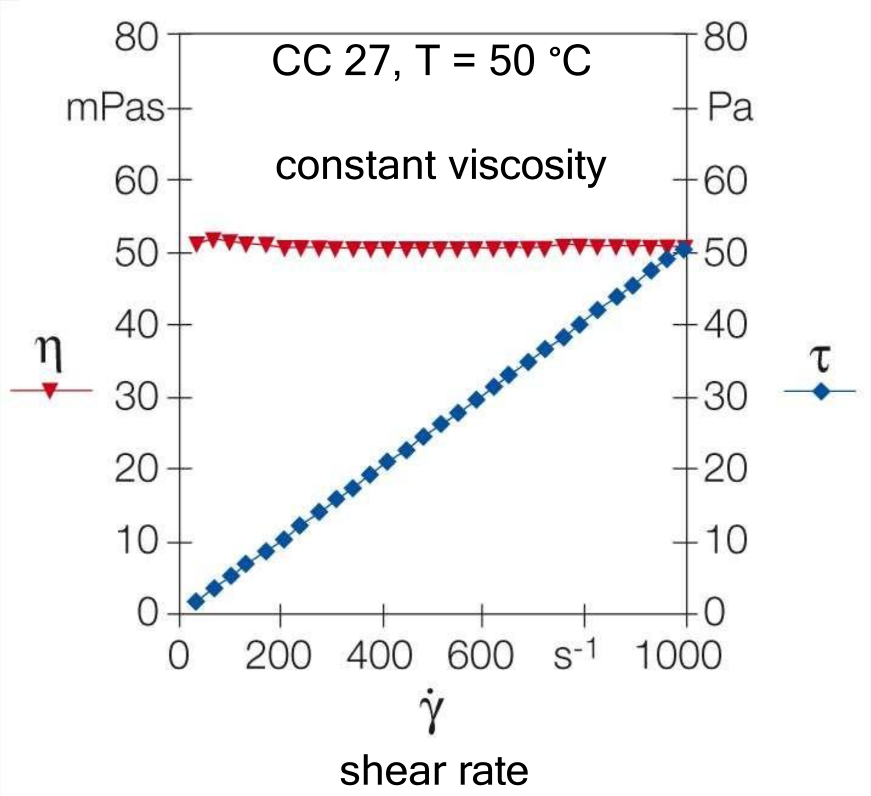


flow curves



viscosity curves

6 Flow Behavior



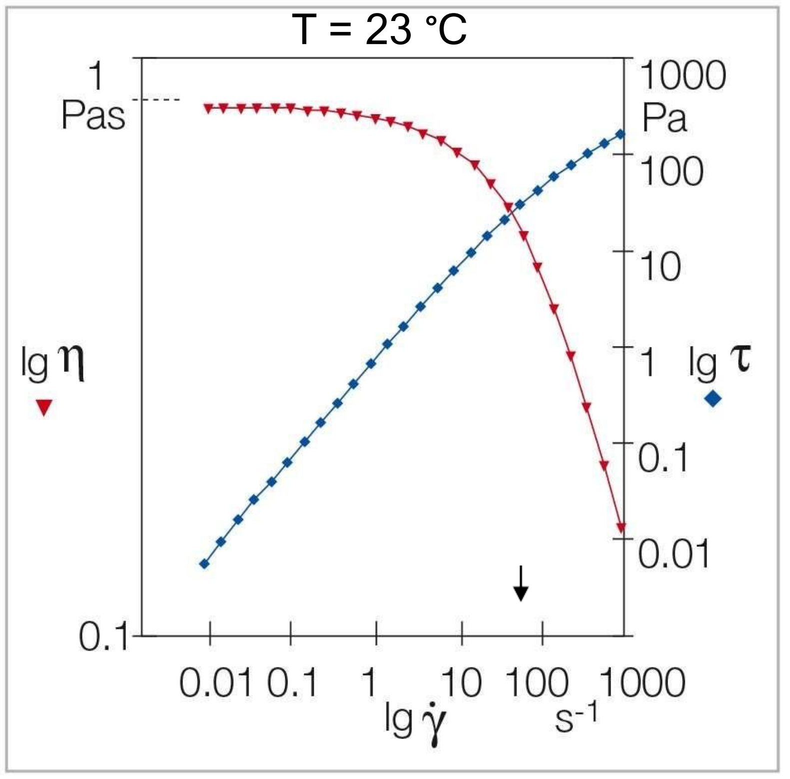
viscosity

shear stress

Mineral oil

concentric cylinders measuring geometry, CC

6 Flow Behavior



Wall paper paste

aqueous
methylcellulose
solution

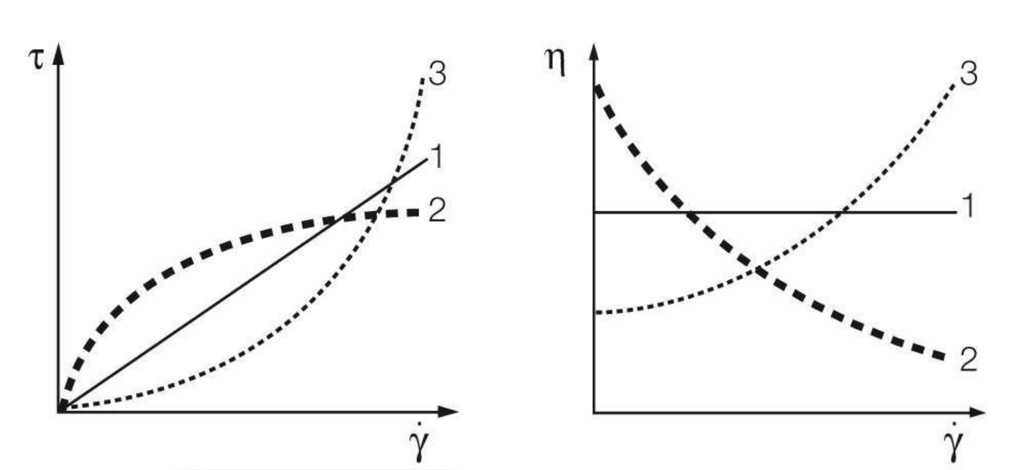
uncrosslinked polymer

for $\dot{\gamma} < 0.1\ s^{-1}$
plateau of the zero-shear viscosity

logarithmic scale
focus on low-shear range

6 Flow Behavior

flow curves **viscosity curves**



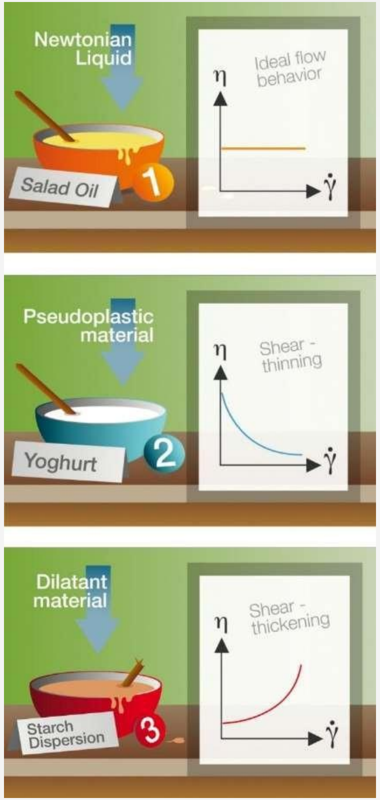
1	ideal-viscous	(Newtonian)
2	shear-thinning	(pseudoplastic)
