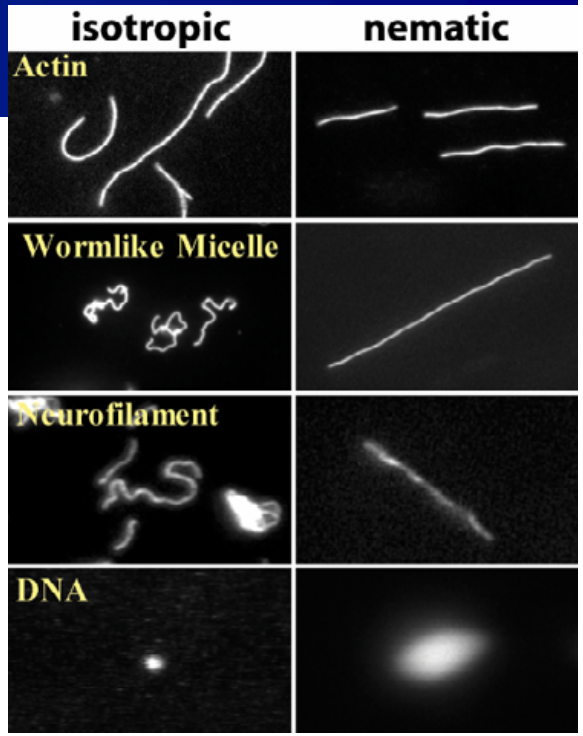
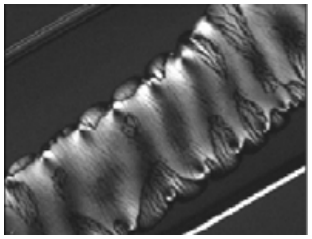
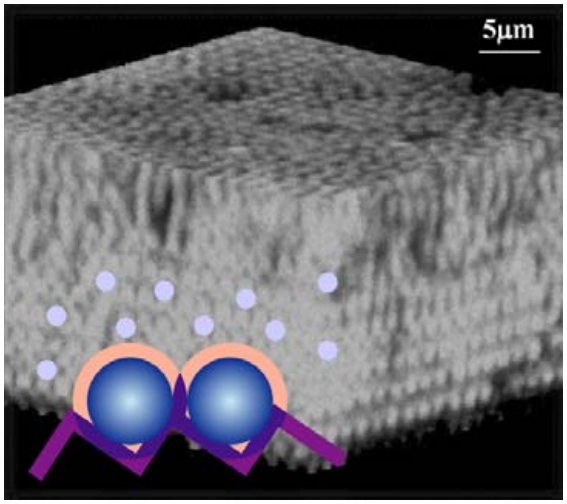
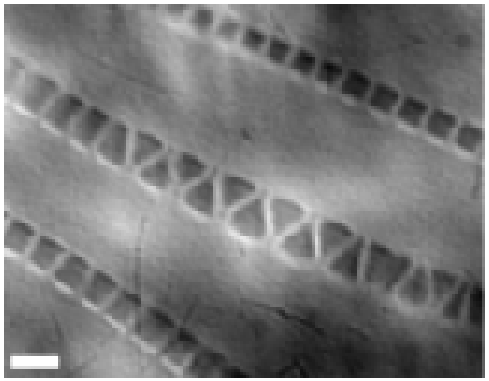
Entropic Forces & Phase Transitions

Arjun G. Yodh, Dept. of Physics & Astronomy



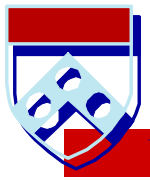




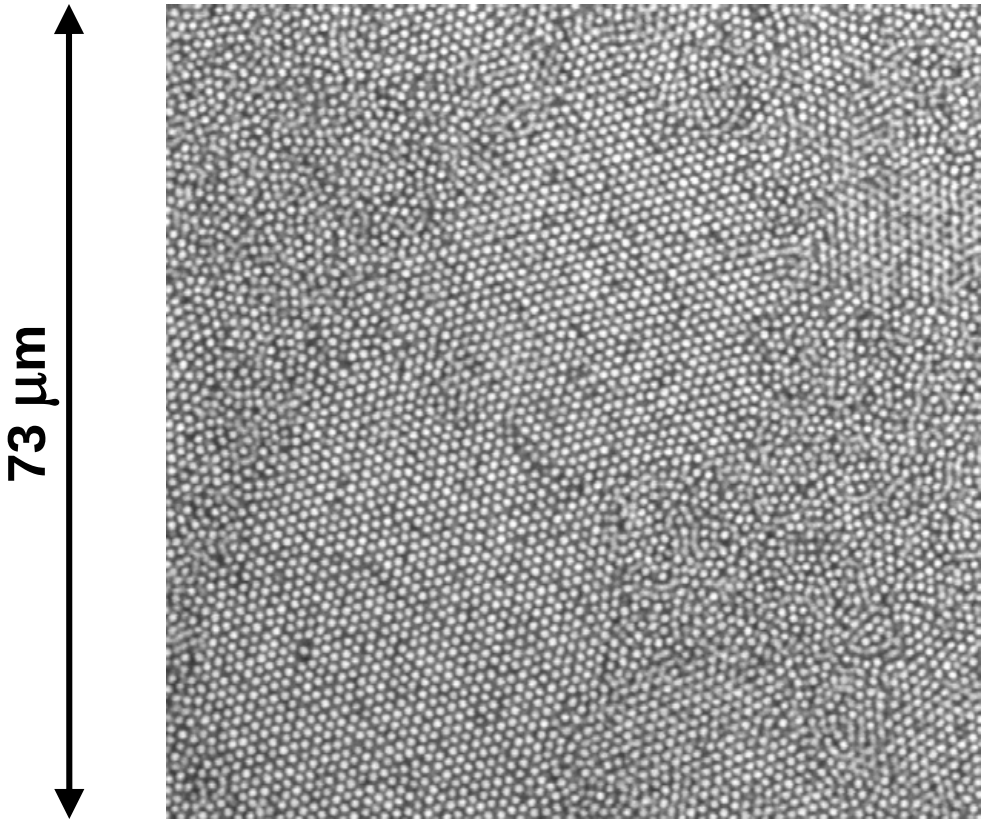


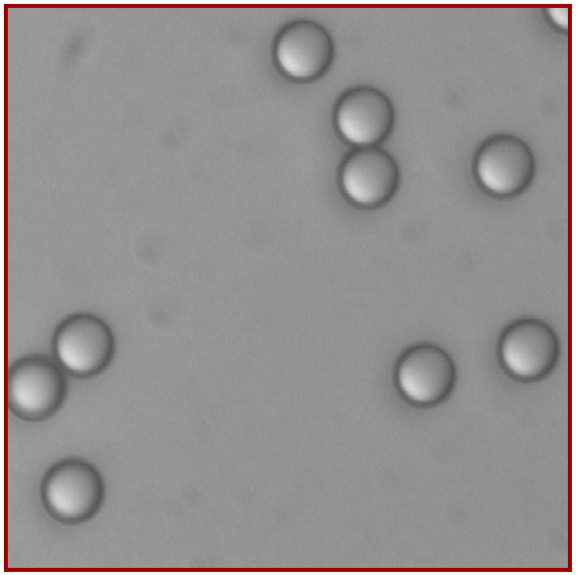
Outline

- General Motivations
- Entropy, Phase Transitions, Entropic Forces
- Interaction Potential Measurements (mainly spheres)
- Self-Assembly (mainly spheres)
- Beyond Spheres

