# Of Small Things and Other Stories

## C. N. R. Rao Lecture, IIT Kanpur, April 13, 2004

**Ashutosh Sharma**

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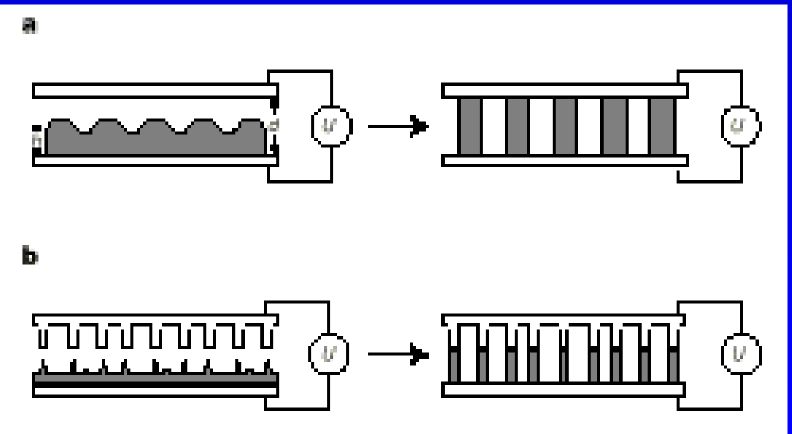
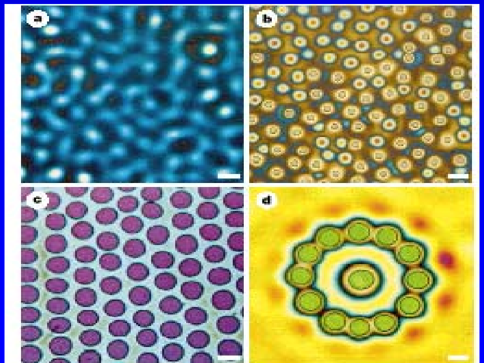
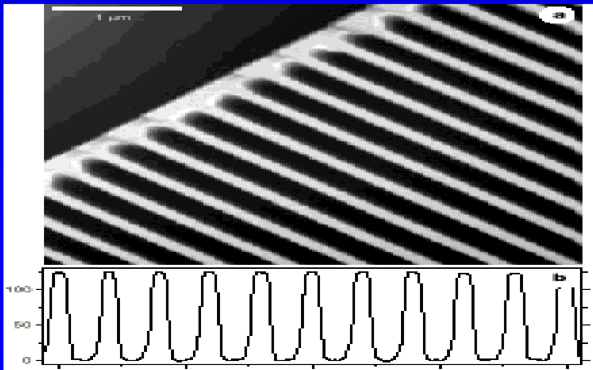
*Indian Institute of Technology, Kanpur*

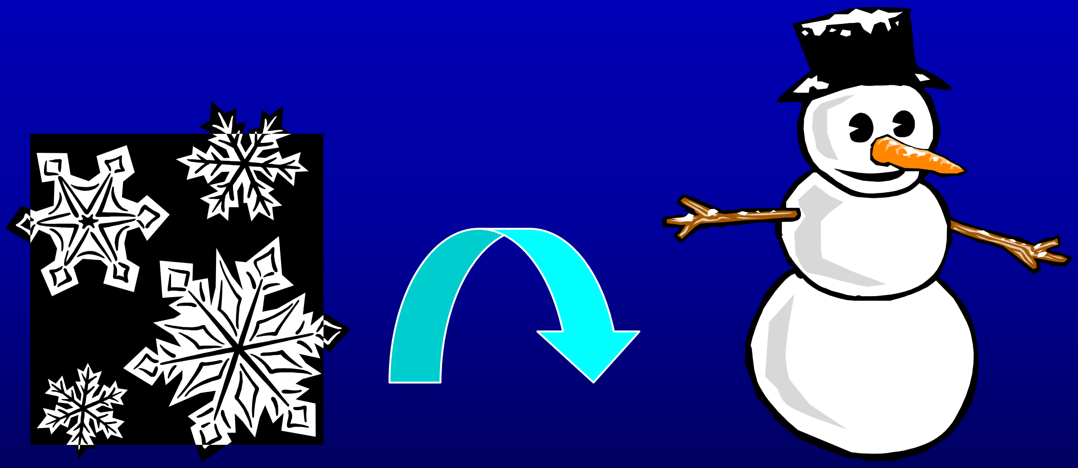






# *Small* Things have *BIG* Consequences……

## Two case studies from everyday life

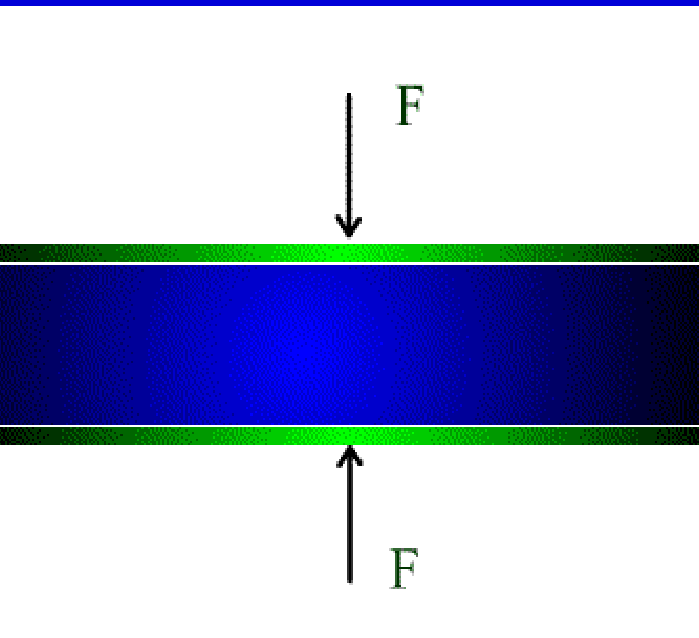


***There is plenty of room at the bottom……***

***Small is Beautiful……..***

# *Small* things have BIG consequences………

## 1. Adhesion of surfaces/particles in a liquid




Velocity ~ Force / resistance

$V \sim F / R$ and $R \sim 1 / H^3$

$V \sim dH / dt \sim F H^3$

as $H \Longrightarrow 0, V \Longrightarrow 0$

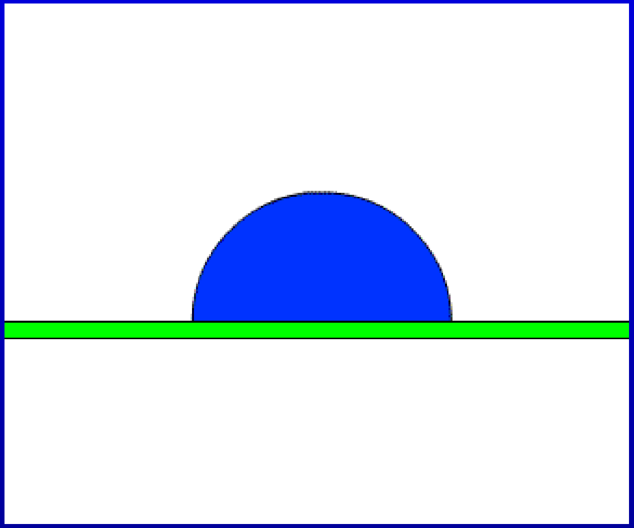
Infinite time for adhesion!

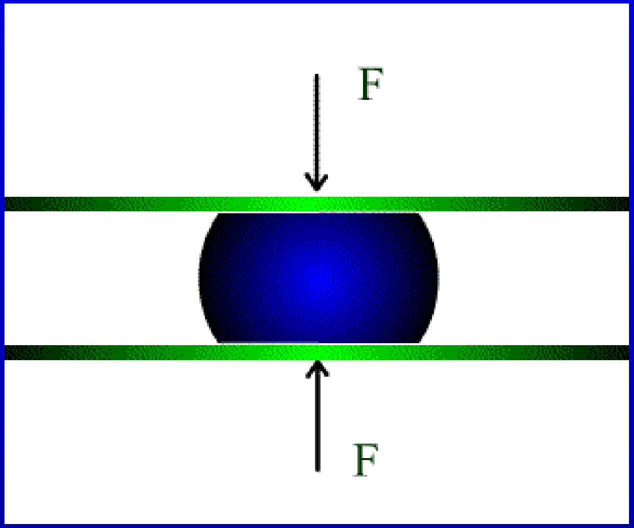
However, for H < 50 nm, van der Waals force,

$F \sim 1/H^3$ and V ~ constant velocity

# *Small* things have BIG consequences…

## 2. Spreading/retraction of a liquid drop






- Slippage of liquid; No-slip condition of classical bulk fluids is violated rather readily!

- Shear stress near contact-line $\Longrightarrow \infty$

- van der Waals force also grows ~ $1/H^3 \Longrightarrow \infty$

# Shaping, patterning and manufacturing of small scale objects by “self-assembly” and “self-organization”

## A NEW PARADIGM

**Micro- and Nano Fabrication;**

**“top-down”**

**“Bottom-Up”**

## • What is MESOSCALE and SELF-ORGANIZATION ?

## • What is the role of CONFINEMENT?

**Highly confined systems (even in 1-D) are usually:**

- ✓ **Far from the equilibrium**
- ✓ **Unstable or metastable**

**and therefore readily self-organize by SHAPE CHANGE to lower their energy……………**

1. Liquid or Soft (< 10 MPa) Solid State Processing

2. Direct uses:

   Protective and Opto-electronic Coatings

   Polymer based Opto-electronic Devices

   MEMS/NEMS

   Sensors; nanocomposites…………

3. Intermediate Structures:

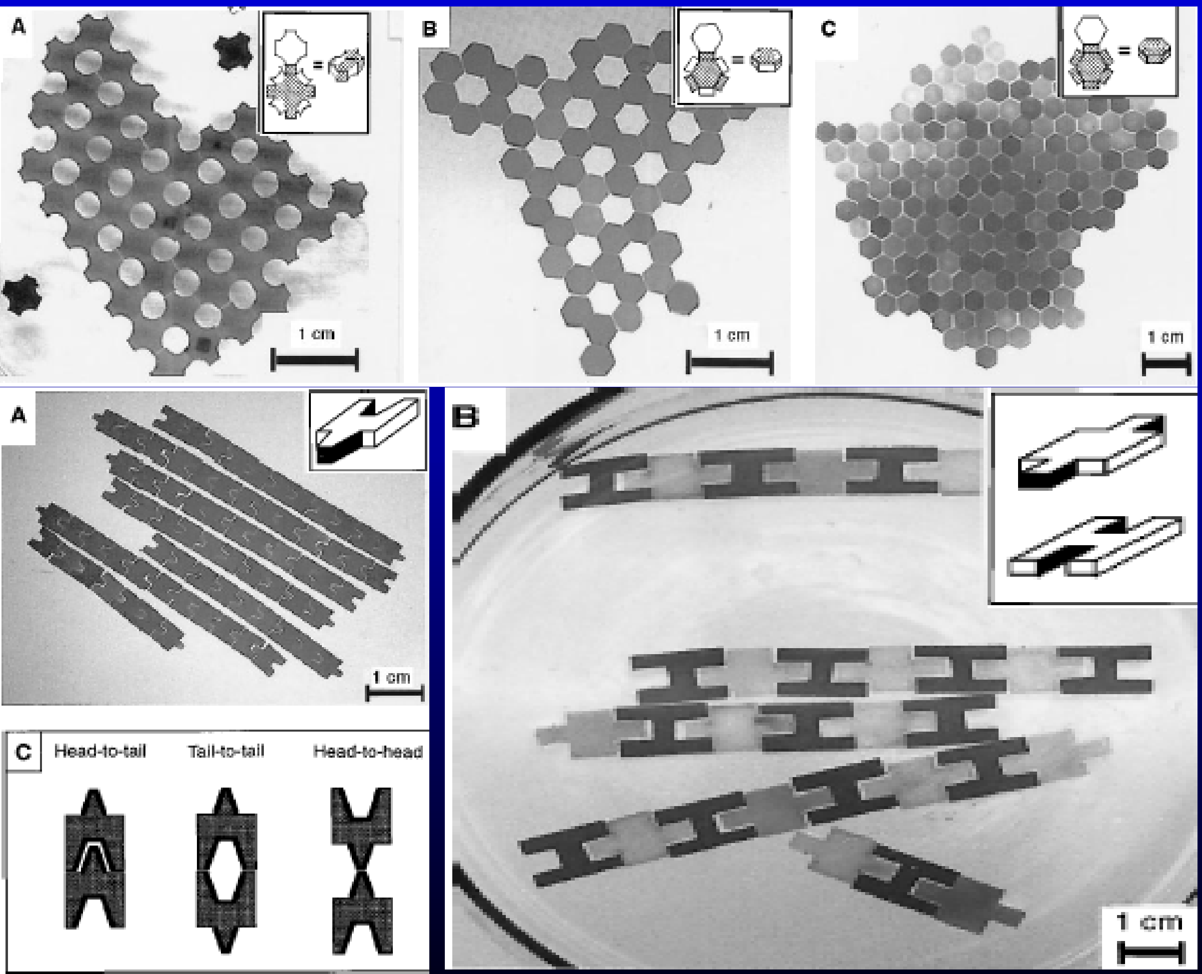
   Masks

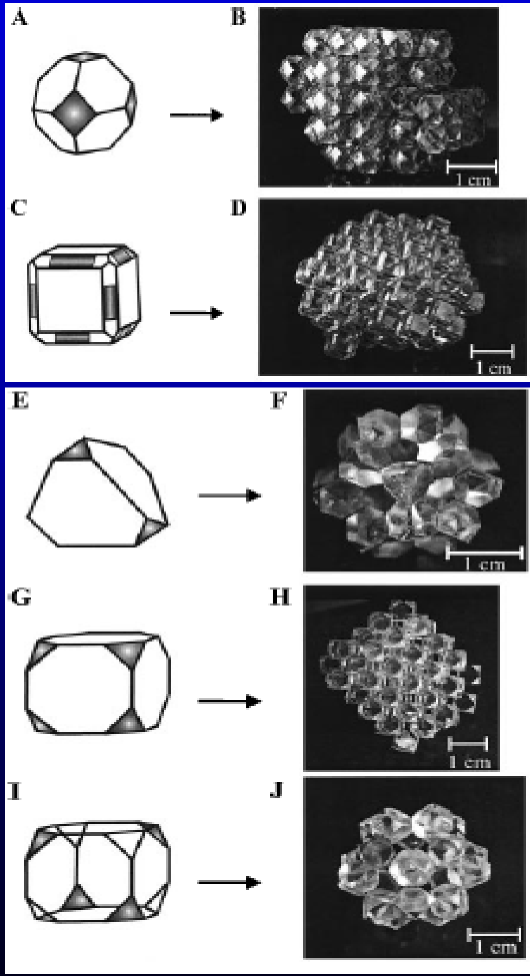
   Sacrificial Layers/Structures

# Mesoscale Self-Assembly of Edge/face modified Floating Objects by Lateral Capilary Forces: Energy Minimization

## 2-D Lattices

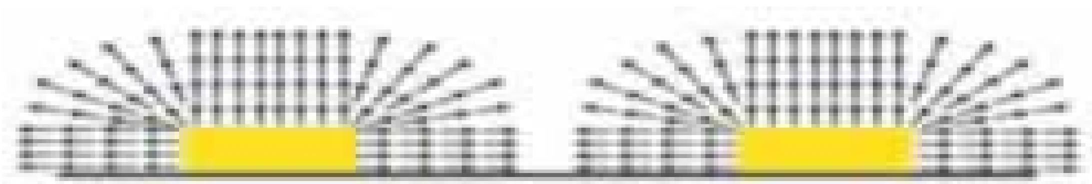
## 3-D "Crystals"