3	shear-thickening	(dilatant)

6 Flow Behavior

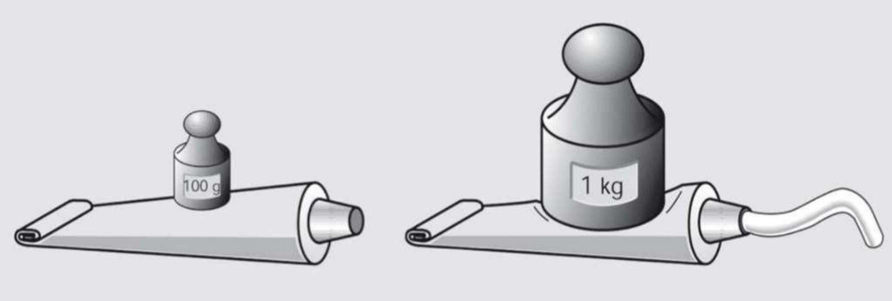
Flow curves
and
viscosity curves

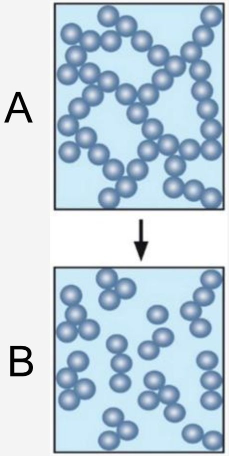
(1) ideal-viscous
(2) shear-thinning
(3) shear-thickening

→ *e-learning*
(the stirring chefs)



7 Yield Point



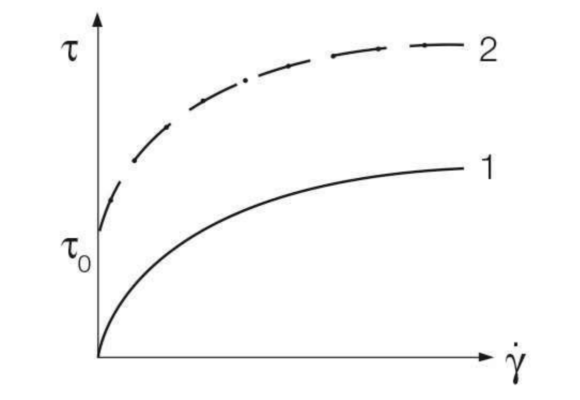


Yield point as the limiting value of the shear stress

(A) super-structure as a **physico-chemical network** of **interactive forces**

(B) break of the structure-at-rest

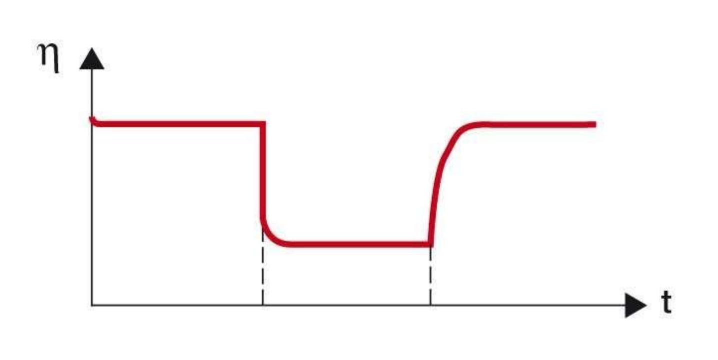
Yield point determination via flow curves on a linear scale