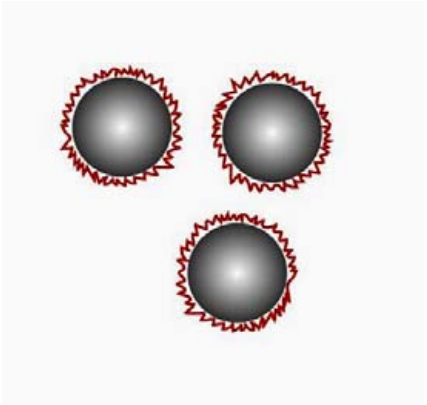


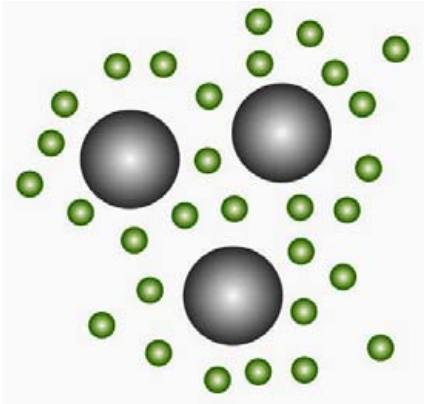
Particles in Water

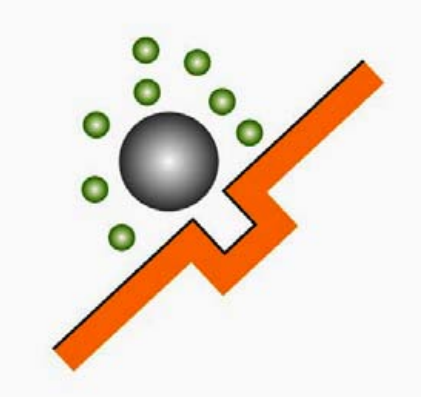


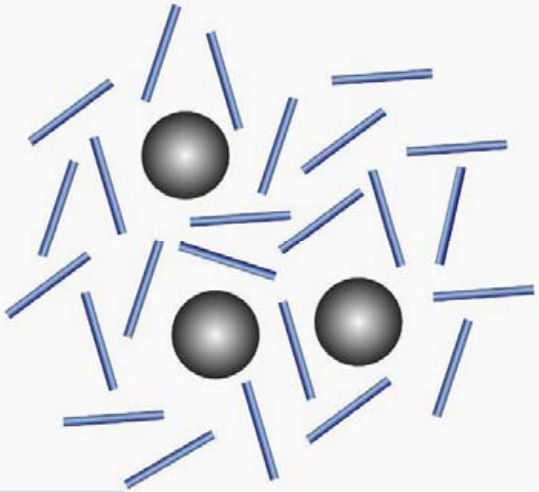


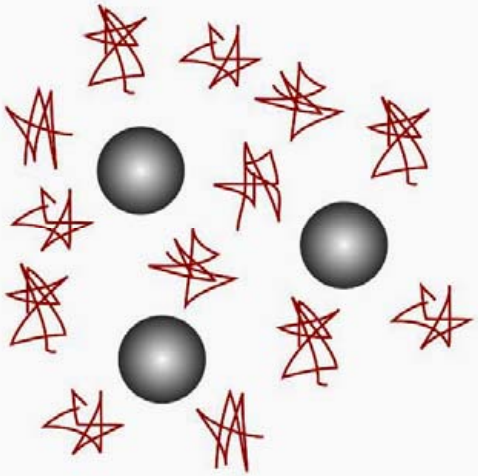
Forces, Potentials ? Self-Assembly?

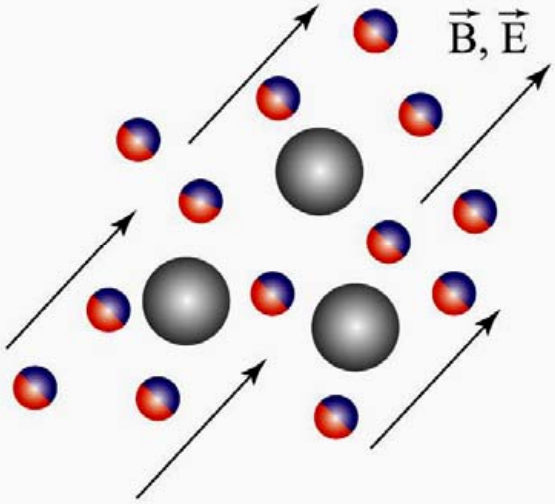








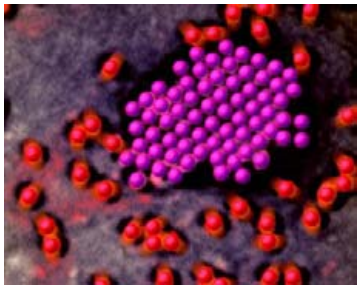




MOTIVATIONS / FUNDAMENTAL

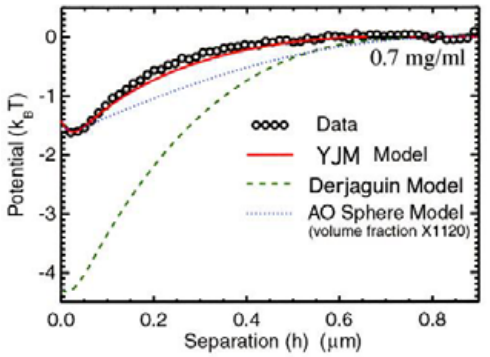
(1) Self-Assembly / Collective Properties

- Novel Phases (Equilibrium Statistical Physics)
  - Role of shape, charge, concentration, conformation, size, ...
- Structure, Dynamics, Rheology, Optical Properties, ...
- Beyond Equilibrium: Metastable phases, glasses, …
  Templates, Nucleation,…
  Sedimentation (Microgravity!)