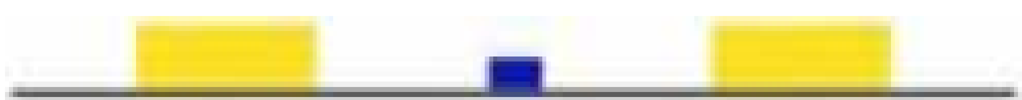

Bowden, Breen, Terfort, Whidesides et al, Science, 1997, 1999

# Molecular Ruler for Scaling Down Nanostructures

**Create gap spacings with multilayer of thiol / carboxylic acid integral multiples of 2 nm layers**

**Evaporate metal & chemical lift-off**



**Penn State Nanofabrication Facility, Stephen Fonash et al.**

# Of Oil and Water

# and Things that Don't Mix

**"You should not, *like water and oil,***

***repel each other,***

**but should, like milk and water,**

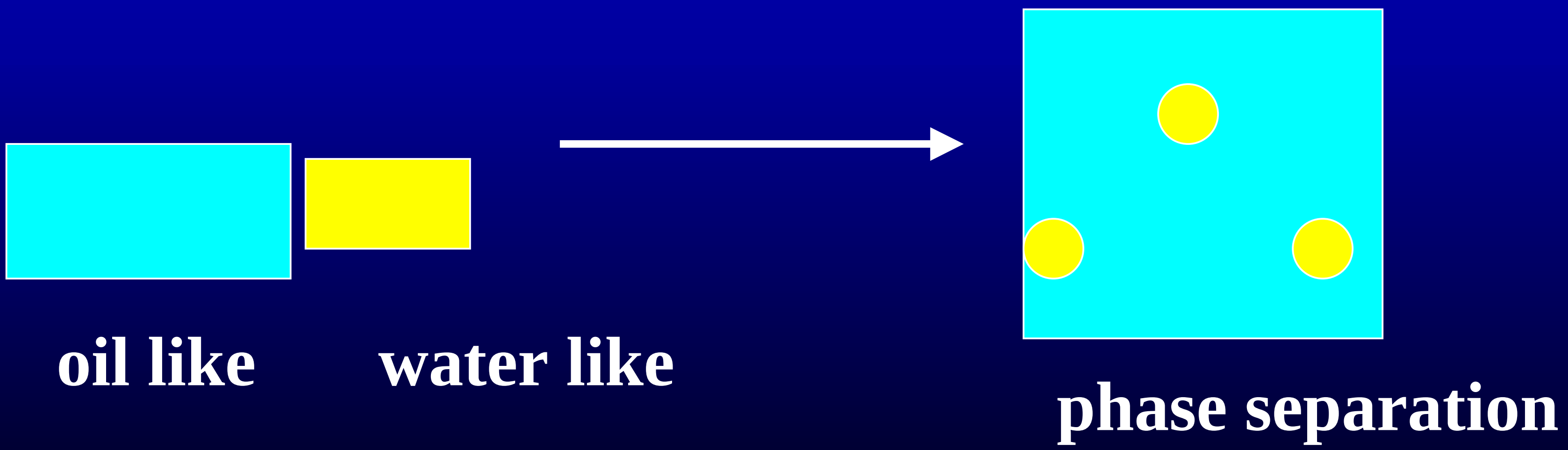
**mingle together."**

**--Gautama Buddha (Advise to Bhikshus)**

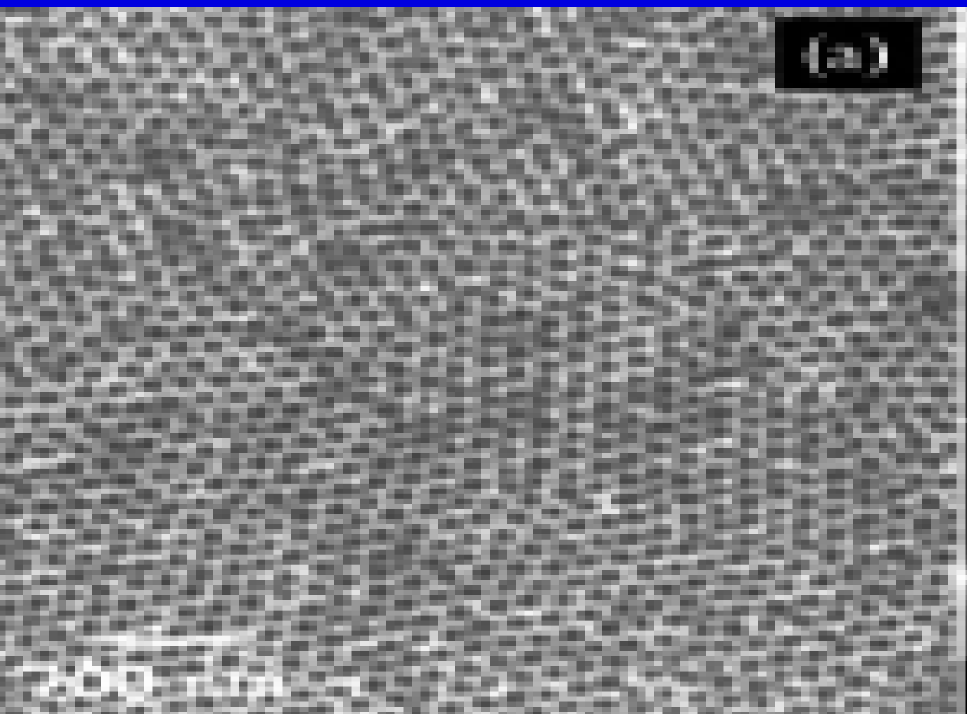
# Self-Organization Driven by Phase Change and Phase Separation

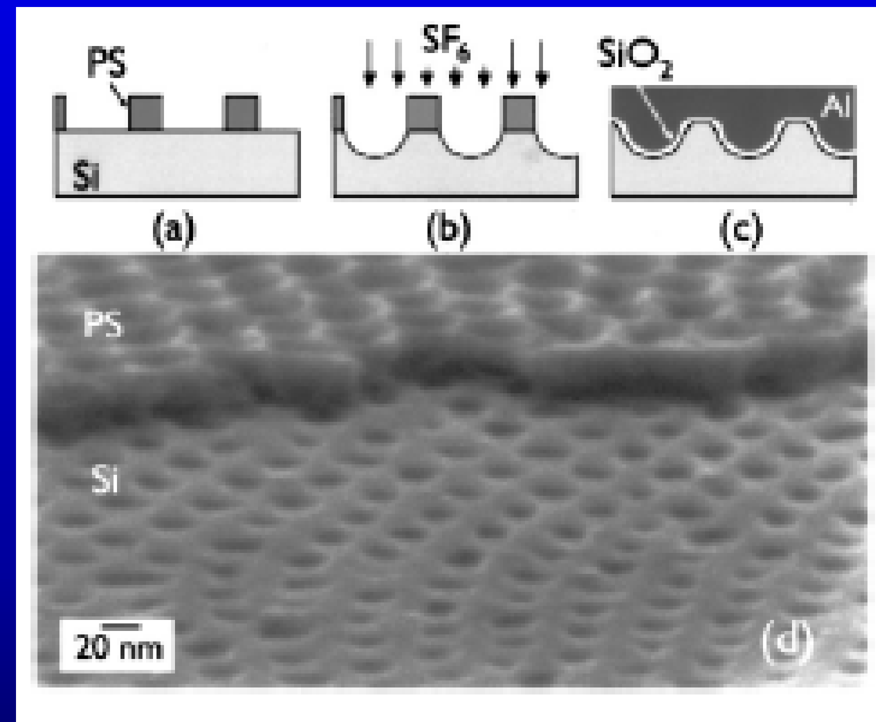
1. Microphase separation in block-copolymers

2. Evaporation-condensation



# Patterned Capacitor Electrode Using Microphase Separated PS-PMMA Diblock Copolymers as Mask



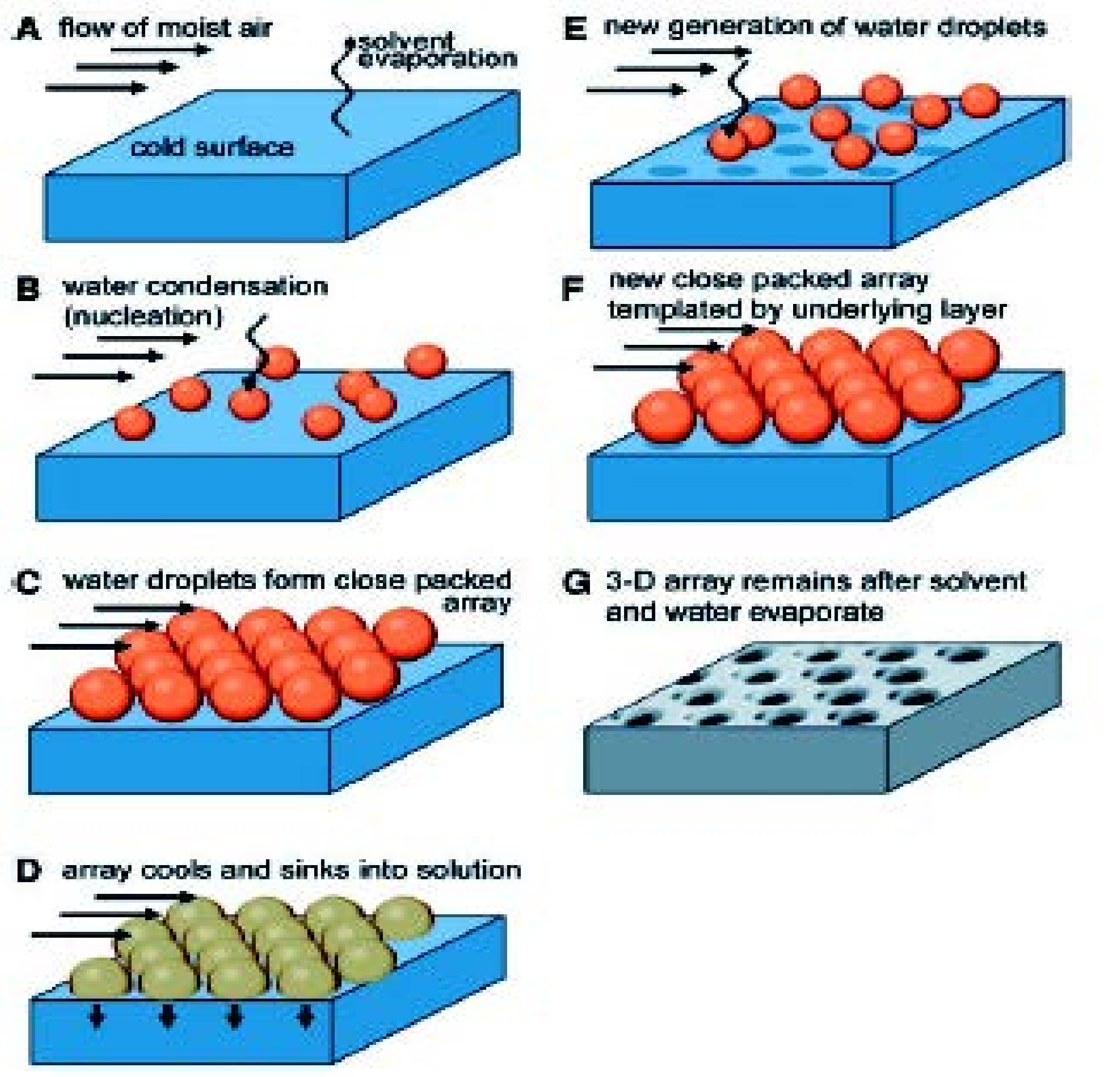



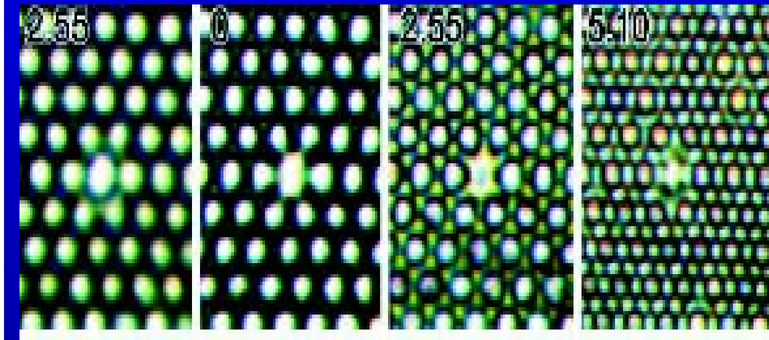

- 1% solution of PS-PMMA diblock copolymer in toluene spun as a 30 nm thick film; Annealed at 160 $^0$C to make hexagonal lattices of PMMA; 45 nm center-to-center (!) without high resolution lithograpgy techniques; Ultraviolet exposure to cross link PS; removal of PMMA by acetic acid leaving polymer mask; Dry etching of silicon followed by thermal growth of oxide and remaining device processing

*Black et al., Appl. Phys. Lett. 79, 409, 2001.*

# *Templating and Self-Assembly:*

# 3-D Mesoporous Materials for Photonic Band Gap Materials, Pico-liter Beakers and Sensors



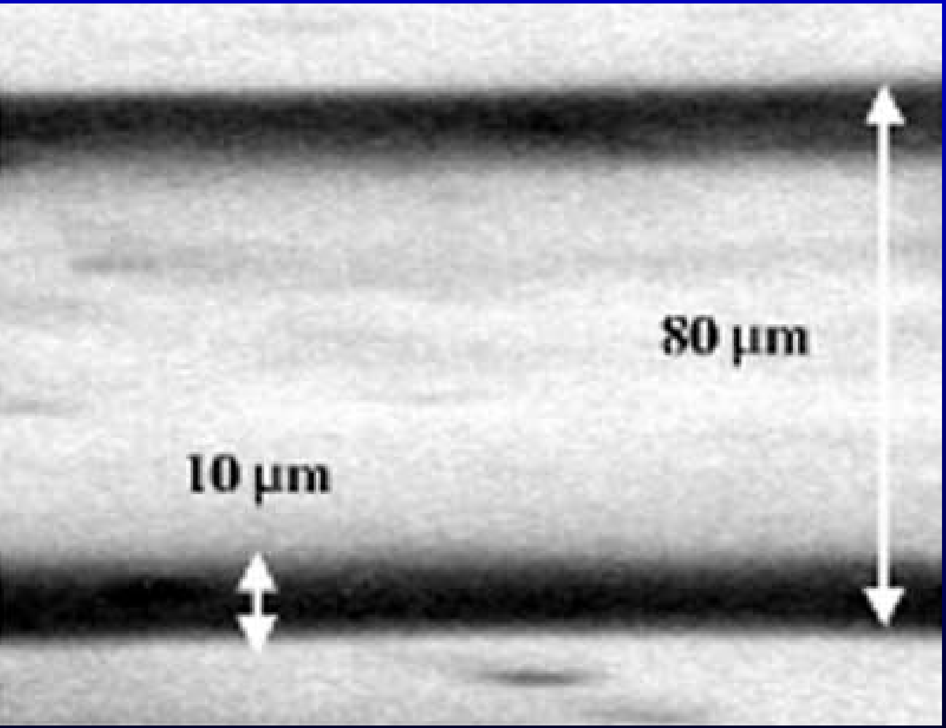

**Polystyrene films with 0.1 to 10 micron holes**

***Srinivasrao et al. Science 292, 79, 2001***

# Mesopatterning by Evaporation of Solutions:

## *The Coffee-Stain Effect*

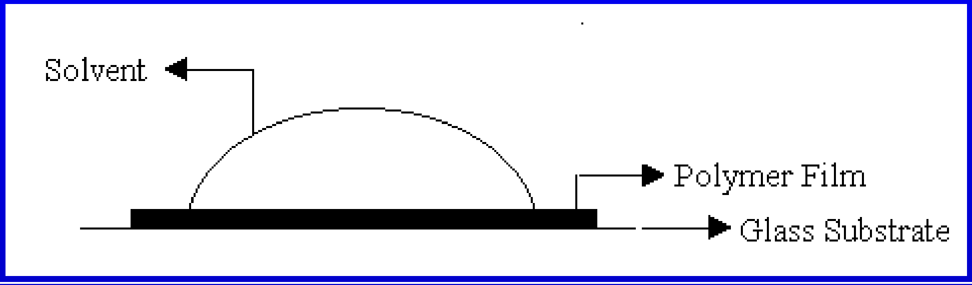
***(solute is transported from droplet center to periphery and deposits near the contact line; Deegan et al. Nature, 1997)***