(1) without a yield point

(2) yield point τ_0 as interception with the τ - axis

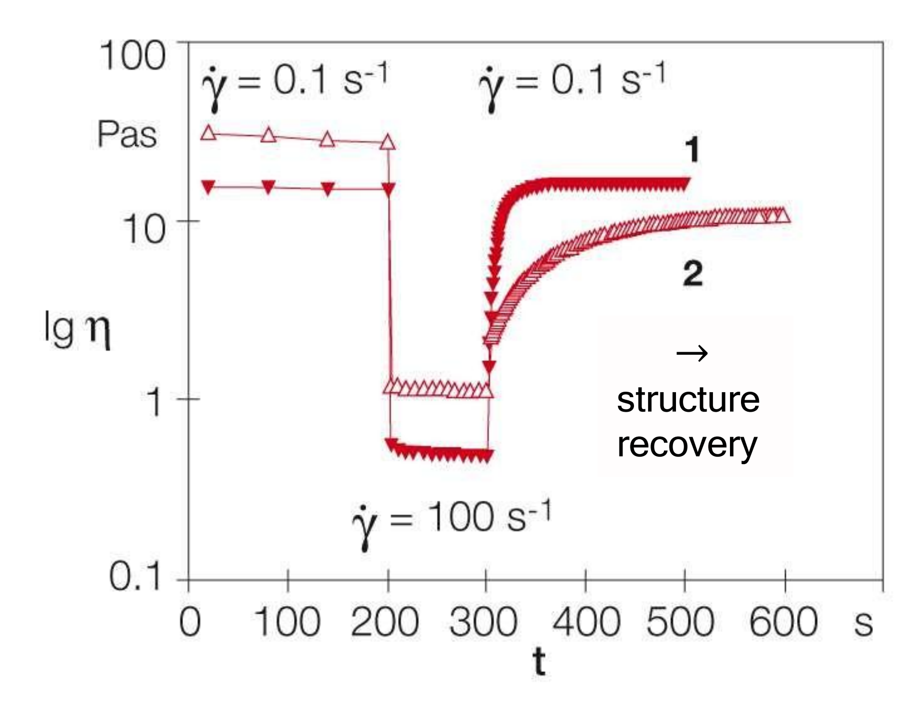
9 Time-dependent Behavior (Rotation)



Structure recovery, step test

Determination of **thixotropic behavior**
(3ITT, 3 interval thixotropy test)

interval	preset shear rate	result	viscosity
1	low	(close to) state of rest	high
2	high	structure break	low
3	low	structure recovery	increasing



Coatings

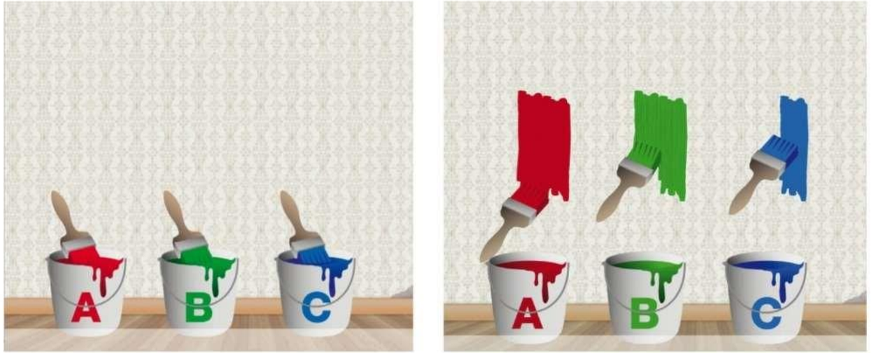
(1) with gellant
fast structural recovery

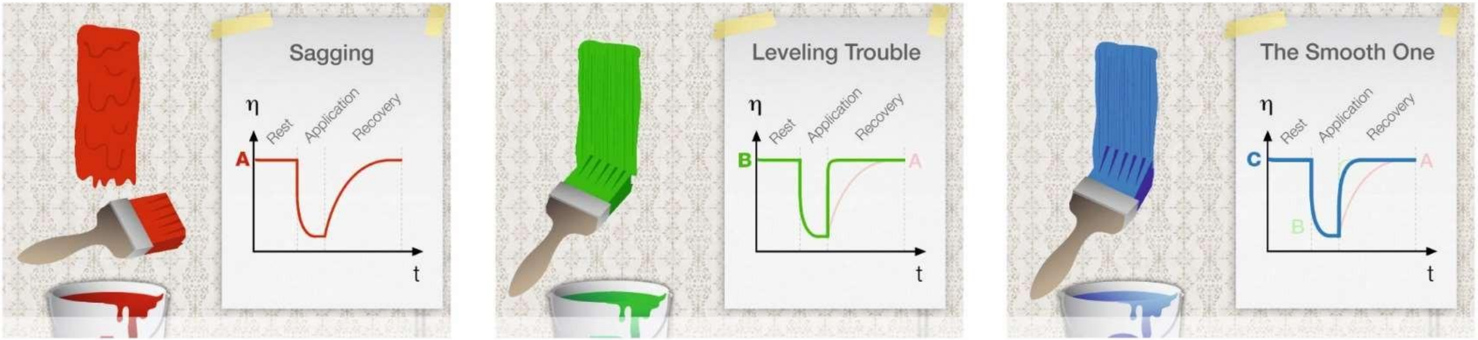
- **less sagging**
- **high wet-layer thickness**
- maybe poor leveling

(2) with viscosifier
slow structural recovery

- **good levelling**
- maybe too much sagging

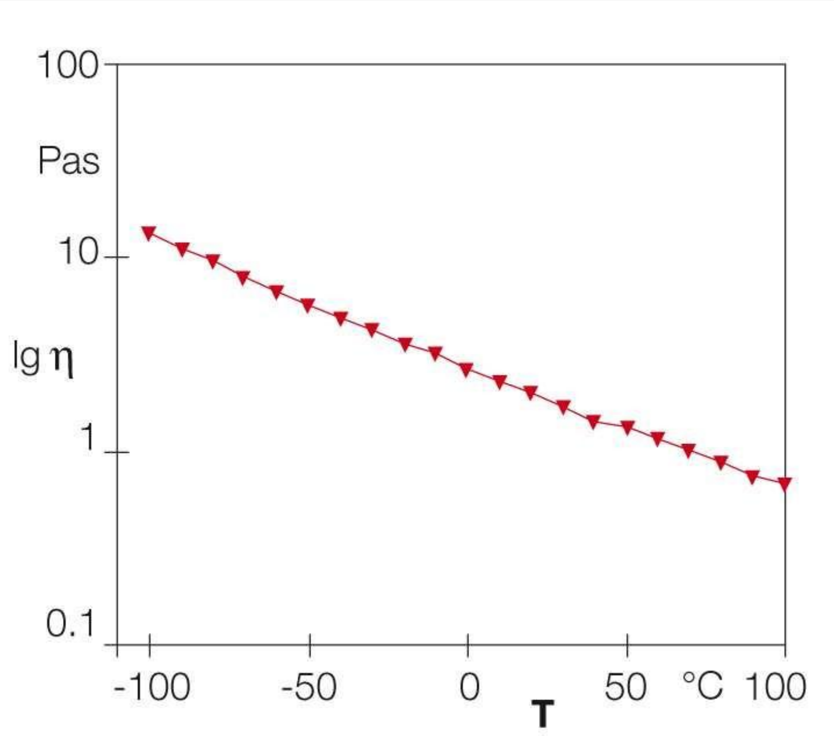
9 Time-dependent Behavior (Rotation)