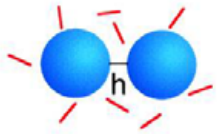
(2) Interactions / Forces

- **What are the interactions between constituents in suspension?**
- **How do these interactions arise?**
- **How do these interactions affect self-assembly, structure, dynamics, rheology, transport properties?**



Silica (1 μm-diam.)

Rod (L=880nm)
Φ ~ .0005



Lin, Crocker, Zeri, Yodh, PRL (2001)

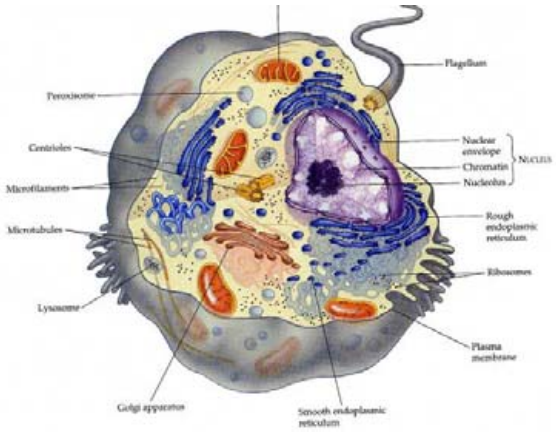
MOTIVATIONS / PRACTICAL

Creation of Novel Structures for "High-Tech" Applications

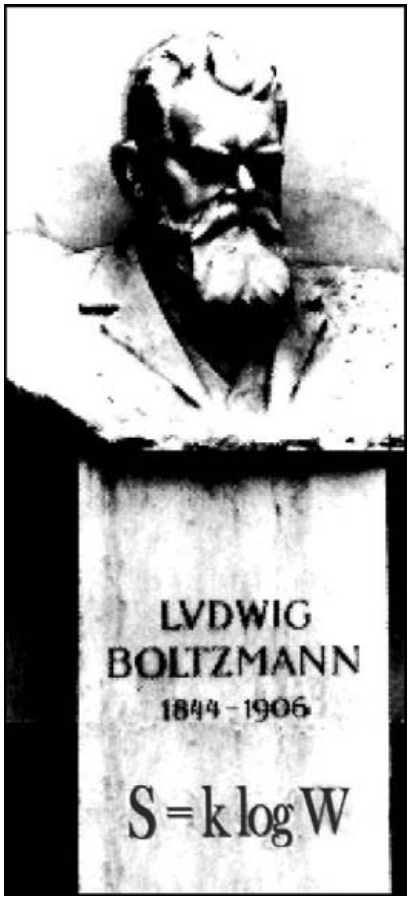
Photonics, Sensors, MicroArrays, Bragg-Switches, Advanced Composites …

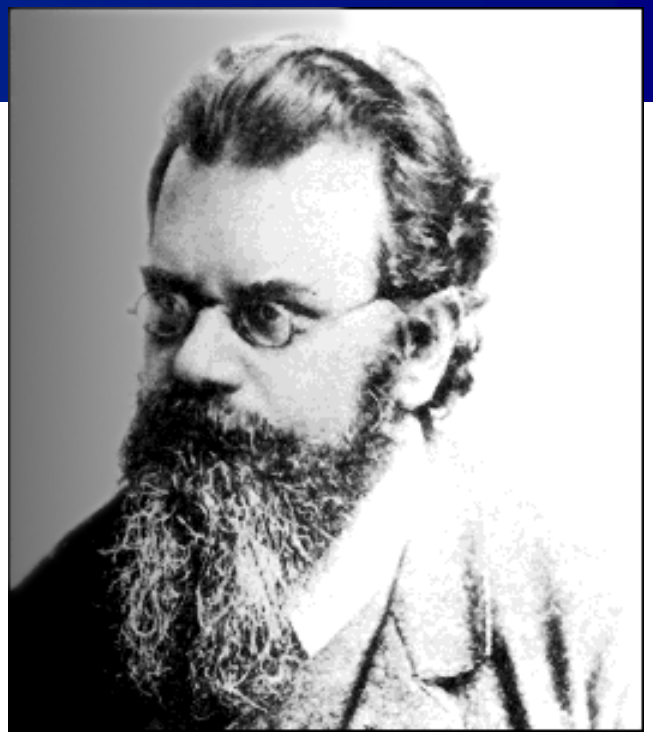
Understanding, CONTROL of many "Practical" soft materials

Insight about crowded environments: cellular interiors



Ludwig Boltzman

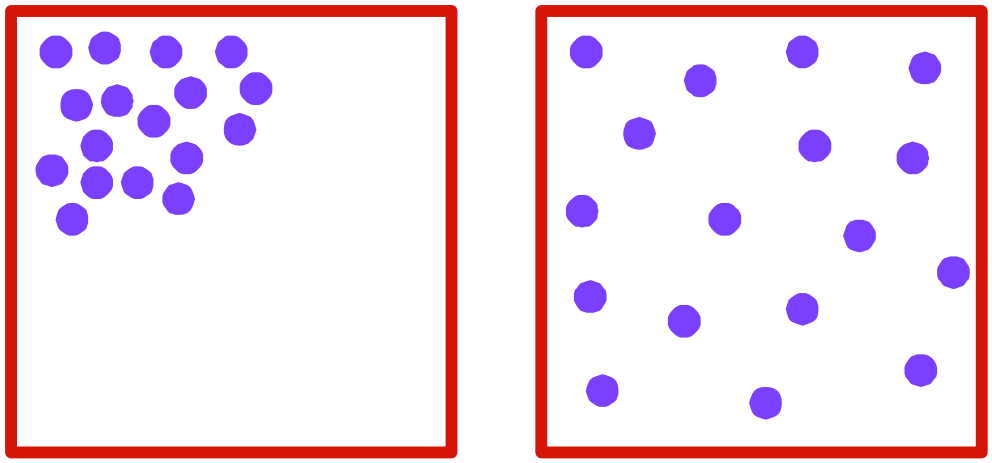




S = ENTROPY

W = Number of states (configurations) Accessible to Thermodynamic System with Energy E

N Gas Particles in a Box



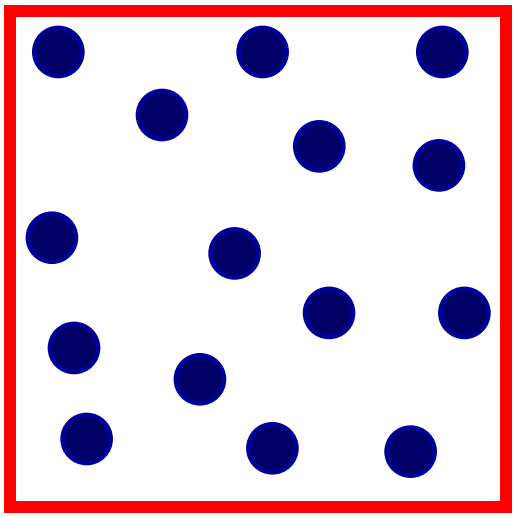
E.g.,

Number of Configurations that fill box far exceed the number of configurations that fill one quarter of the box.