**ink-jet printed Copper hexanoate in a volatile solvent**

**Troian et al. APL 2000**

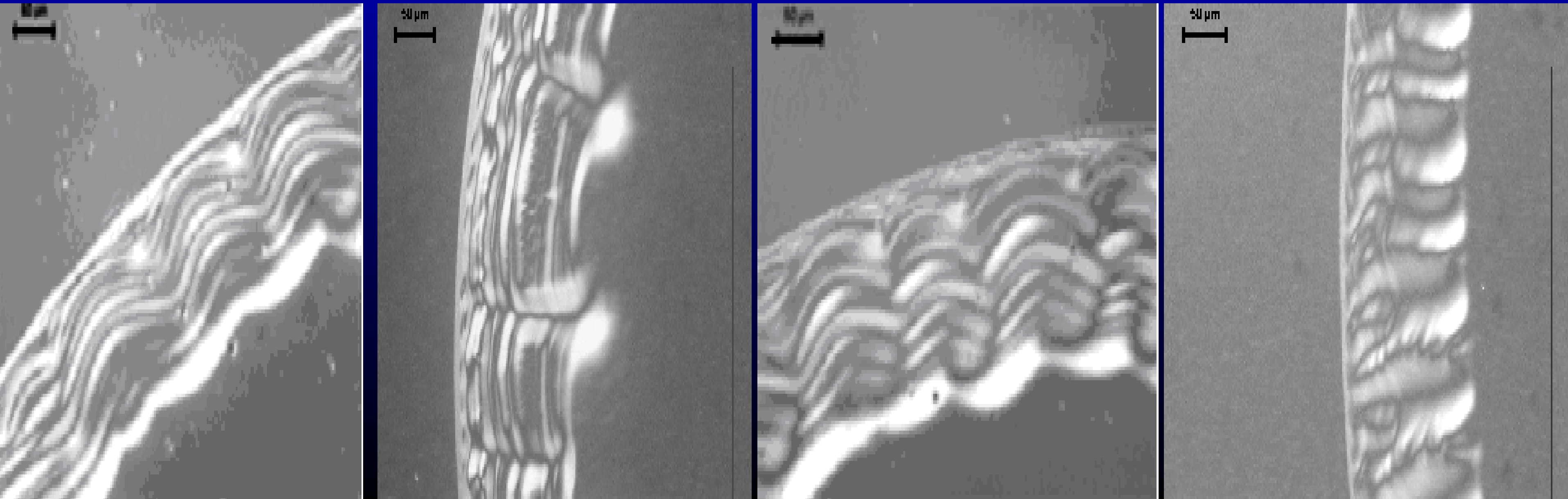
# Evaporating Solvent on a Dissolving Polymeric Substrate




**Flows bringing polymer to drop periphery and instabilities**

**Contact-line pinning; Benard, Marangoni, Thermocapillary convections; Osmotic pressure difference**

**Patterns at IITK (Sharma and Gonuguntla, Langmuir, 04)**



# Array of Polymer Droplets by Evaporation of Toluene Layer (70 $\mu$m) on a Polystyrene Film (43 nm): IITK study

100 $\mu$m

T = $15^0$ C; nearly saturated vapor phase; RH = 70%; Time > 10 min

# Stability of Nanostructures

1. Intermolecular forces and their measurement

## Self-organization under External Fields: Gaining Control

2. Controlled Dewetting on patterned Substrates

3. E-Field induced patterning

# *Intermolecular Force Driven Spinodal Dewetting on Homogeneous Surfaces*

**water**

**PDMS film**

**quartz**

**Spontaneous Dewetting of PDMS Film under Water on Quartz**

# FLUID THIN FILMS: EQUATION OF MOTION

$$3\mu\,(\partial H/\partial T) + \nabla.[\gamma\, H^3\, \nabla\nabla^2 H] - \nabla.[H^3\, \nabla\Phi] = 0$$

$$\nabla\Phi = \Phi_H \nabla H + \nabla\Phi|_{H=constant}$$

Where, $\Phi=\Phi(X,Y,H)$

1. Condition for Spinodal Instability:

$$\Phi_H = \partial^2 \Delta G/\partial H^2 < 0$$

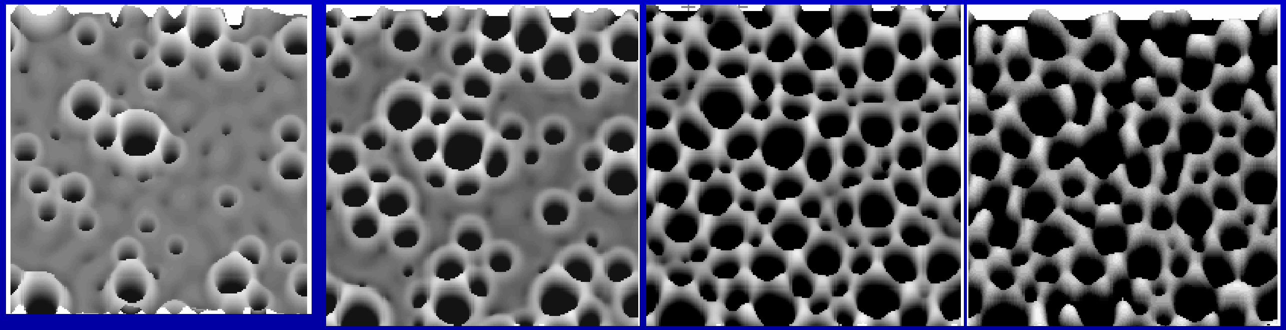
2. Heterogeneous Instability:

$$\nabla\Phi|_{H=constant} = f(X,Y)$$

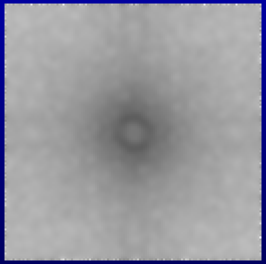
# Spontaneous Dewetting by Hole Formation

## Large Scale (10 λ x 10 λ) Simulation

time



FFT

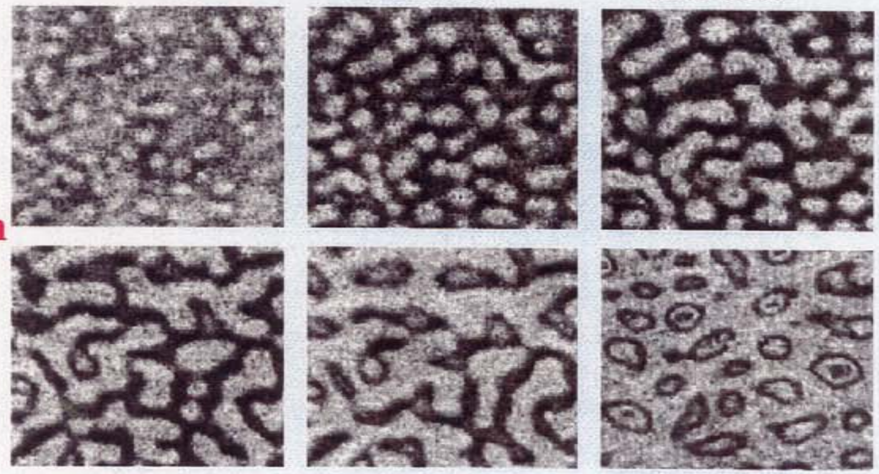


- Length scale and time scales as given by the linear stability
- Morphology: formation of satellite holes

# Instability driven by the surroundings: Thicker films: hole formation

64 sec | 122 sec | 200 sec

60 nm

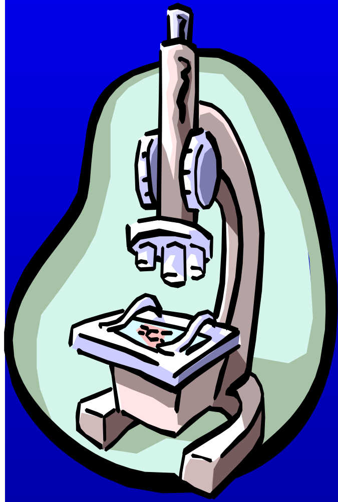


330 sec | 507 sec | 970 sec

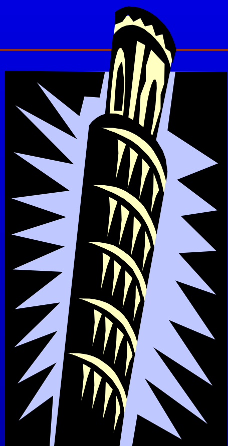
darker = thicker
lighter = thinner


size: 150 x 150 $\mu m^2$

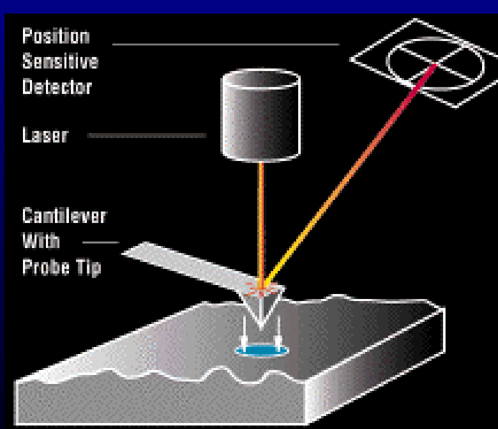
[ PDMS (60 nm) on PDMS bimodal brush ]



# *Thin liquid films as cantilevers for intermolecular forces !!*

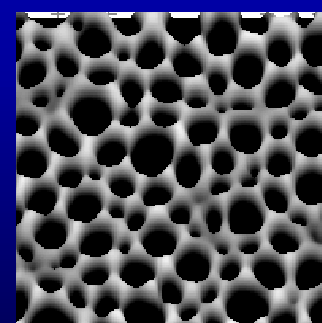


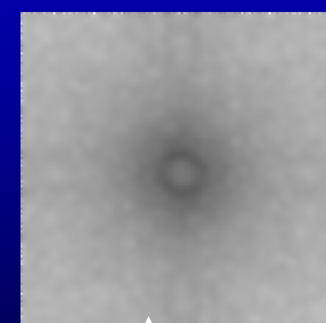
**solid-fluid film-solid system**




**Solid-fluid film-fluid system**

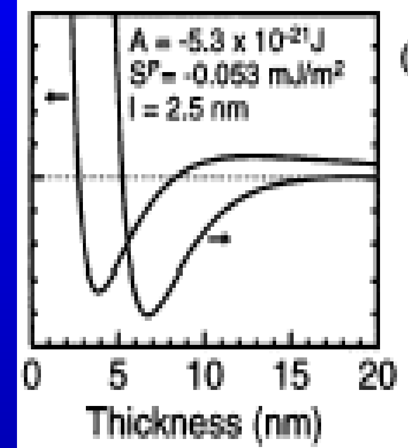
$$\lambda^2 \sim 1 / [\partial^2 \Delta G/\partial H^2]$$





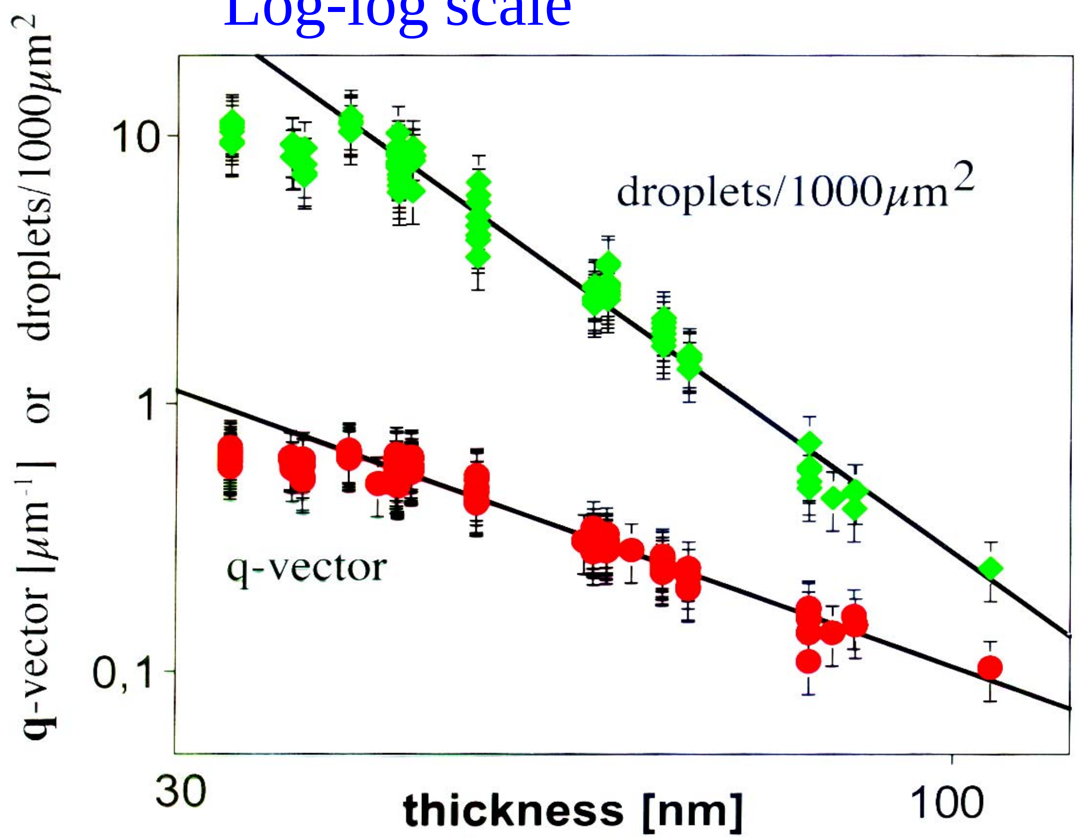
**$\lambda$ From FFT**

# Number Density of Holes




## Liquid Cantilevers: Thin Film Force Microscopy

Log-log scale




***Signature of van der Waals force***

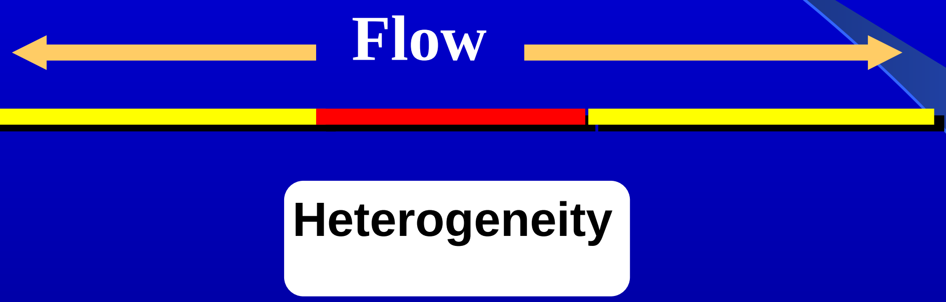
$$q^2 \sim \partial^2 \Delta G / \partial H^2$$