→ *e-learning*
(brushing of 3 paints)

10 Temperature-dependent Behavior (Rotation)



Silicone oil

Heating:
viscosity decrease

Without phase change:
Linear viscosity functions
in semi-logarithmic
log η / lin T diagram

The Rheology Road

viscous	viscoelastic	elastic

ideal-viscous liquids
water, oils
Viscosity Law

viscoelastic liquids
glues, shampoos

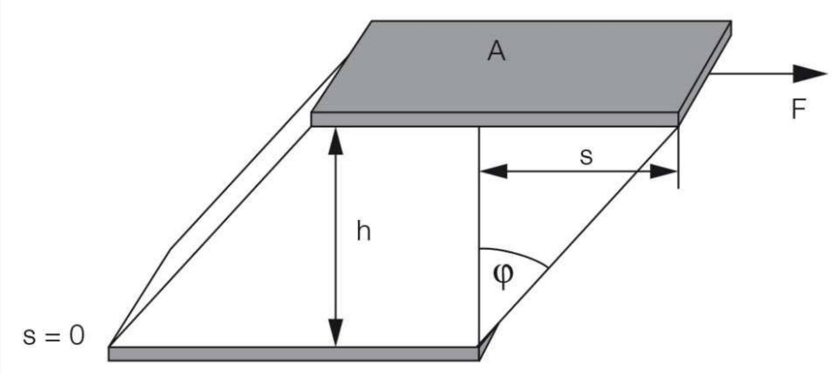
viscoelastic solids
pastes, gels, elastomers

ideal-elastic solids
stone, steel
Elasticity Law

rotational tests

oscillatory tests

12 Definitions:
Deformation, Strain, Shear Modulus



Two-plates model

shear stress

$$\tau = F / A$$

unit: 1 N / m² = **1 Pa**

shear deformation or **shear strain**

$$\gamma = s / h$$

unit: 1 m / m = **1 = 100 %**

12 Definitions: Deformation, Strain, Shear Modulus

Robert Hooke (1635 to 1703),
in 1676 he states **for solids proportionality of force and deformation**.

The later so-called
Elasticity Law of Hooke
was formulated in the
19. century (e.g. by T. Young in 1807, or A.L. Cauchy in 1827).

Shear modulus

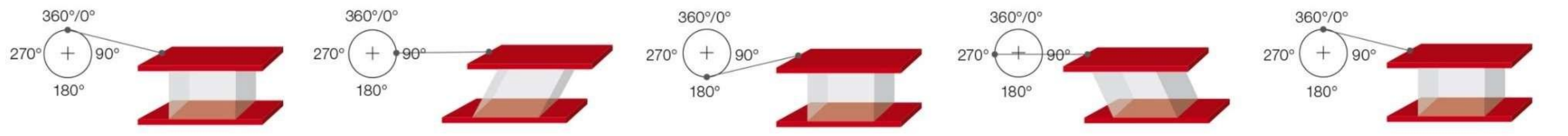
$$G = \tau / \gamma$$

unit: (1 Pa / 1 =) **1 Pa**

1 GPa = 1000 MPa = 10^6 kPa = 10^9 Pa

Giga-pascal, Mega-pascal, kilo-pascal

spring force	F
deflection path	s
spring constant	C (stiffness)
law of springs:	F / s = C



Two- plates model, equipped with two sensors,

top preset of deflection path (strain or deformation)

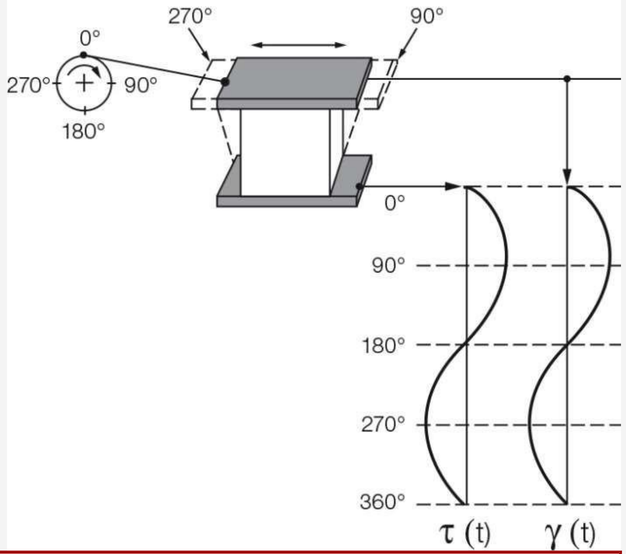
bottom measurement of resulting force (shear stress)