In the absence of external influences systems tend to maximize entropy (i.e. become more disordered).

Entropy of N Particles in a Box

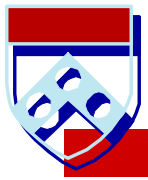
Indistinguishable non-interacting particles in a box



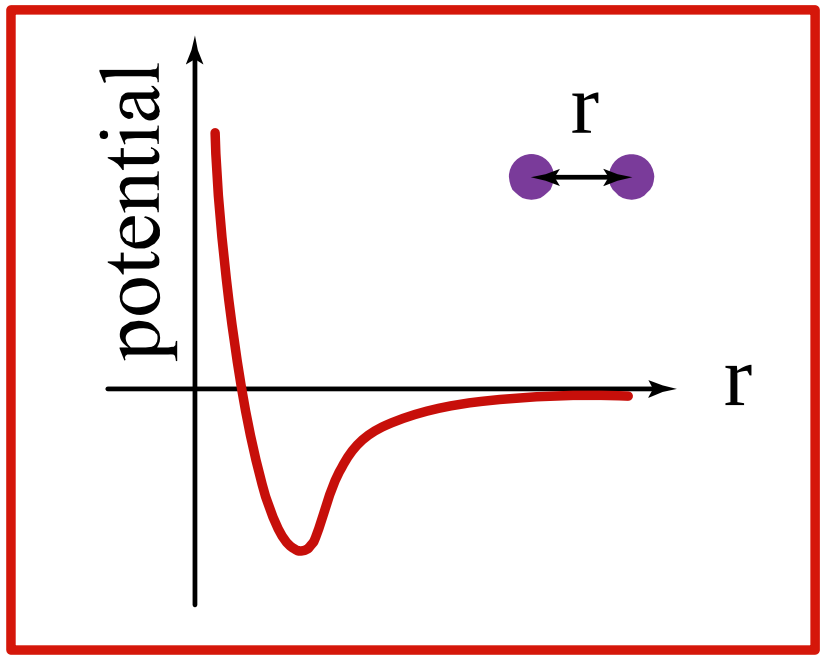
V, T, N

$$S \sim k\,N\,ln\left(\frac{V}{N}/\lambda^3_{\text{deBroglie}}\right)$$

$$\text{If } V \to V + \Delta V: \quad \Delta S \approx kN\left(\frac{\Delta V}{V}\right)$$



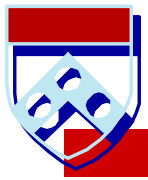
Free Energy (F)



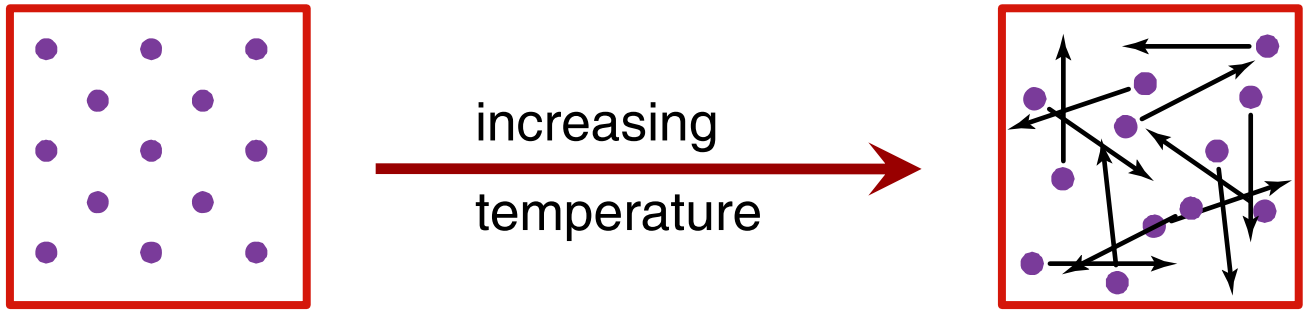
$$F = U - TS$$

- U: internal energy associated with particle positions
- TS: tendency to disorder

Phases of Matter (solid, liquid, gas) minimize free energy



Conventional Solids & Liquids/Gases



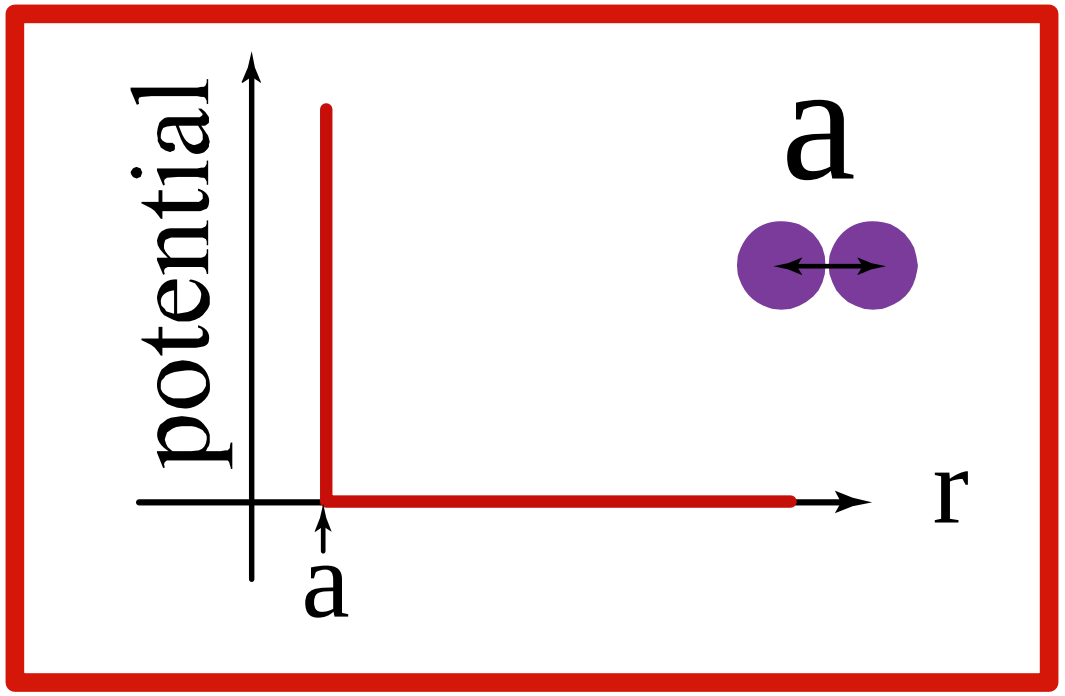
solid **liquid, gas**

U dominates S

S dominates U

Hard Sphere Systems

No attractive energy from U !