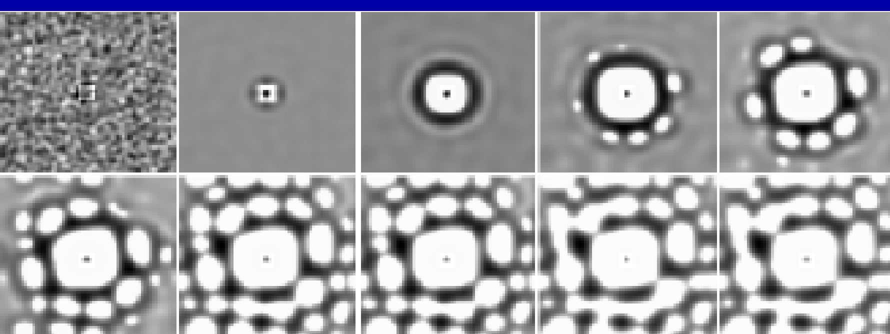
**if** $\Delta G \sim 1/H^2$

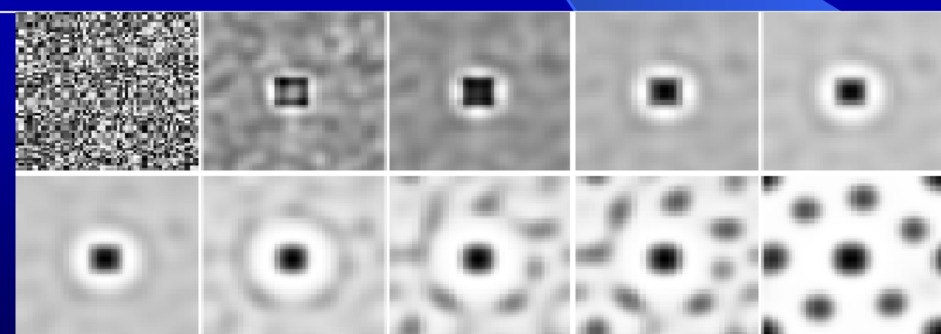
$$\Rightarrow q \sim 1/H^2$$

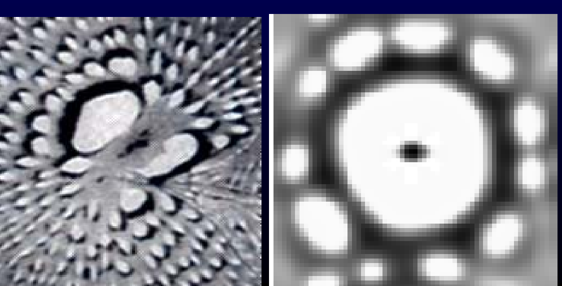
# Gaining Control: Ordered Dewetting Patterns on Chemically Heterogeneous Surfaces

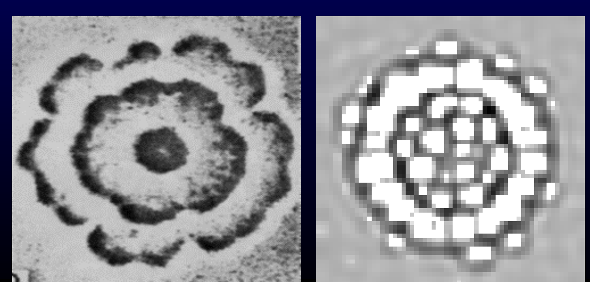
## Flow Engendered by Potential (Wettability) Gradients



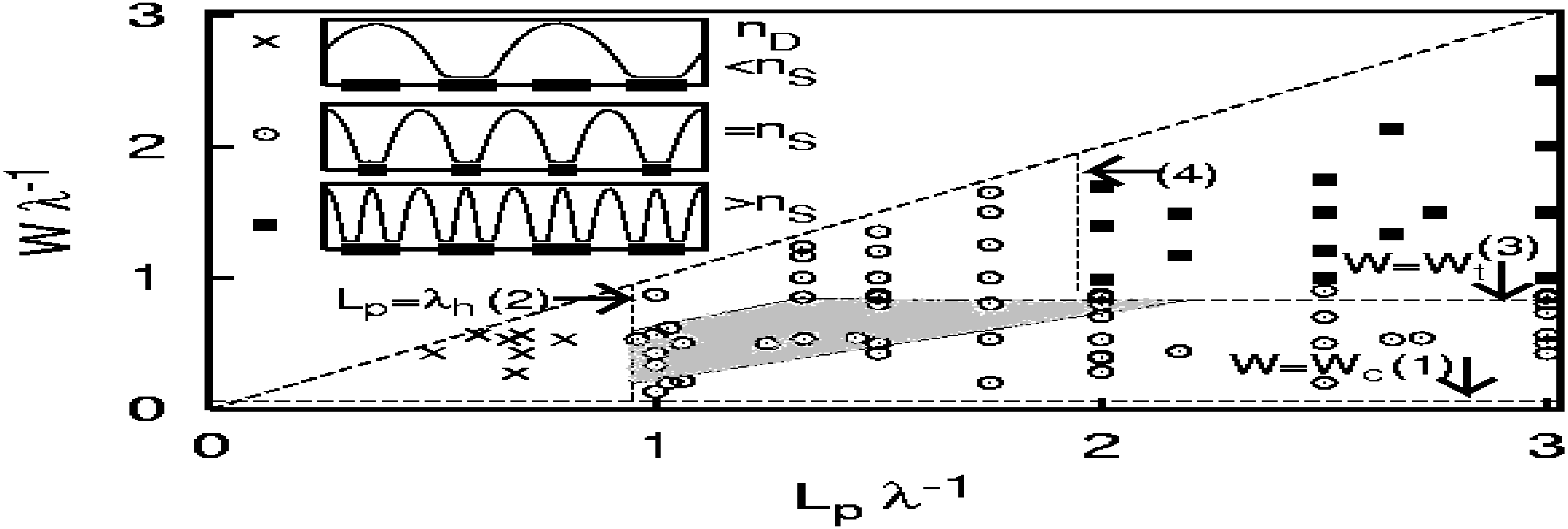









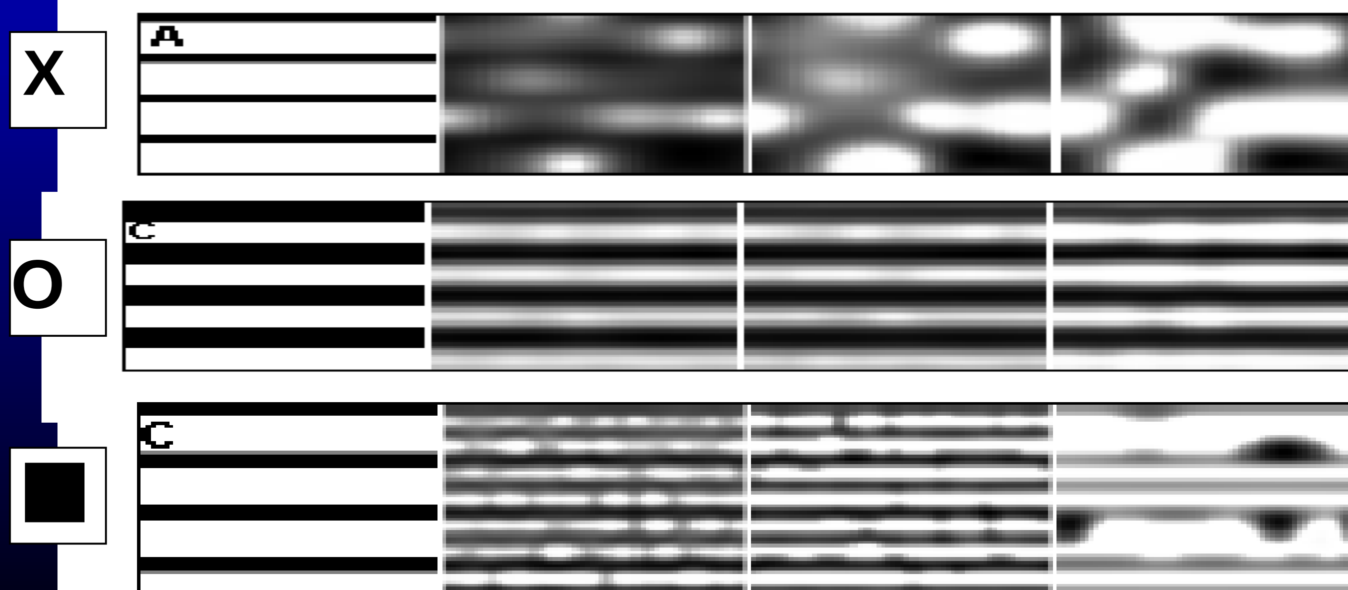
# MORPHOLOGY PHASE DIAGRAM

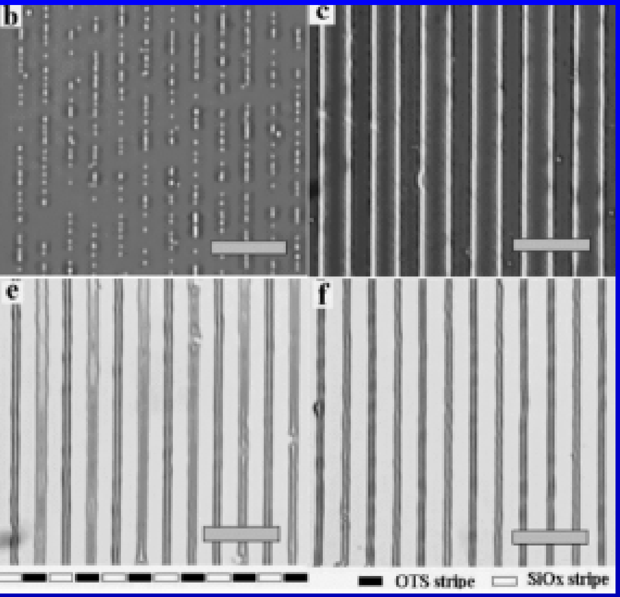



ideal case

$2\lambda > L > \lambda$

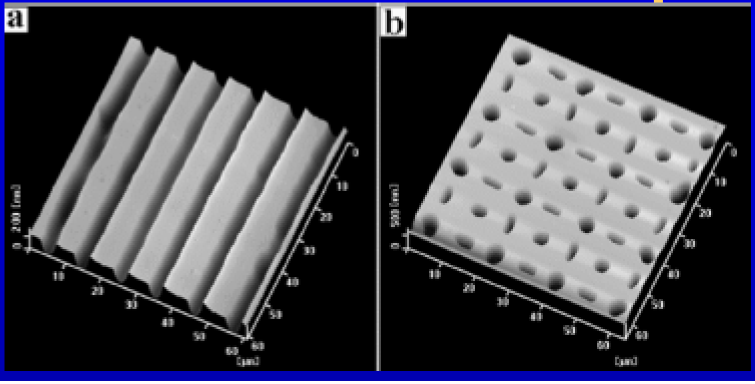
$W < \lambda$

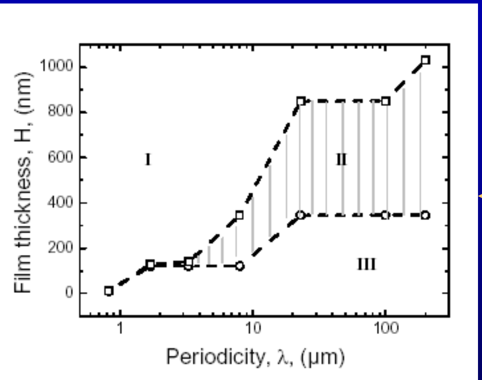





# Zhang et al. Polymer, 44, 3737, 2003

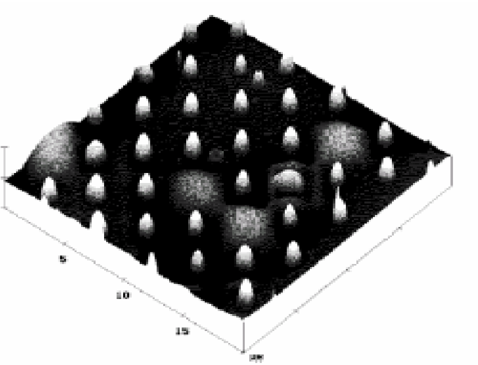
**45 nm PS film on OTS and SiO stripes.**
**Below: pattern transfer to PDMS stamp**

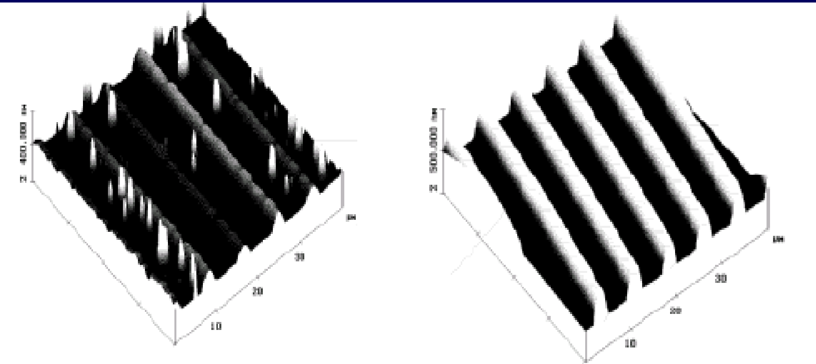


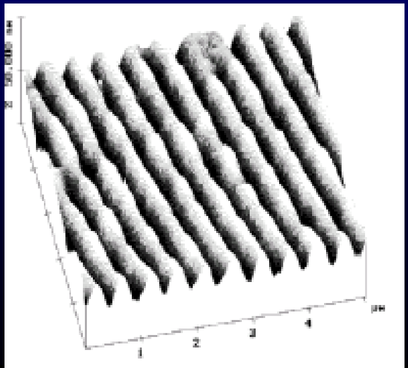




# Wang et al. Adv Func Mat, 2004

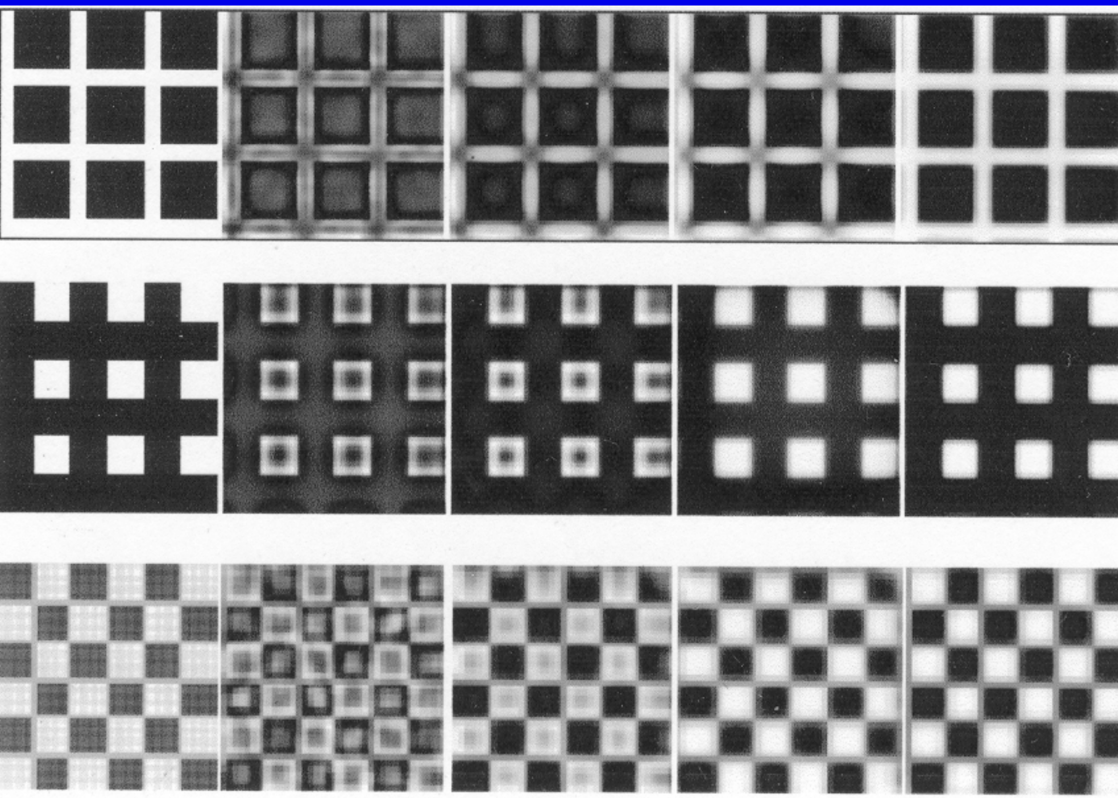
← **Ideal patterning for intermediate film thickness**