sinusoidal preset

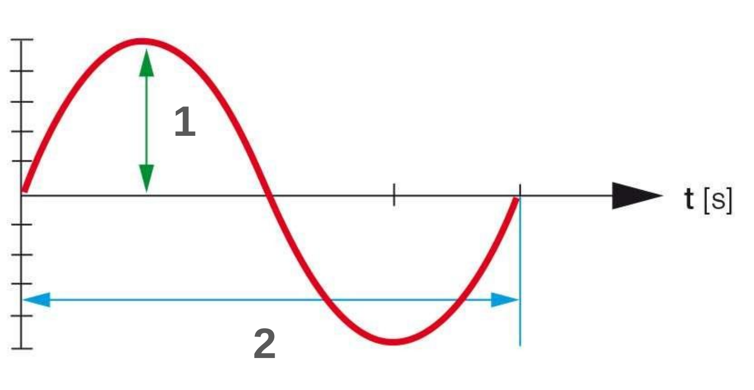
ideal-elastic behavior

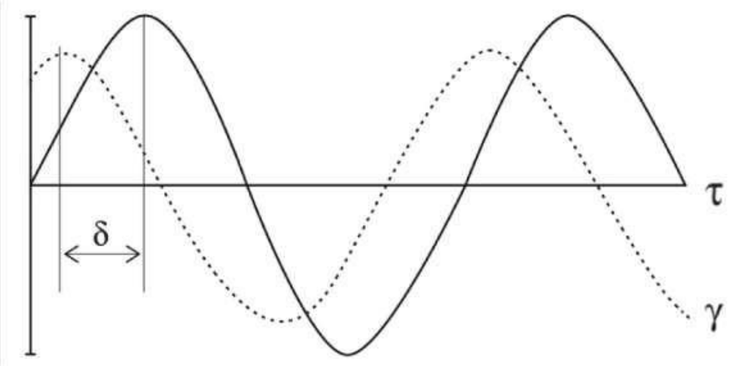
stiff sample (e.g. a stone or steel):
no time shift between the sine curves of preset strain and resulting shear stress:

the curves of γ and τ are "in phase"



→ *movie (2-plates-model, ideal-elastic behavior)*





Preset
constant amplitude (1) and constant frequency (2)

Result
Most samples show
viscoelastic behavior
with a
phase shift δ
between the maxima of the sine curves as the
retardation of the measuring response
compared to the preset.

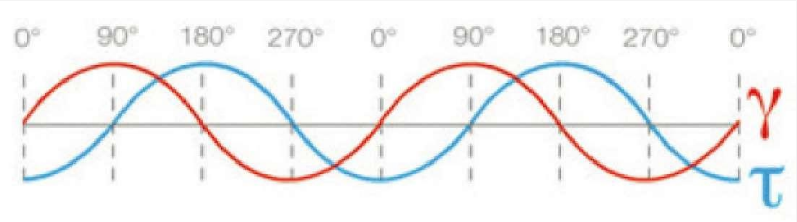
→ *movie (2-plates-model, viscoelastic behavior)*

ideal-viscous behavior
fluid, liquid: **90° ≥ δ > 45°**

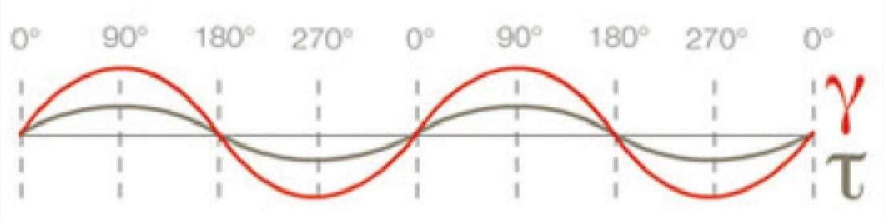
and

ideal-elastic behavior
solid, gel-like: **45° > δ ≥ 0°**

Illustrative concept: δ as the "street number in Rheology Road"



ideal-viscous: **δ** = 90°



ideal-elastic: **δ** = 0°

Vector diagram

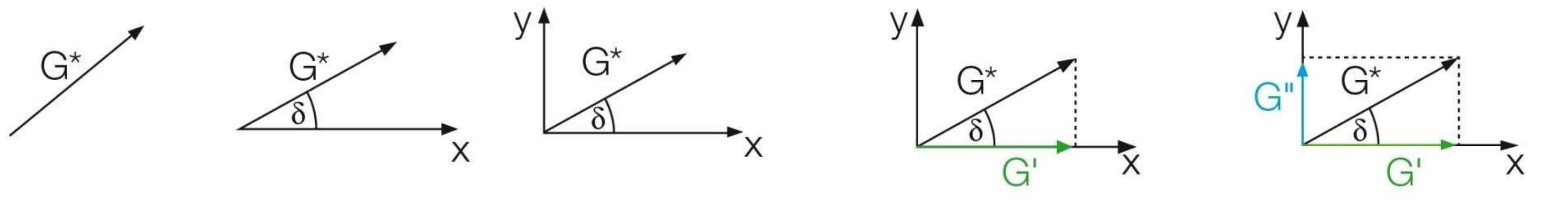
to determine the parameters G' and G'' based on the Elasticity Law

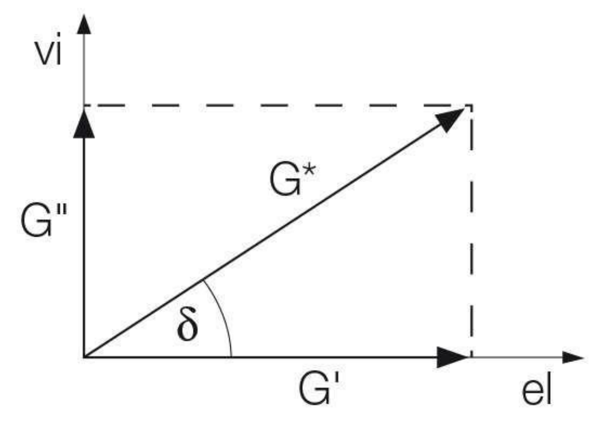
- preset of y_A
- measurement of τ_A and phase shift angle δ (index A for amplitude)

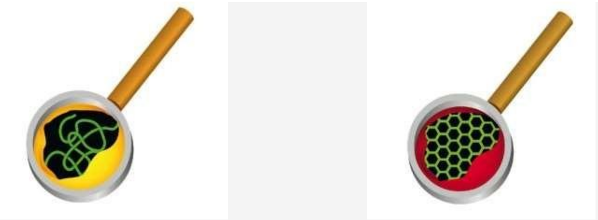
Calculation:

complex shear modulus G*

$$G^* = \tau_A / y_A$$







Molecules
left: freely moveable, uncrosslinked
right: crosslinked

Vector diagram

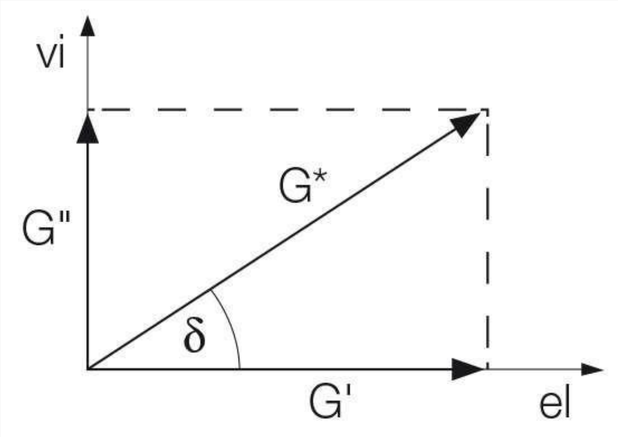
G* **complex shear modulus, viscoelastic behavior in total**