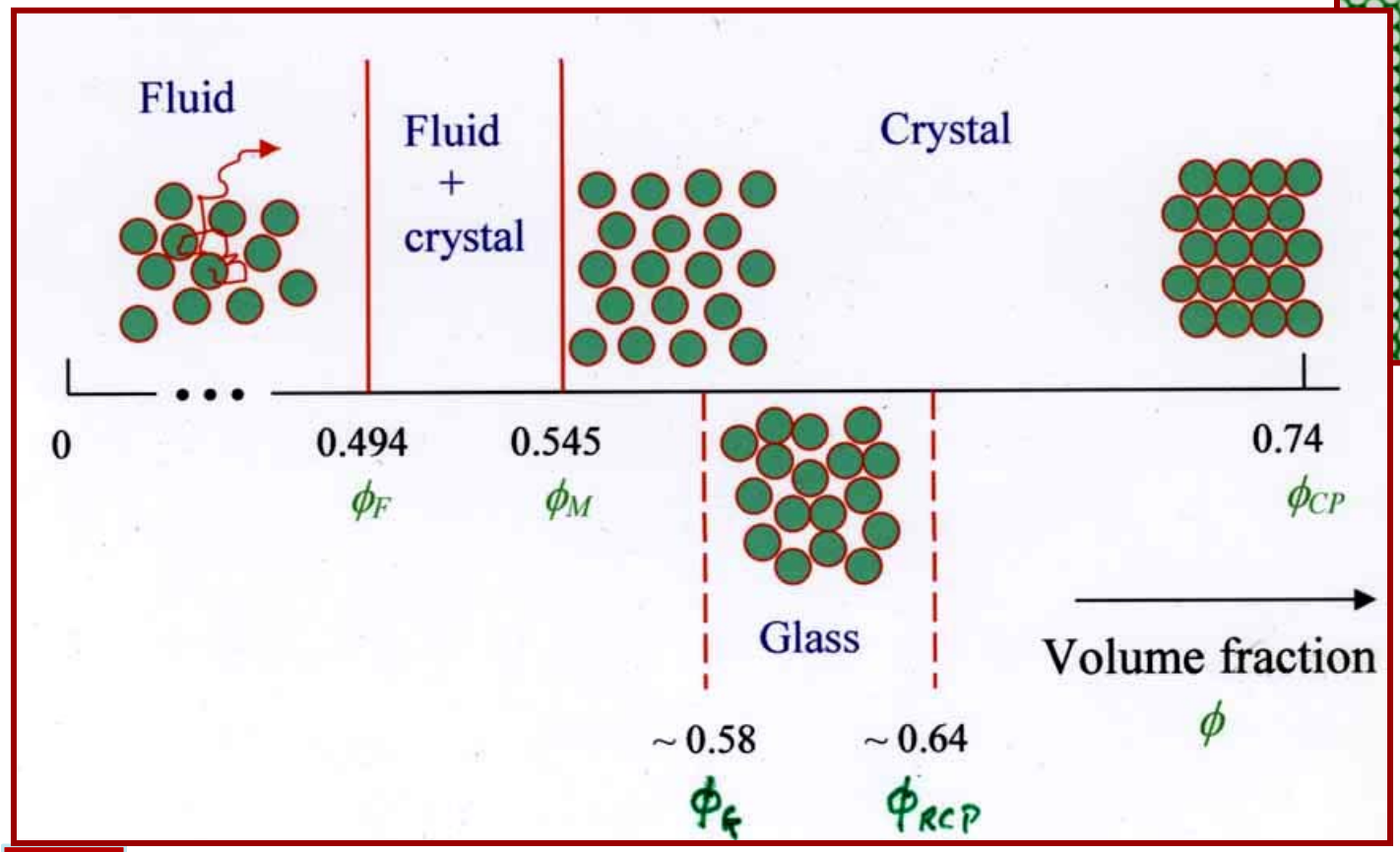


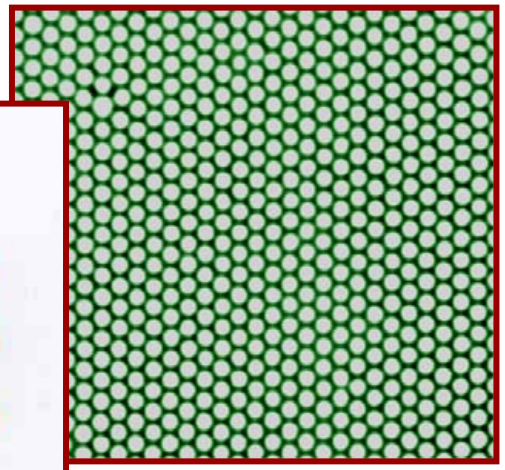
F = -TS

only depends on entropy

Monodisperse Hard Sphere Phase Behavior

Phase diagram – one-component



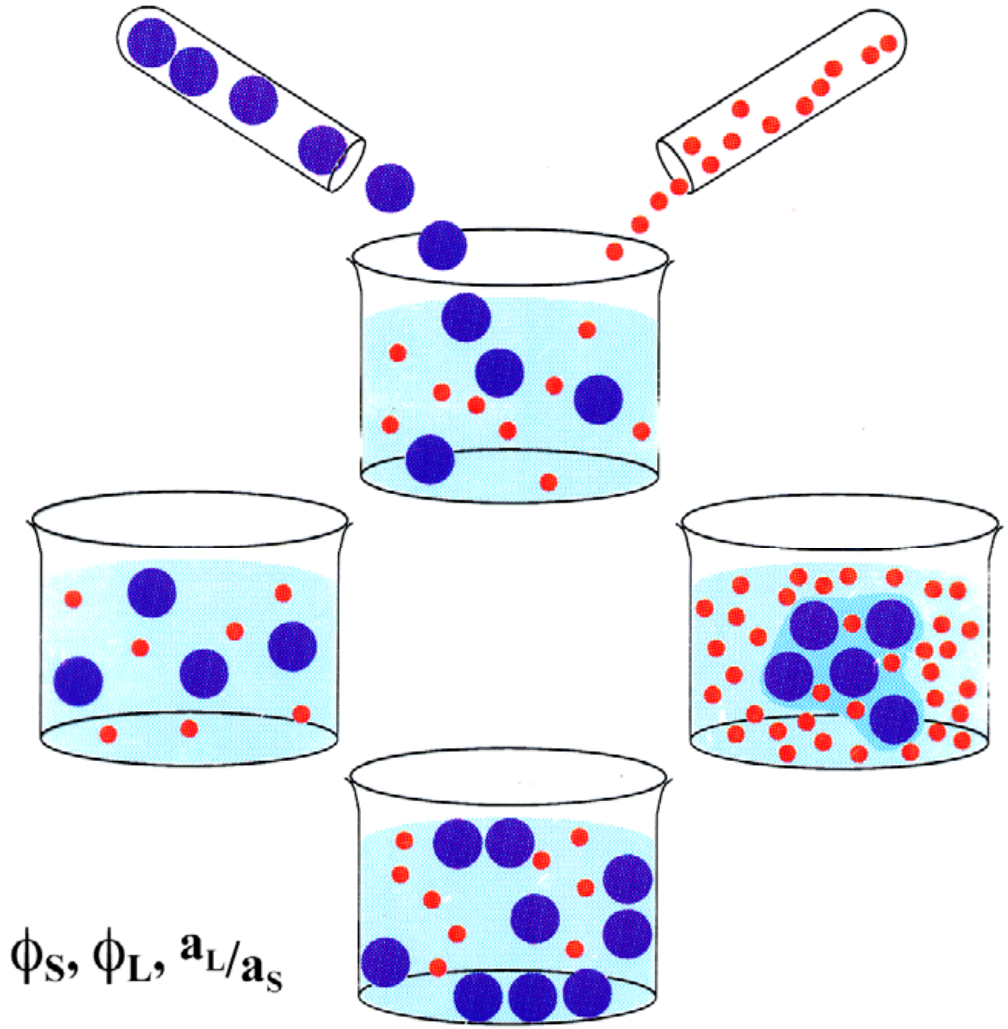


Real colloidal crystal

Pusey, P.N., van Megen, W. Nature 320, 340-342 (1986).

Zhu, J.X., Li, M., Rogers, R., Meyer, W., Ottewill, R.H., Russell, W.B., Chaikin, P.M. Nature 387, 883-885 (1997).

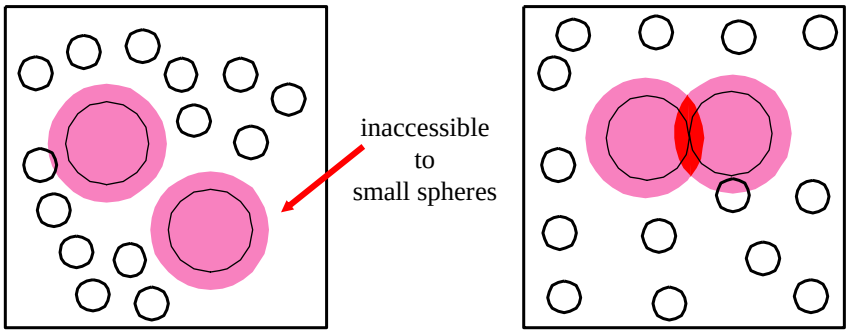
Binary Systems



Role of Surfaces

Entropic Forces