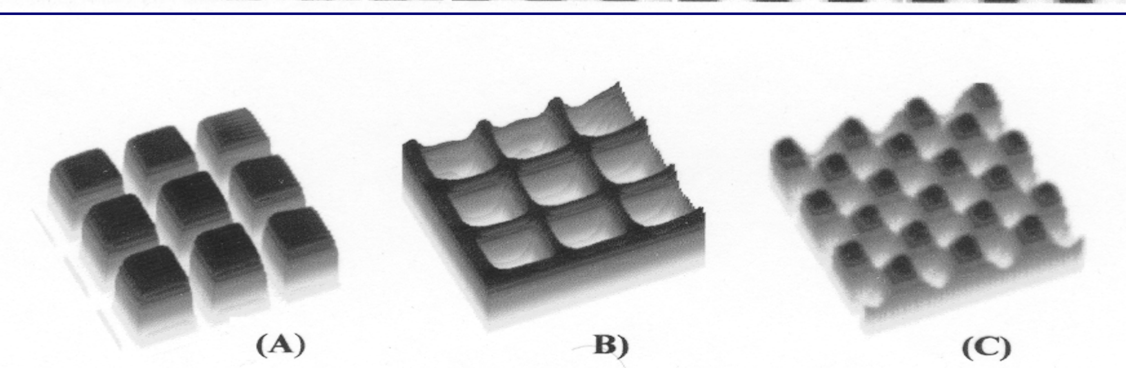






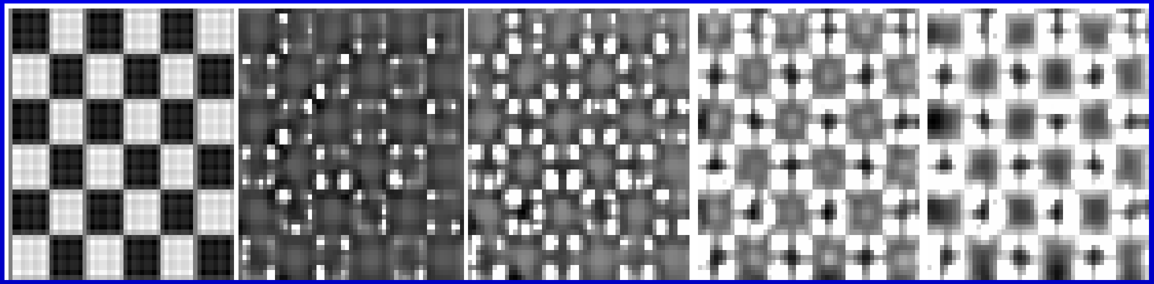
# Ideal Templating: $L_p \sim \lambda_m$





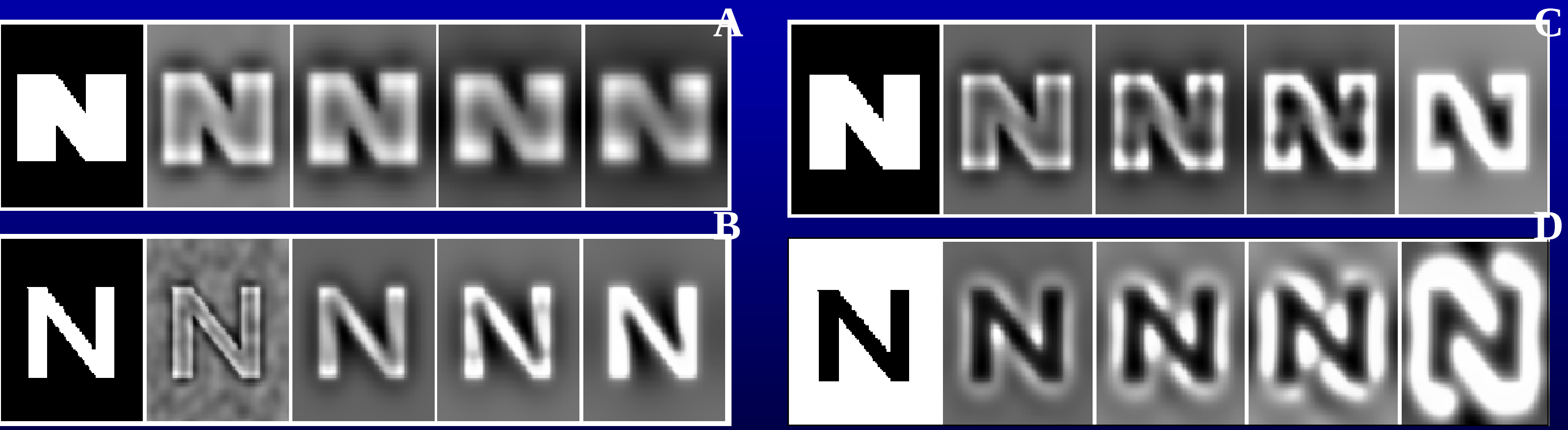

**Increased nonwettable area fraction,**
**Keeping $L_p \sim \lambda_m$**

# TEMPLATING OF COMPLEX PATTERNS



***CHECHERBOARD***

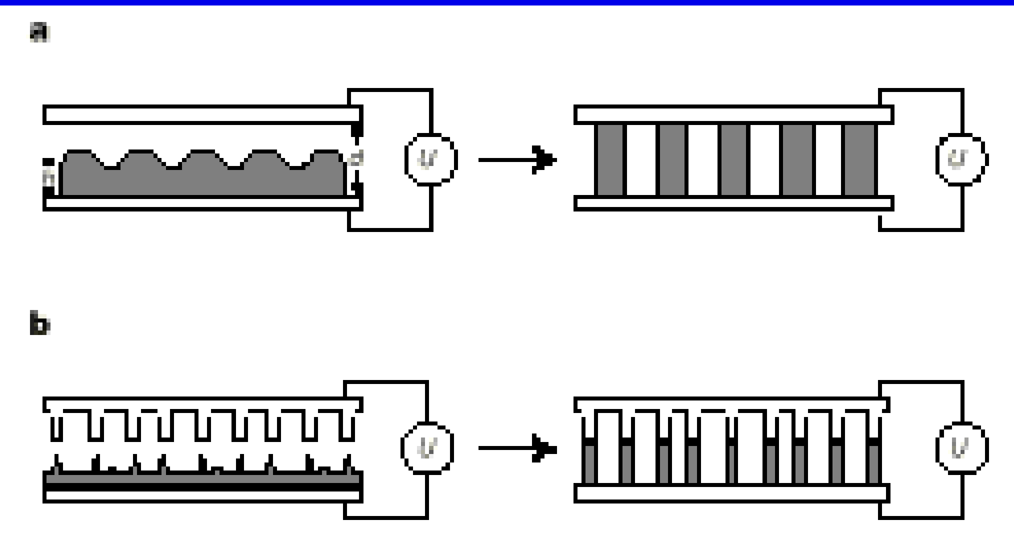
**6.7 nm thin film on a checkerboard patterned substrate having a large periodicity, $L_p$ = 2.5 $\lambda_m$.** ***The amplitude of energy heterogeneity,*** **$\varepsilon_H$ = 0.5 .**

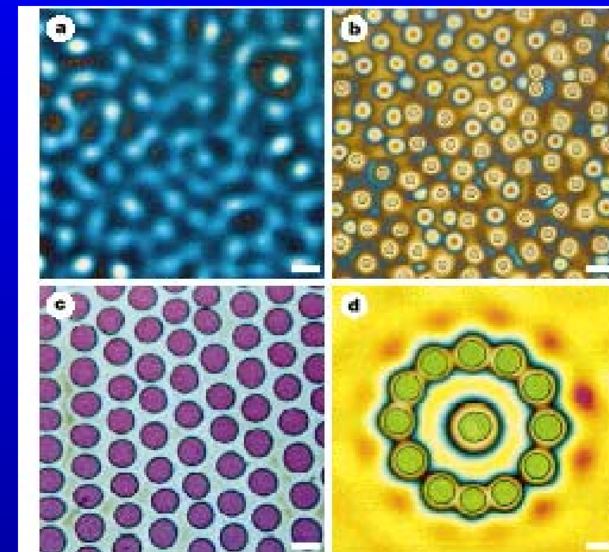


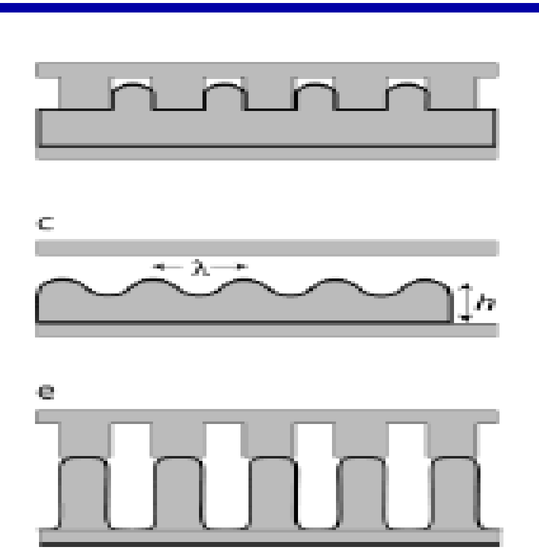

***ALBHABET***

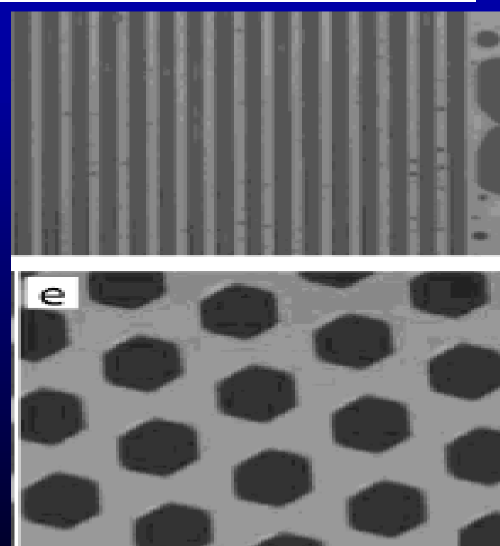
**5 nm film. For figs A-D, the pattern "N" is the less wettable part and in fig. D, "N" is the completely wettable part.**

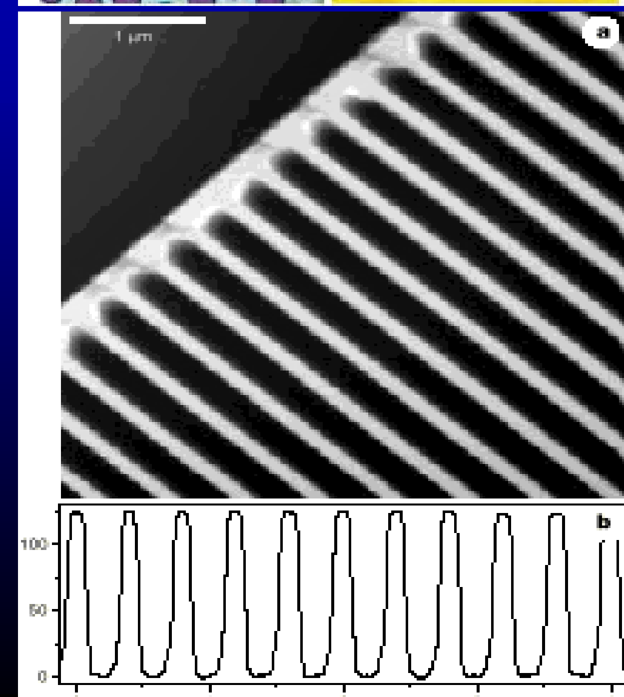
# Pattern Transfer: E- Field and Confinement Induced Structures in Thin Liquid Films



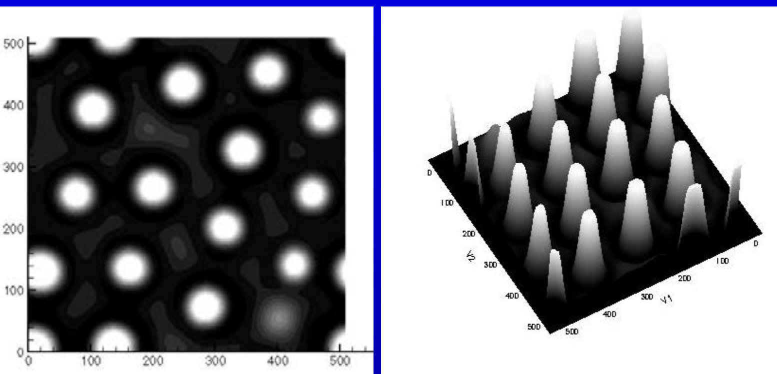




**E. Schaffar et al., Nature 2000**

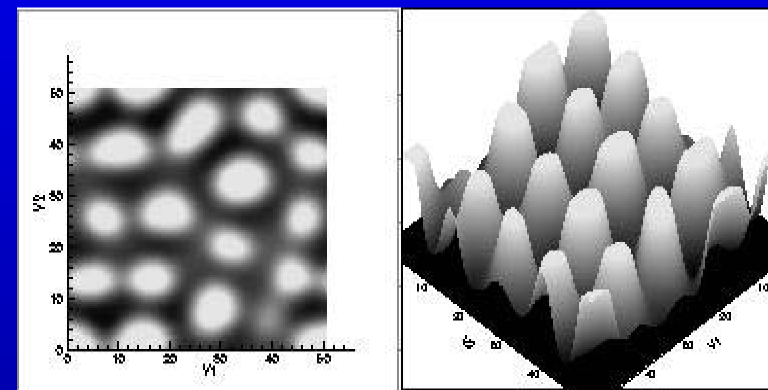
**Harkema et al., Langmur 2003**

# Simulations at IITK: E-field

$$3\mu\,(\partial H/\partial T) + \nabla.[\gamma\, H^3\, \nabla\nabla^2 H] - \nabla.[H^3\, \nabla\Phi] = 0$$