G' **(shear) storage modulus, elastic shear modulus**

G" **(shear) loss modulus, viscous shear modulus**

G' (G-prime) for the **stored**,
G" (G-double prime) for the **lost** (dissipated)

deformation energy
internal friction when flowing



$\tan\delta$ = G''/ G'

loss factor (or **damping factor**)

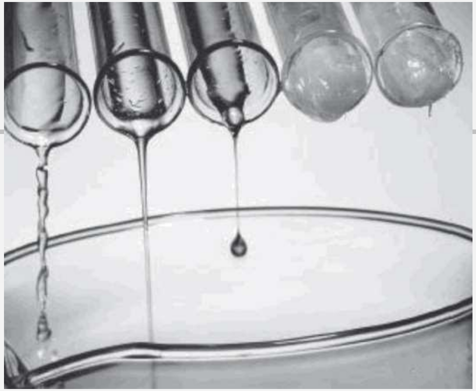
tangent delta
unit: dimensionless (or 1)

“viscoelastic ratio”

of viscous and elastic portions

use case
point of phase transition

G' = G'' or **$\tan\delta$ = 1** or **δ = 45°**



viscous		viscoelastic		elastic
G'' >> G'	G'' > G'	G'' = G'	G' > G''	G' >> G''
liquid, fluid state		sol / gel transition	gel-like, solid state	

tanδ = G'' / G'				
tanδ >> 1 → ⍰	tanδ > 1	tanδ = 1	tanδ < 1	tanδ << 1 → 0

ideal-viscous: tanδ > 100:1 = 100
for scientists: tanδ > 1000

ideal-elastic: tanδ < 1:100 = 0.01
for scientists: tanδ < 0.001

Source: Society of Cosmetic Chemists: Viscosity, Rheology and Rheology Modifiers

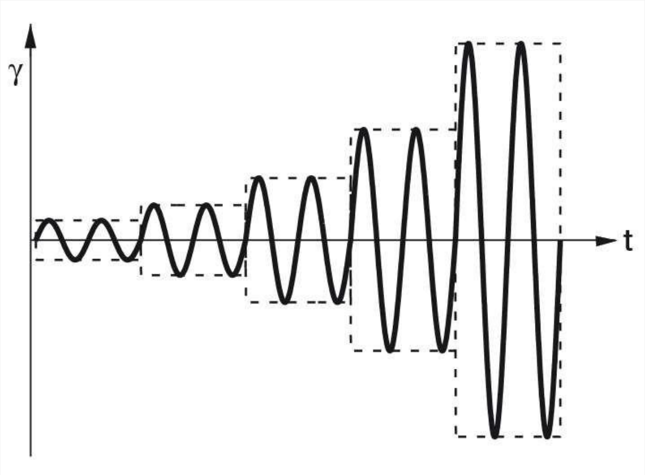
Anton Paar

Oscillation CSD **contr. shear deformation**	**test preset**		**result**	
raw data	**deflection angle φ(t)**	[rad]	**torque M(t)** **phase shift δ**	[Nm] [degrees]
rheological parameters	Deformation/strain γ(t)	[%]	shear stress τ(t) phase shift δ	[Pa] [degrees]

Oscillation CSS **controlled shear stress**	**test preset**		**result**	
raw data	**torque M(t)**	[Nm]	**deflection angle φ(t)** **phase shift δ**	[rad] [degrees]
rheological parameters	shear stress τ(t)	[Pa]	deformation/strain γ(t) phase shift δ	[%] [degrees]

φ in degrees or in 1 rad; 360° corresponds to 2π rad

15 Amplitude Sweeps



Preset

constant frequency

(e.g. angular frequency **x** = 10 rad/s)

variable strain (deformation)

strain sweep

or variable stress

stress sweep

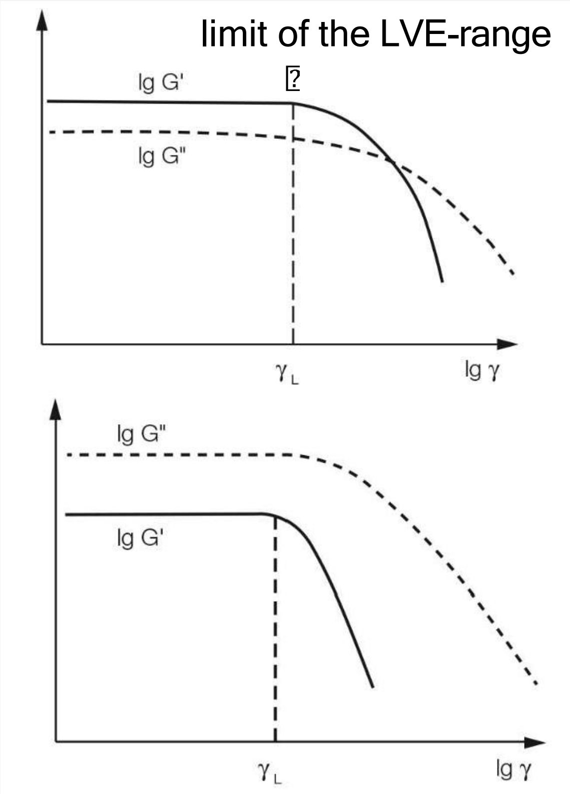
Frequency conversion: **x = 2π f**

with **angular frequency x in rad/s** (or s^{-1}) and **frequency f in Hz**

Please note: Hz is not a SI unit.