Depletion Force: (HARD SPHERES)



$$U(r) = \pi(\Phi_S)\,\Delta V(r, a_S, a_L)$$

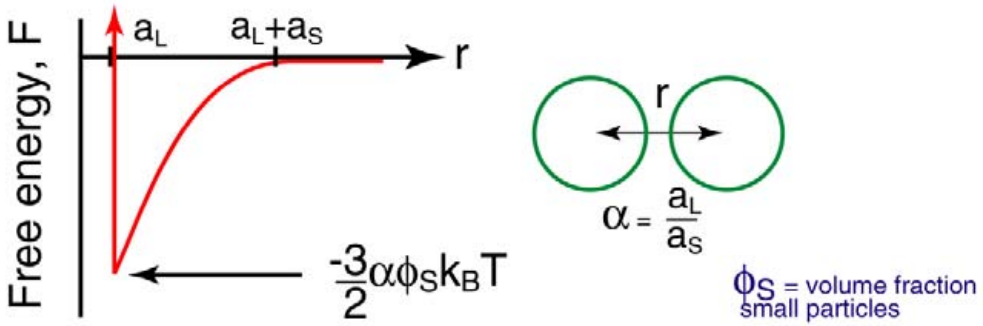
Osmotic pressure — **Free Volume Change**

→ Moving 2 large spheres together increases volume accessible to small spheres

↓

increases total entopy

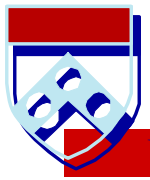
$\Delta F = \Delta U - T\Delta S$



Free-energy gradient ⟷ **Force**

Asakura, Oosawa, J. Polym. Sci. v.33, 1983 (1958)

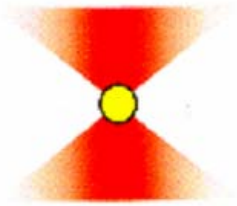
Vrij, Pure Appl. Chem. v.48, 471 (1976)