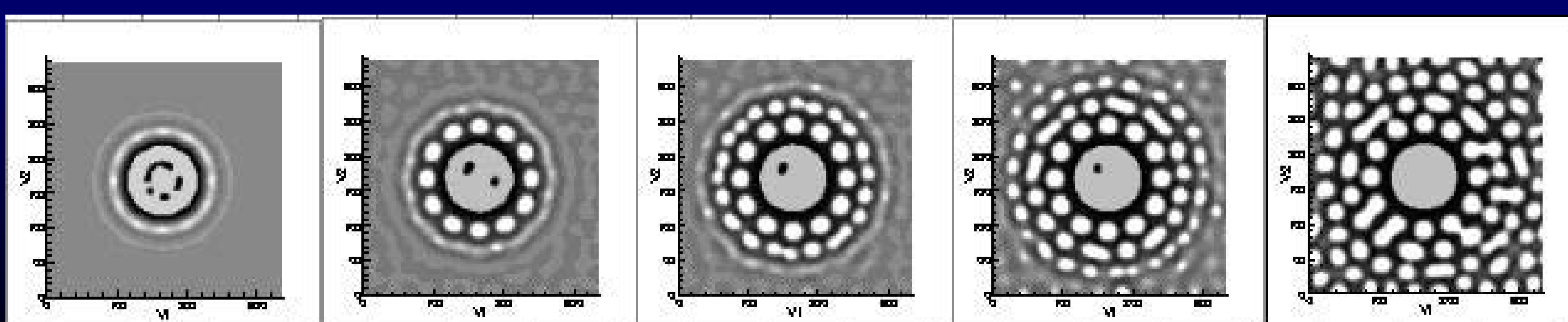


h=25 nm, d=100 nm,U=50V



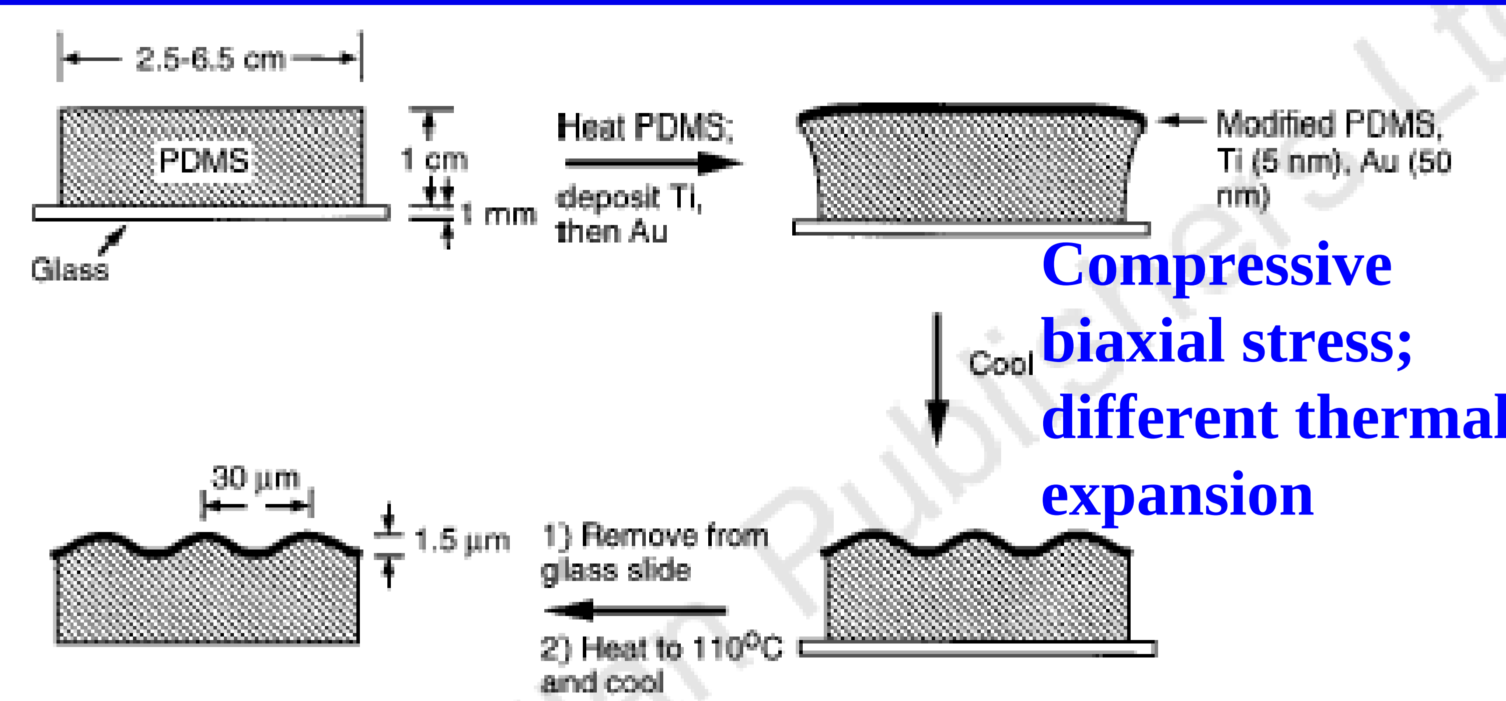
h=75nm, d=100 nm,U=50V

## Patterned Electrode Assisted Ordering

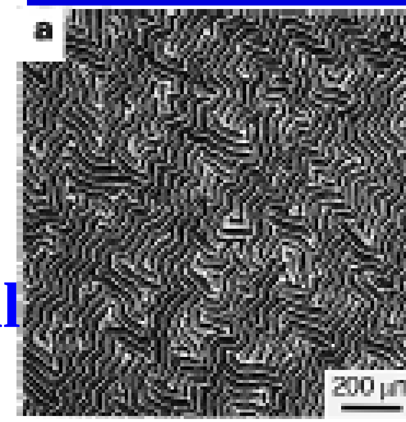


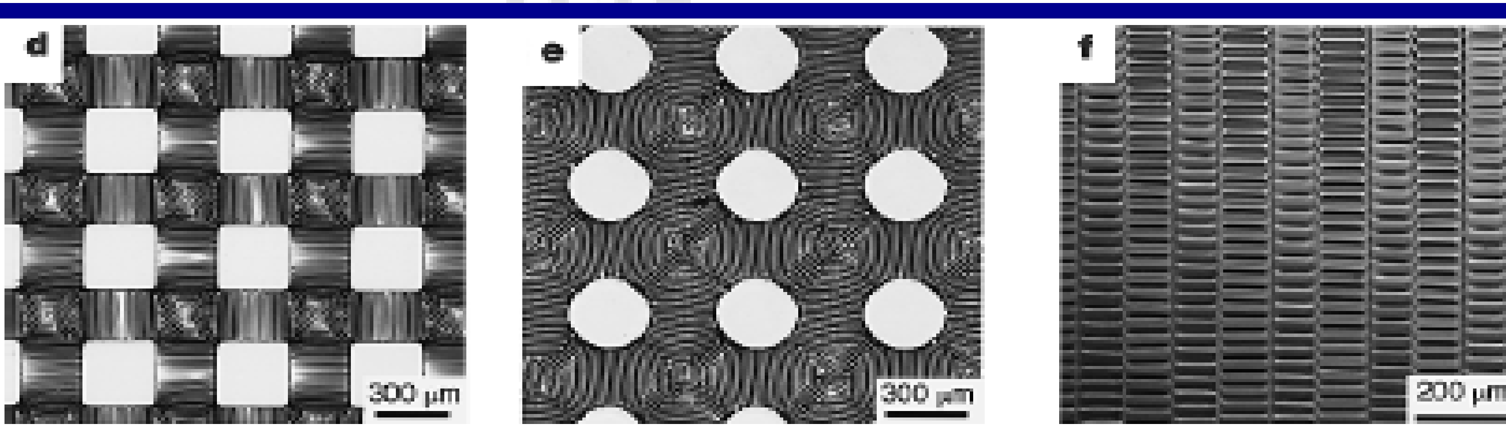
Verma and Kargupta

# Patterning by Stress Engineering




**Compressive biaxial stress; different thermal expansion**




**Patterned PDMS**

**Whitesides et al., Nature 1998**

# Direct Compressive Buckling of a thin polystyrene film on a softer PDMS Substrate

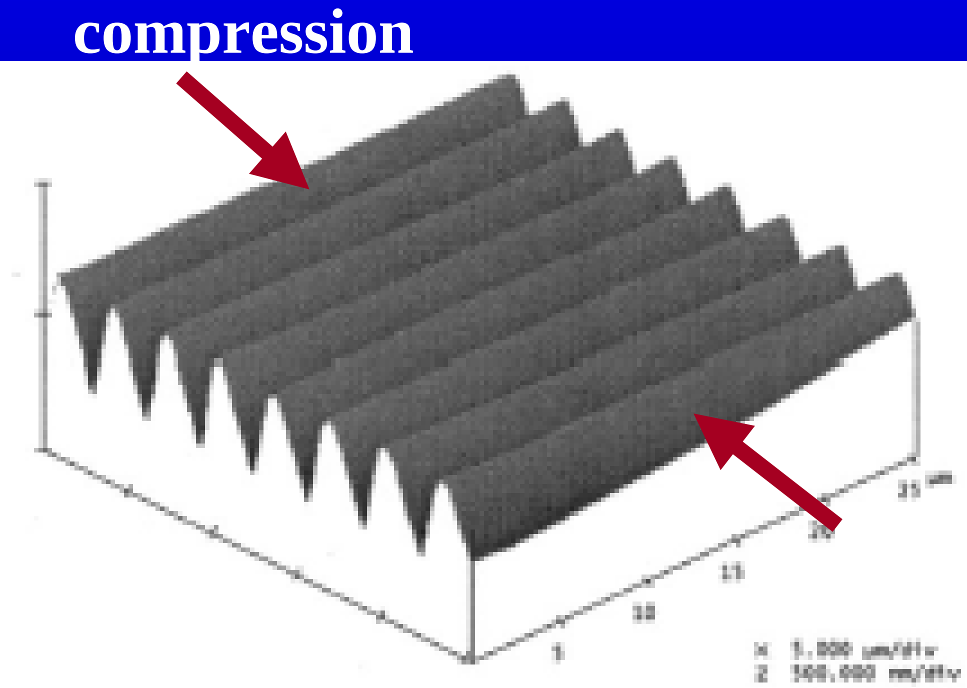
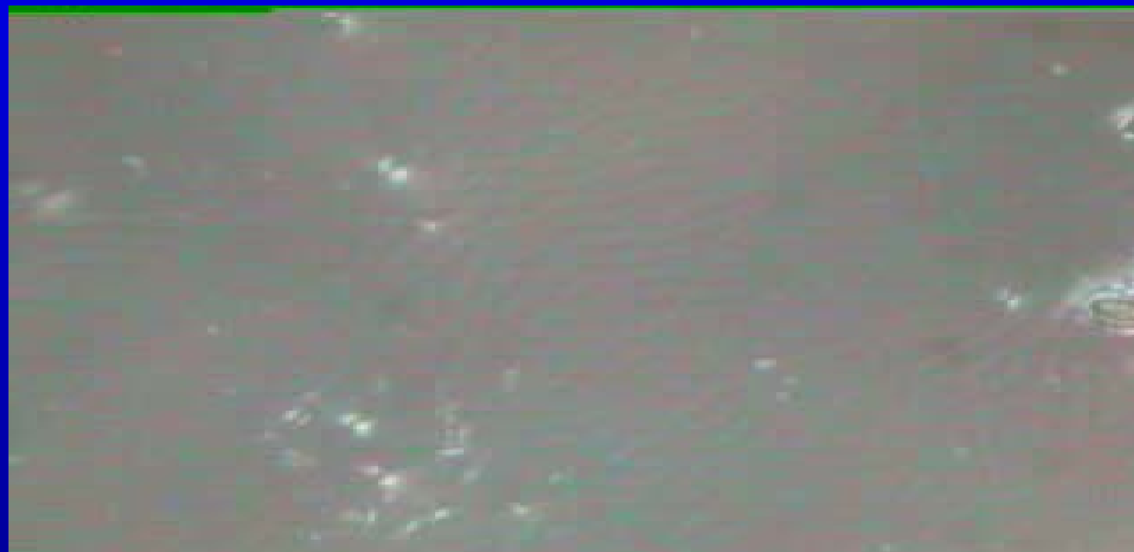



Figure 1. AFM micrograph of a buckled film of polystyrene, having a thickness, *h*, of 59.7 nm ± 0.5 nm, supported by and adhered to PDMS.

C. M. Stafford, NIST, Adhesion Society Meeting, 2004.

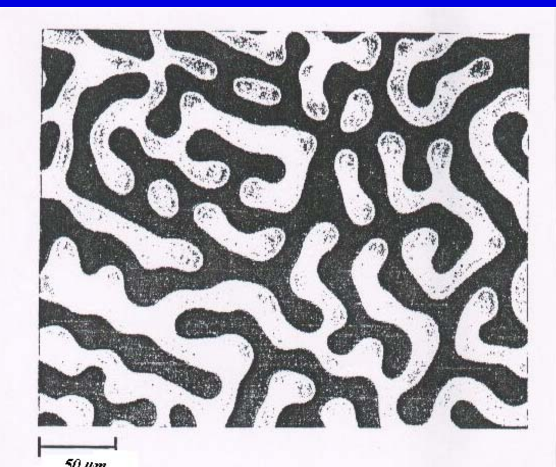
# Stress Engineering II: Patterning of Thin Elastic Films by Adhesion and Debonding