→ *movie (amplitude sweep)*

15 Amplitude Sweeps



Result

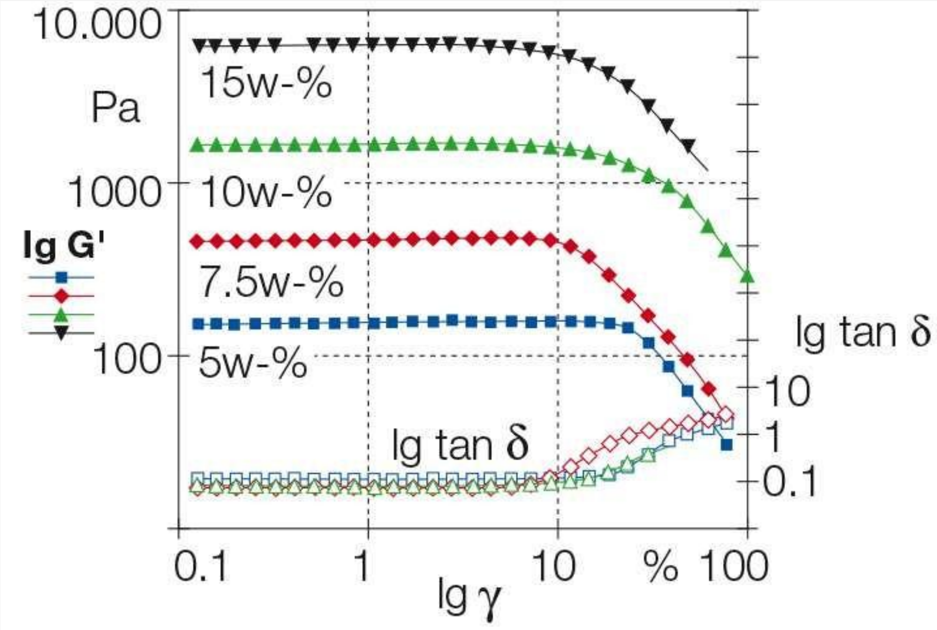
storage modulus **G'** (elastic behavior)
loss modulus **G''** (viscous behavior)

limiting value of the
linear viscoelastic (LVE-) range when reaching y_L
linearity limit of shear strain

at **given** conditions,
i.e., at the **preset** frequency

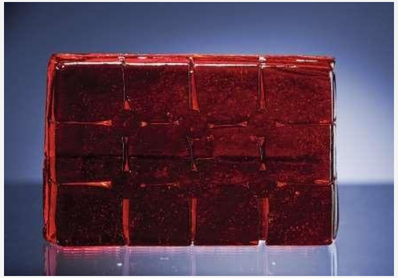
in the LVE-range
top: **G' > G'' (gel-like, solid structure)**
bottom: **G'' > G' (liquid, fluid structure)**

15 Amplitude Sweeps



ω = 10 rad/s, T = 23 °C

Starch gels
in water



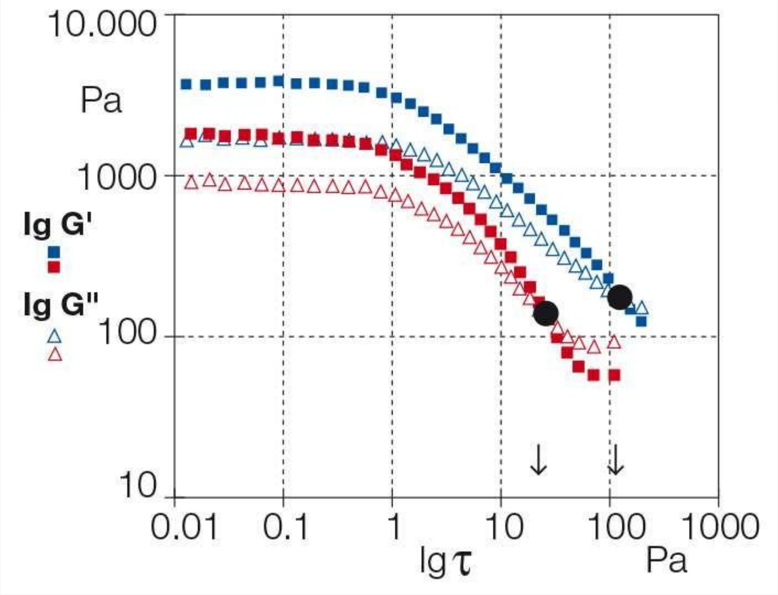
gel strength
as the G'-value in the LVE-range

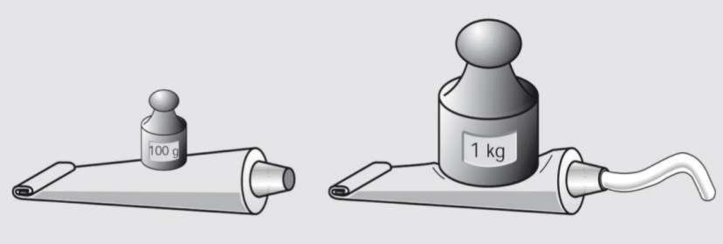
First check:

LVE-range: tanδ < 1 for all samples
(= gel-like structure)? Yes !

tanδ = G'' / G'