Optical Micromanipulation

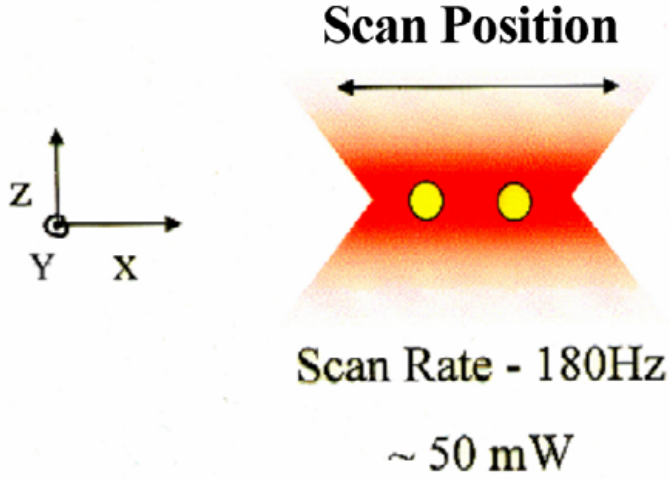
Optical Tweezers

Gradiant Force >> Radiation Pressure



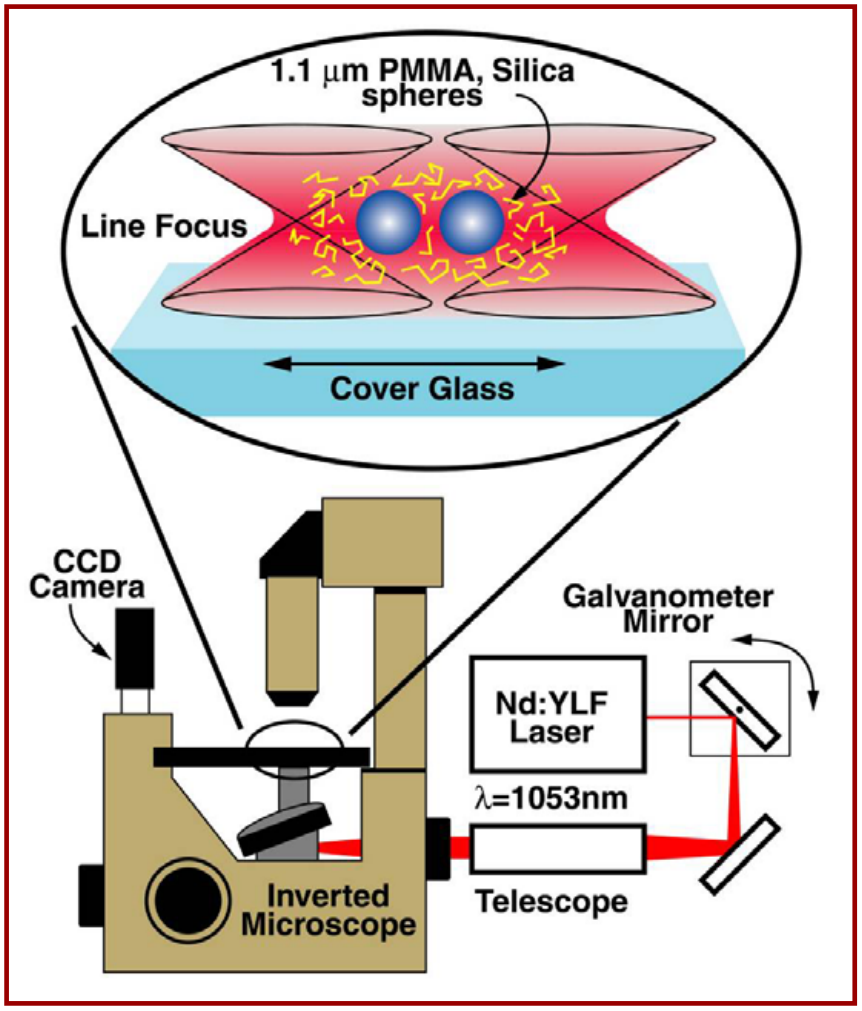
- **Strongly Focused Beam**
  Microscope objectives with high NA provide an easy solution
- **Non-Destructive**
  Can manipulate small dielectric particles with piconewton forces

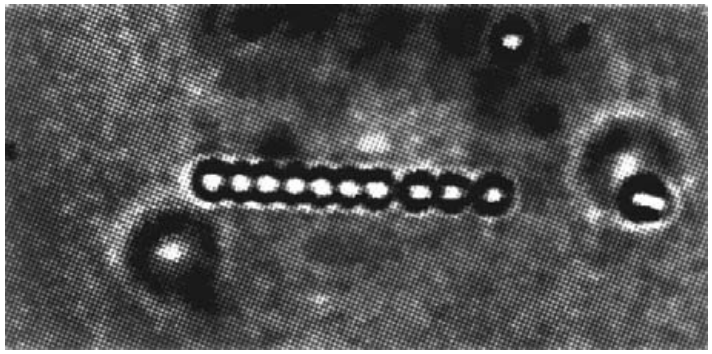
Optical Line Tweezers



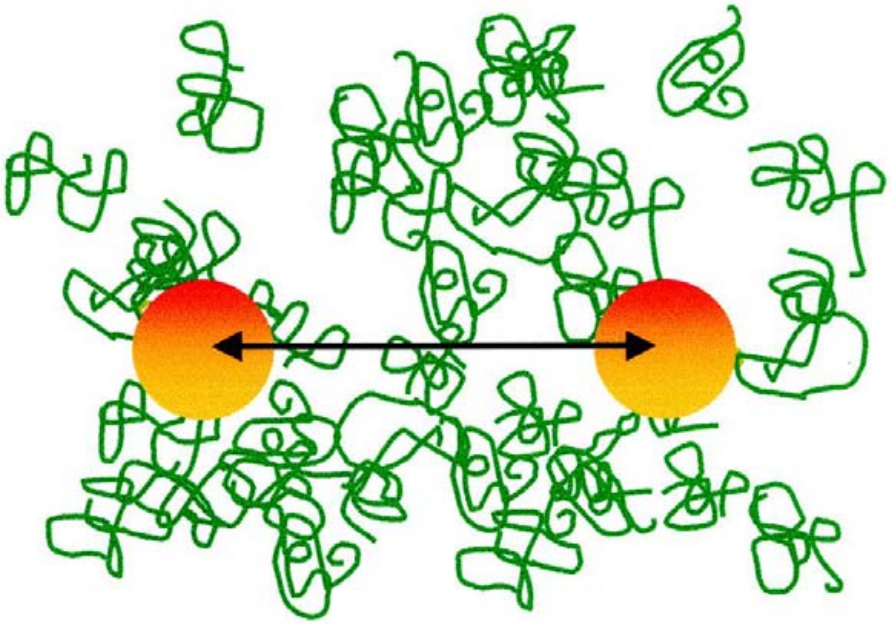
- **Measure Actual 3-Dimensional Separations**
  Particles are confined in the yz-direction
- **Confine Motion of Particles**
  Improves Statistics

A Line-scanned Optical Tweezer

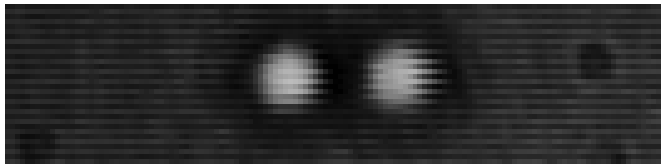




Measuring the Interaction



Center separation (**r**)