**Contact Instability**

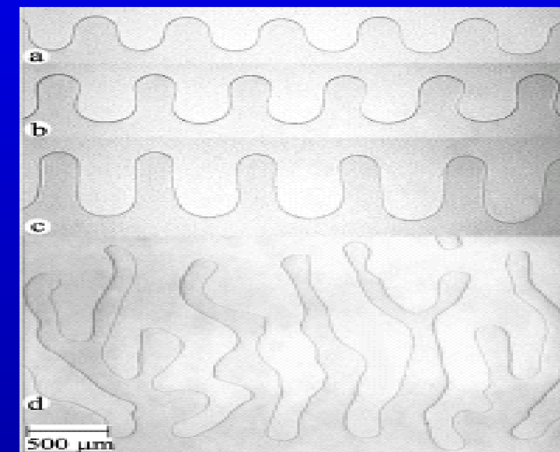

Moniraj Ghosh

# Cracks and Debonding Patterns of Soft Elastic Films in Different Geometries



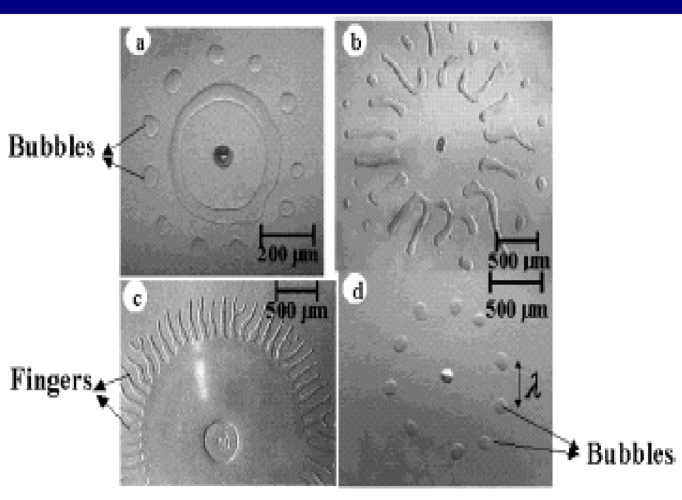

**Euro.Let. <u>53</u>, 525 (2001)**

**Phys. Rev. Let., <u>84</u>,3057 (2000)**



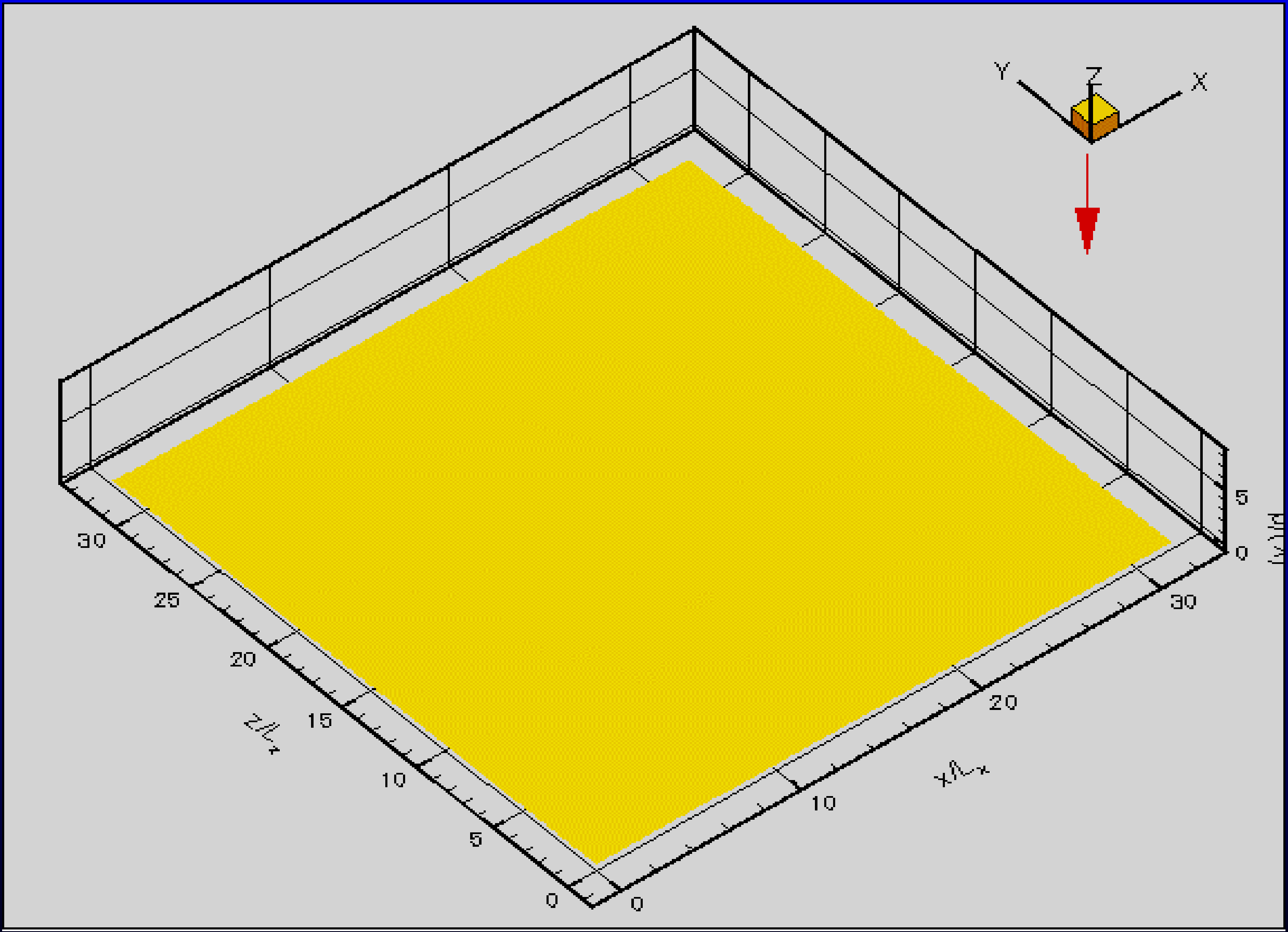

**Phys. Rev. Let., <u>85</u>, 4329 (2000)**

$$\lambda \sim 3h - 4h$$



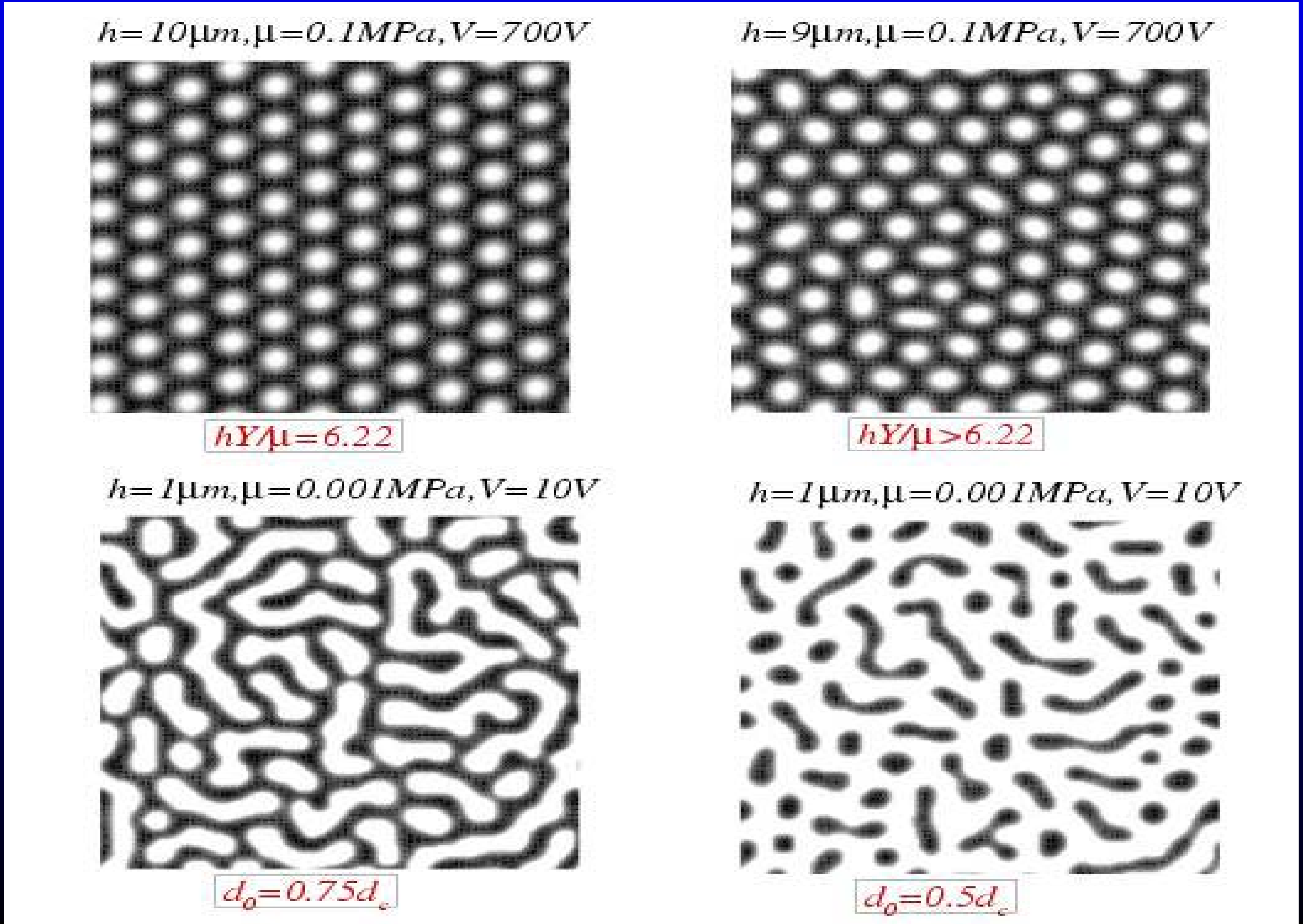

**Langmuir, <u>19</u>, 2621 (2003)**

# Patterns during Approach and Retraction of a Contactor



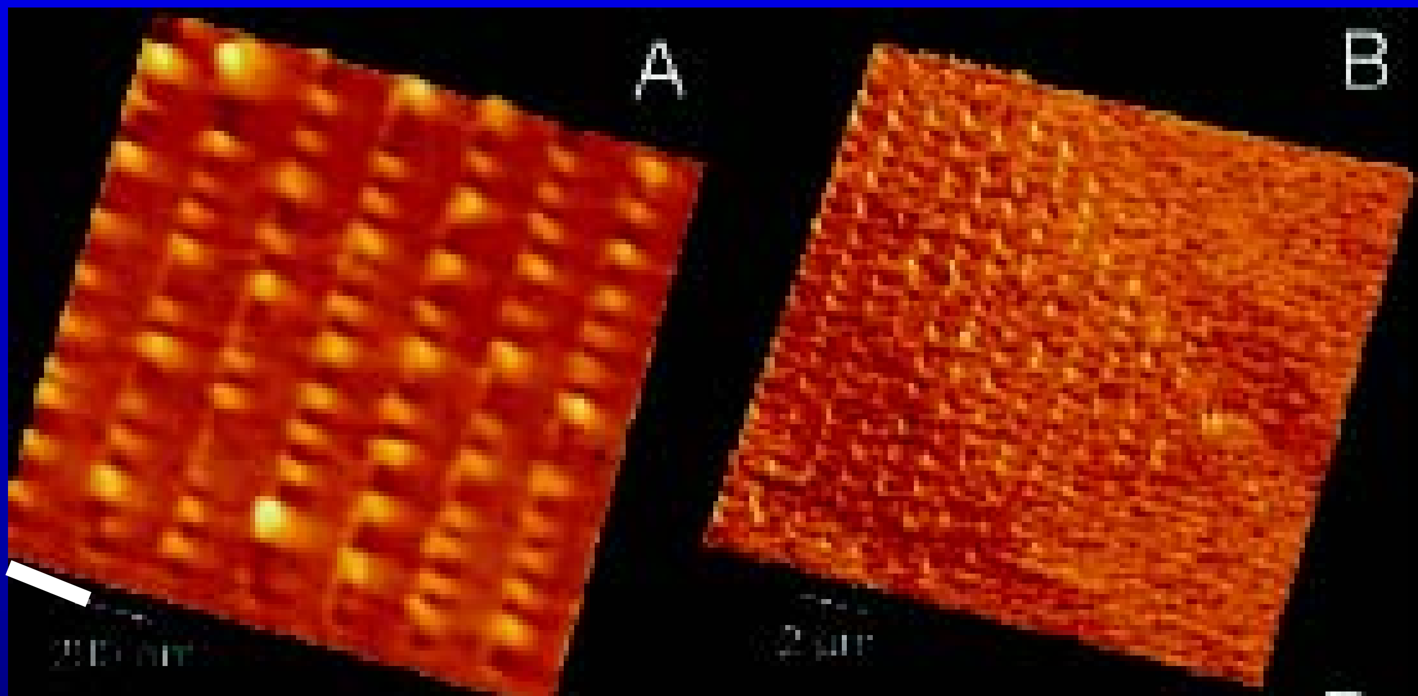

J. Sarkar

# Simulations on E-Field Patterning of Soft Solid Films: Origins of Order & Disorder



# Self-Organized Dots in Thin Elastic Film

200 nm



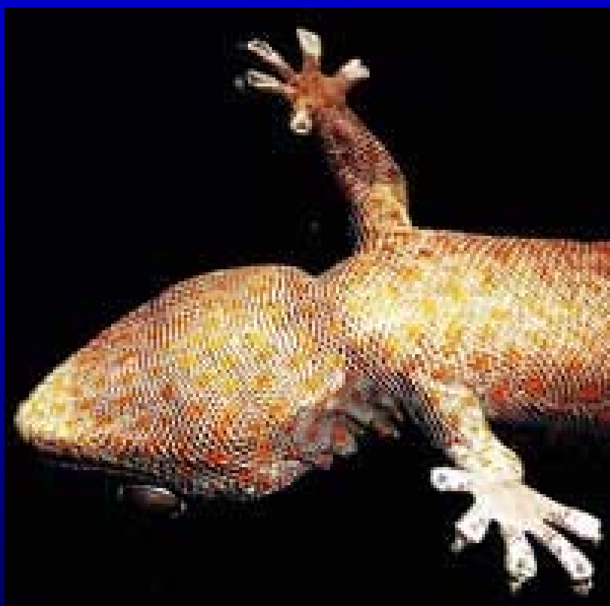

**Dots created by line scans of the AFM tip on 3nm -35 nm thick rotaxane films on HOPG.**

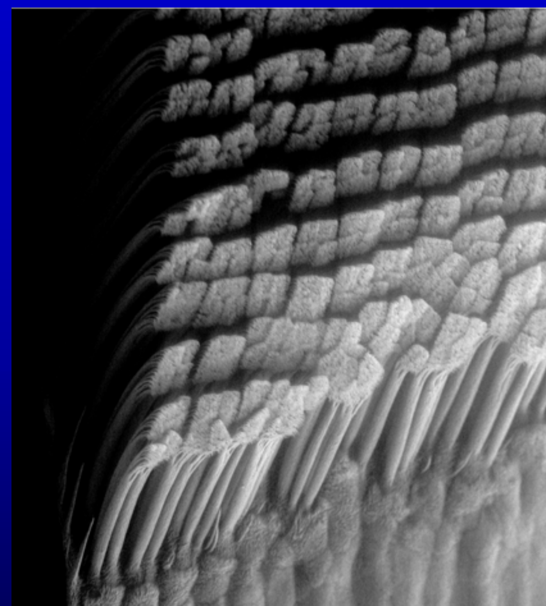
**Interdot distance ~ 100 nm – 500 nm; height 1nm -20 nm.**

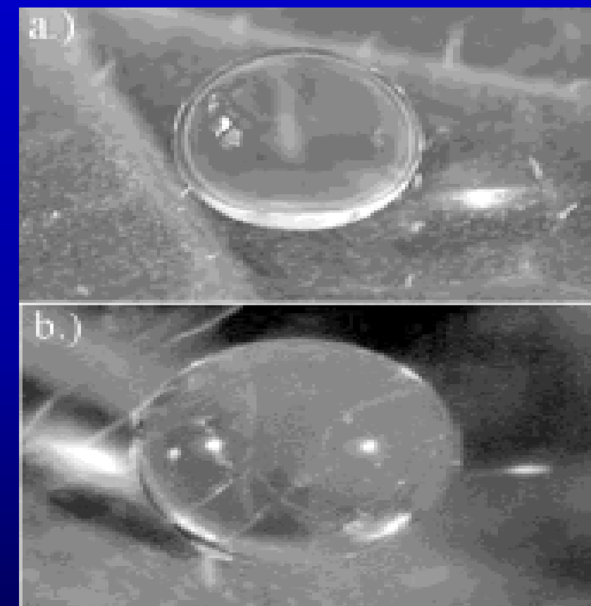
**Source: Cavallini *et al.*, *299 Science (2003)***