15 Amplitude Sweeps





Tooth pastes

paste 1

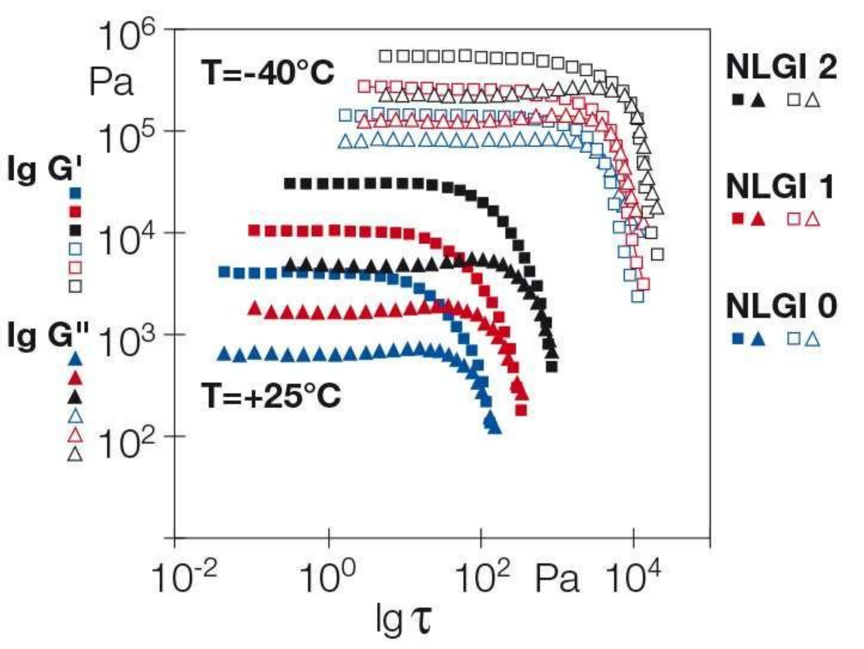
flow point τ_f = 125 Pa

paste 2

flow point τ_f = 24.9 Pa

the same yield point (linearity limit), but different flow points

15 Amplitude Sweeps

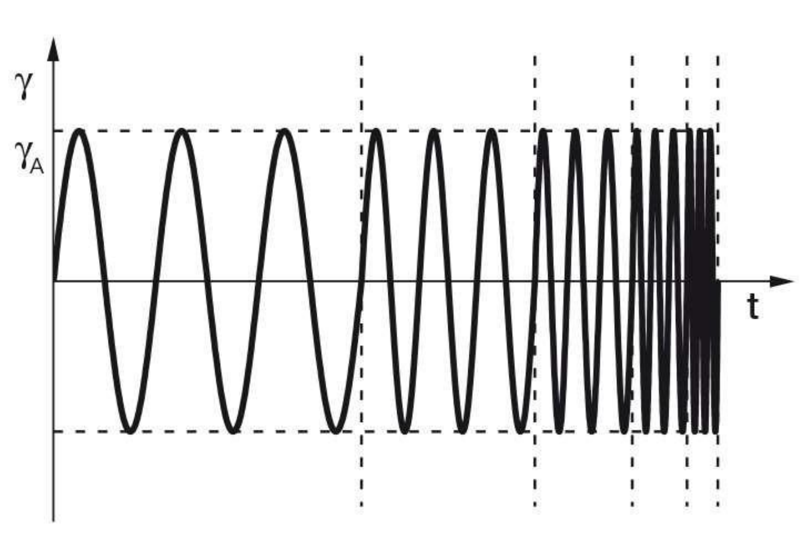


Lubrication greases
flow point τ_f
acc. to DIN 51810-2
crossover point G' = G''

NLGI classification	T = +25 °C	T = -40 °C
NLGI 0	100 Pa	5 kPa
NLGI 1	200 Pa	7 kPa
NLGI 2	400 Pa	10 kPa

Consistency according to *NLGI*-classification (*National Lubrification Grease Institute*, USA) via pen-values, using a penetrometer

16 Frequency Sweeps



Preset

constant amplitude

shear strain (or shear stress)
within the LVE-range

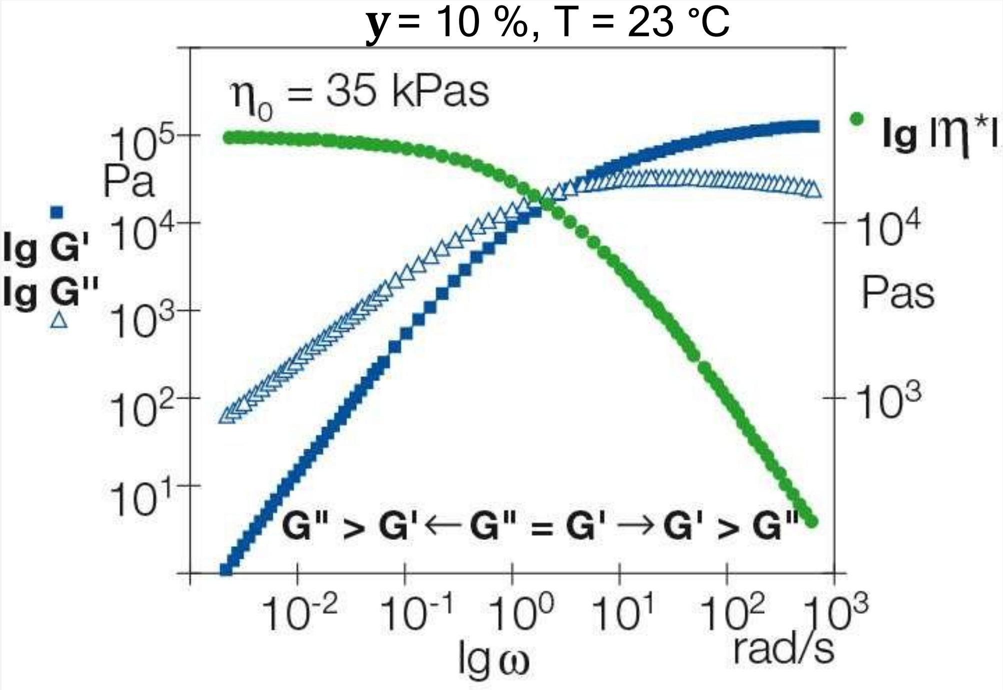
and

variable frequency

Precondition:
LVE-range has been checked by an amplitude sweep.

→ *movie (frequency sweep)*

16 Frequency Sweeps



PDMS
poly-
di-methyl
siloxane

typical behavior of
uncrosslinked polymers
showing a crossover point G' = G''

Anton Paar

Thank you.