# Bio-inspired Meso-Mechanics

## Two Examples





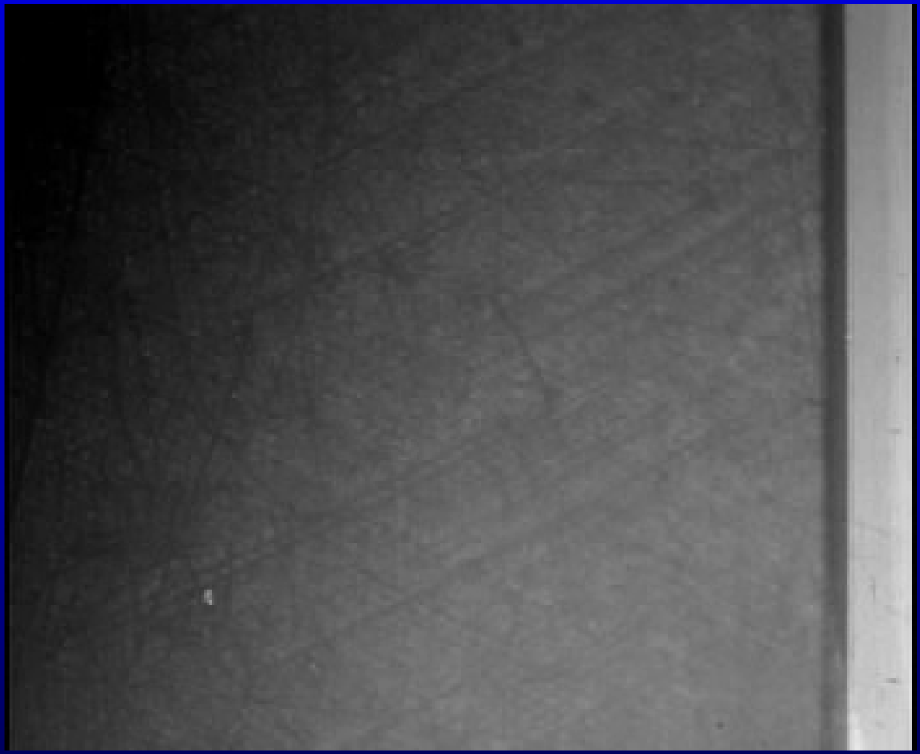


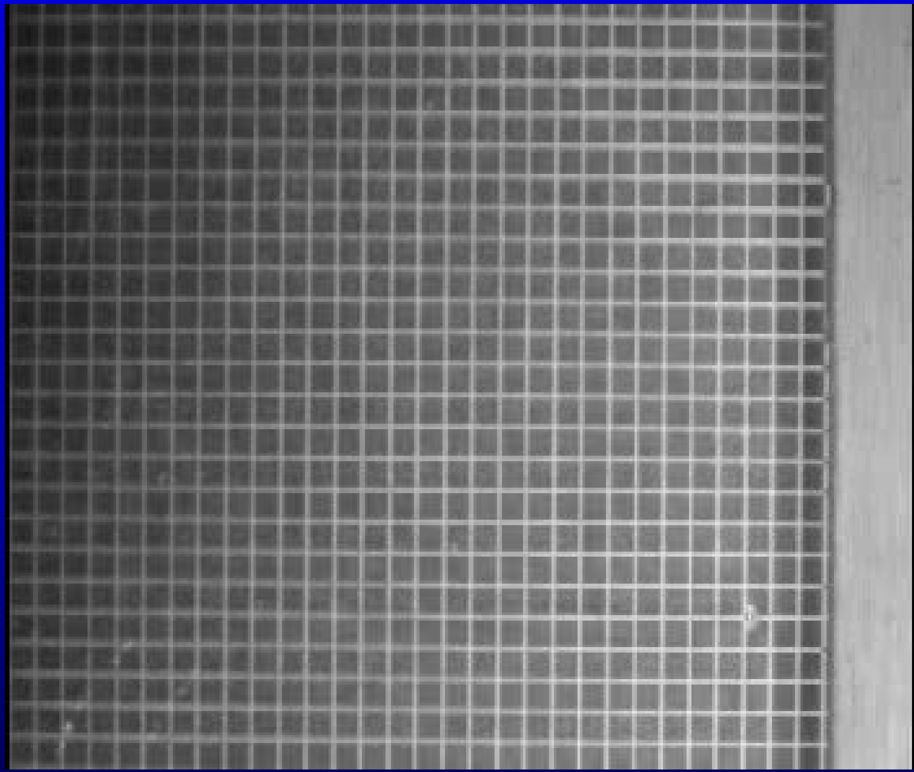

**van der Waals force mediated adhesion in gecko**

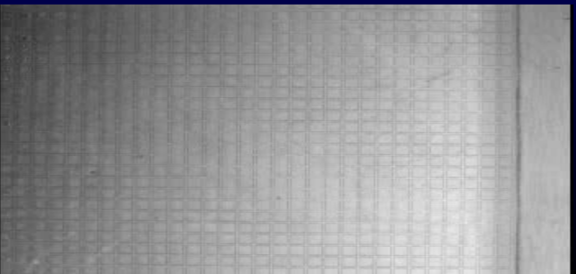
**Full et al, Nature 2000**

**Lotus effect**

# Mechanics of Gecko Adhesion and Optimal Pressure Sensitive Adhesives







Choudhary and Ghatak (Lehigh U.)

# Superhydrophobicity and Self-cleaning:

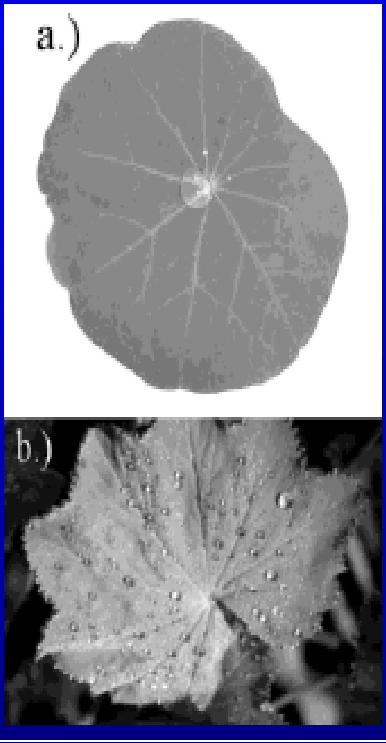
## Bird-feathers, “Fakir Droplets” and “Lotus” Effect

*“….like the lotus, be of the world,*

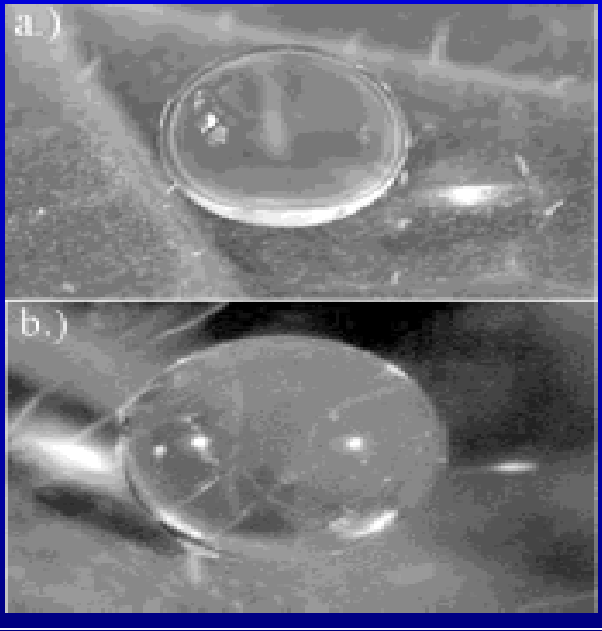
*but untouched by it”*

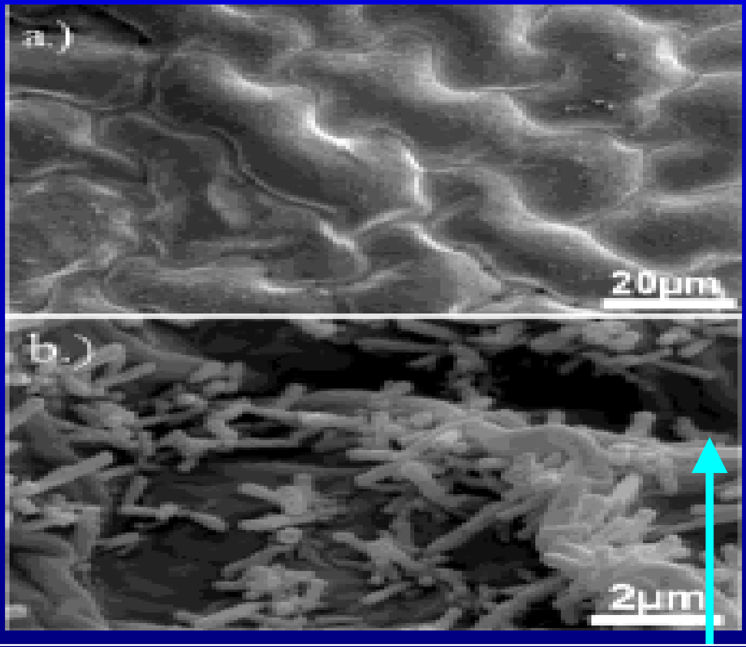
*--Buddha*

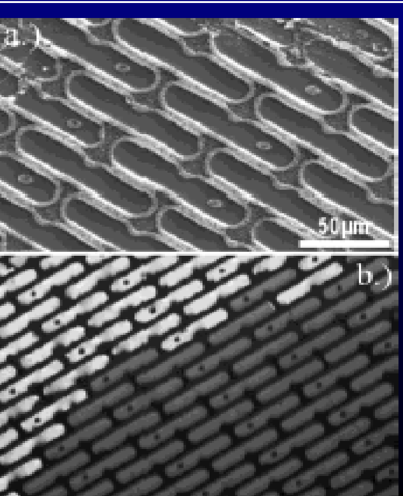
# Superhydrophobicity and Self-cleaning: “Fakir Droplets” and “Lotus” Effect

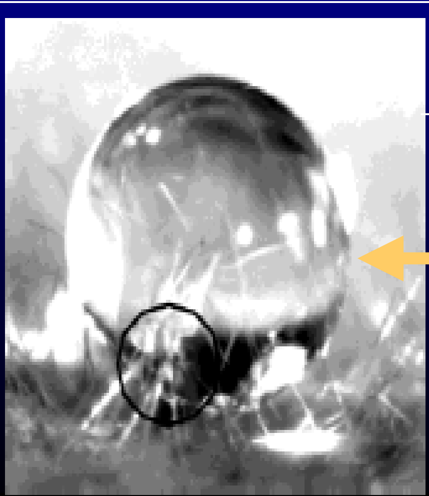



## Water droplets on Indian cress and Lady’s Mantle



**Indian cress leaf; wax crystals**

**Nanotube pattern and condensed hair cluster holding a drop**

**Herminghaus, Langmuir 04**

**Many a small thing has been made large by the right kind of advertising**

**--Mark Twain**

# Top 10 Nanotechnology Products of 2003: A case study of nanotech hype, hope and realities

1. **High-Performance Ski Wax:** "intelligent" nanowax with hard, fast-gliding surface that lasts longer and hardens in with temperature drop….

2. **Breathable Waterproof Ski Jacket:** the two-layer laminate windproof, waterproof, breathable and grime resistant

3. **Wrinkle-Resistant, Stain-Repellent Threads:** Attached molecular structures to cotton fibers; water-proof, wrinkle-proof and repels stains from perennial offenders like soda, coffee, wine, mayonnaise and syrup.

http://www.forbes.com/home/2003/12/29/cz_jw_1229soapbox.html

**4. Deep-Penetrating Skin Cream:** 200-nanometer polymer "capsule” holds vitamin A until the outer shell dissolves under your skin.


**5. World's First OLED Digital Camera:**

**6. Nanotech DVD and Book Collection:**

**7. Performance Sunglasses:** antireflection and scratch-resistance functionality, Nanofilm deposits coating layers of 150 nanometers and 20 microns thick, respectively. Then it uses chemical self-assembly to form a polymer coating, three to ten nanometers thin, on the outer layer of the antireflective lenses.

**8. Nanocrystalline Sunscreen:** Nano-dispersed zinc oxide makes it clear rather than a white pasty goop

**9 & 10. High-Tech Tennis Rackets And Balls:**

>In the 1970s, it was aluminum; the 1980s, graphite; the 1990s, titanium. Now comes nanotechnology. high modulus graphite with carbon nanotubes hundred times stronger than steel, yet one-sixth the weight, carbon nanotubes increase the rigidity of the stabilizers….

>Barrier for the air to escape by coating the ball's inner core with 20 microns thick of layered sheets of clay polymer nanocomposites--each 1 nanometer thin.

**Always be nice to those younger than you, because they are the ones who will be writing about you.**

**--Cyril Connolly**

## Multidisciplinary vs. Interdisciplinary

**Discipline X + Discipline Y**
**$\Longrightarrow$ Problem solved (product made)**
**$\Longrightarrow$ Discipline X + Discipline Y**

**Discipline X + Discipline Y $\Longrightarrow$ Discipline Z**

***--"Nonlinear mixing" of different "scientific silos" or a "chemical reaction"***

***--Nanotechnology is yet to fully progress from white to yellow.***

**We can lick gravity, but sometimes the paperwork is overwhelming.**

**Author: Werner von Braun**

**Source:** ***in the Chicago "Sun Times", July 10, 1958***

**Science is a wonderful thing if one does not have to earn one's living at it.**

**Author: Sir Humphrey Davy**

**Source:** ***Consolations in Travel--Dialogue V--The Chemical Philosopher***

**“…….and precisely those scientists who have labored not with the aim of producing this or that, but who have worked with the sole desire to advance knowledge, ultimately prove to be greatest benefactors of human kind.”**

***-- Sir C. V. Raman***

# The art of our era is not art, but technology. Today Rembrandt is painting automobiles; Shakespeare is writing research reports; Michelangelo is designing more efficient bank lobbies…

**--Howard Sparks**

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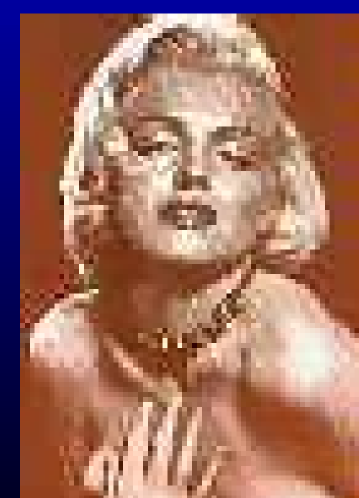
- **Of course, what works for Sir Raman, doesn’t work for Bill Gates (!) ………..**

# The Middle Way

"…there are two extremes that should be carefully avoided…"

**--Guatama Buddha**



- **Small things have BIG implications even in macroscopic world and products of everyday**
- **Self-assembly and self-organization are efficient, cheaper and often the only ways ways of forming structures and patterns on small scales**
- **Nano-structures and devices are often NOT stable, which is both bad and good !**
- **Bio-processes and structures can inspire novel and optimal engineering ideas**

# *Acknowledgements*

Vijay Shenoy (IISc, Bangalore)

Manoj Choudhary (Lehigh U.)

Animangsu Ghatak (Harvard; soon to be at IITK?)

Guenter Reiter (CNRS, Mulhouse)

Rajesh Khanna (IIT Delhi)

Kajari Kargupta (Jadavpur U)

Rahul Konnur (TRDDC, Pune)

Jayati Sarkar (IIT Kanpur)

Manoj Gonuguntla (IIT Kanpur)

Subasis Sarkar (IIT Kanpur)

Moniraj Ghosh (IIT Kanpur)