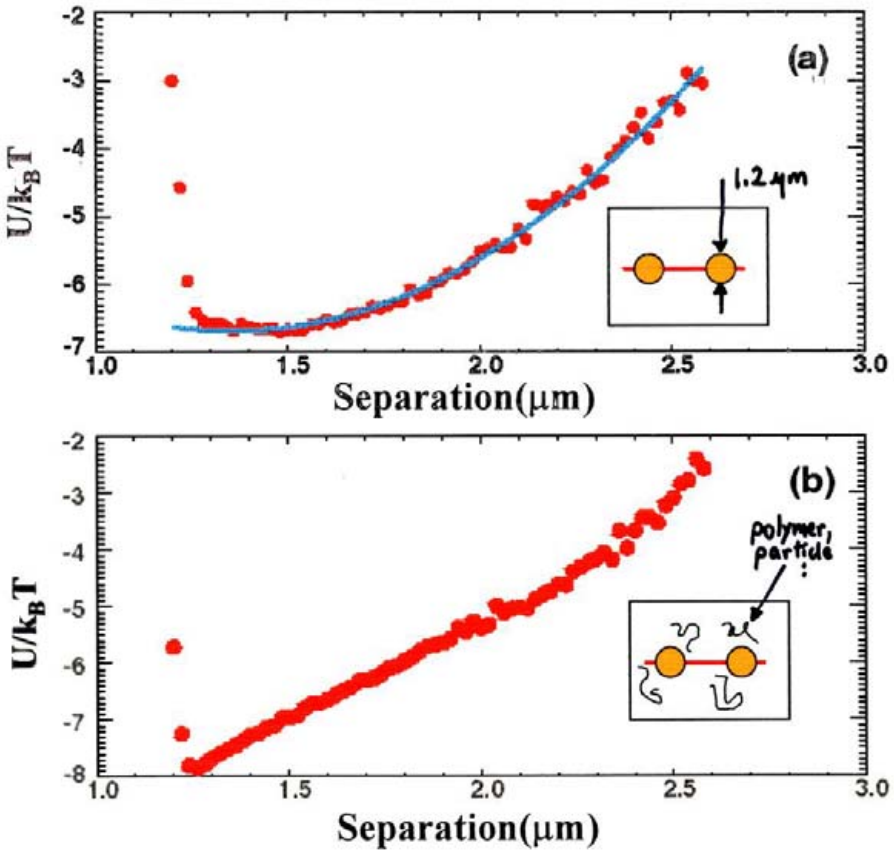
Probability of finding the separation between two particles to be **r**

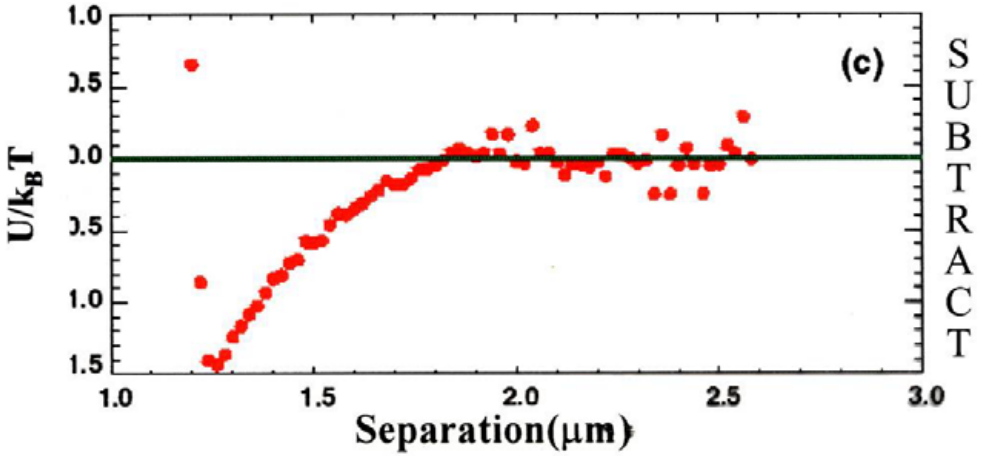
$$P(r_i) = \frac{N(r_i)}{\sum_i N(r_i)}$$

$$P(r_i) \propto e^{-U(r_i)/k_B T}$$

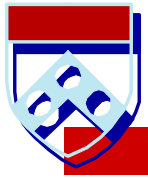
$$U(r_i) \propto -k_B T \ln(P(r_i))$$

Isolating the Entropic Effects of the Background Fluid



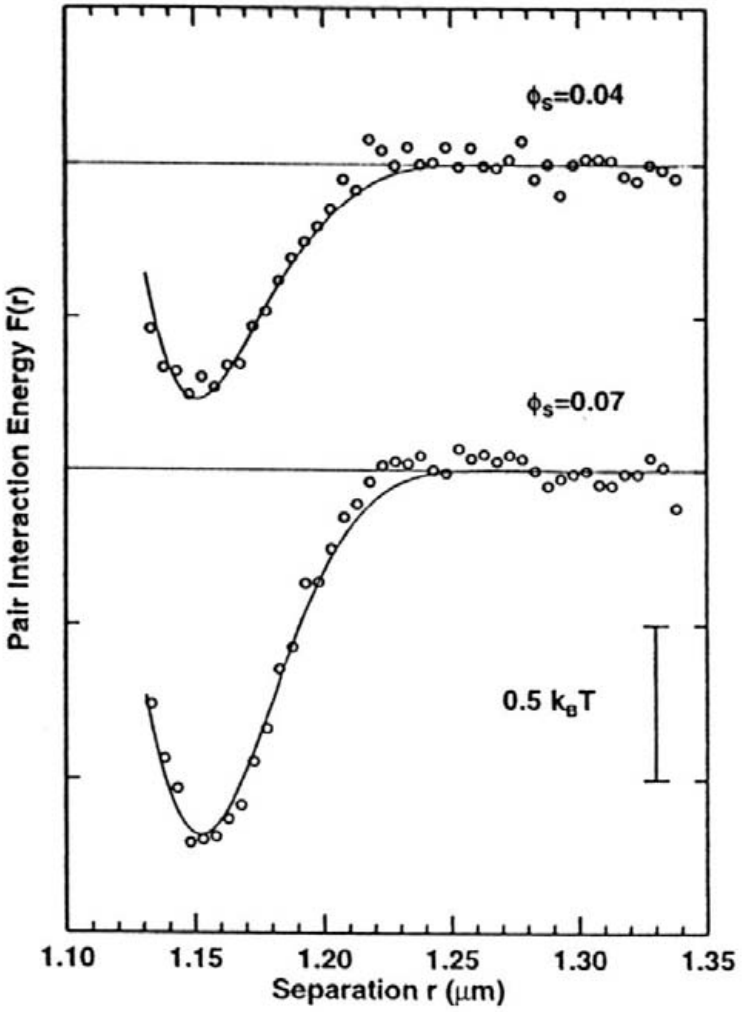


Energy Resolution ~ 0.05kT
Spatial Resolution ~ 15-30nm



Big Spheres and Little Spheres

$$F_{AO}(r) = (kT\,\Phi_s^*)\,(2a_s^*)^{-3}\,(2a_s^* + 2a_L - r)^2\,(2a_s^* + 2a_L + r/2)$$



$a_s^* = a_s + \delta a_s$; $\Phi_s^* = \Phi_s\,(1 + \delta a_s/a_s)^3$

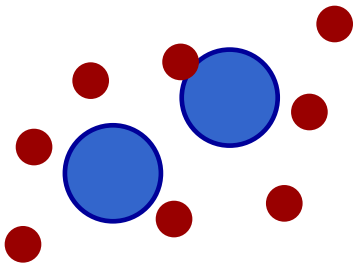
$2a_s = 83$ nm (PS)

$2a_L = 1100 \pm 15$ nm (PMMA)

$\delta a_s = 7 \pm 3$ nm

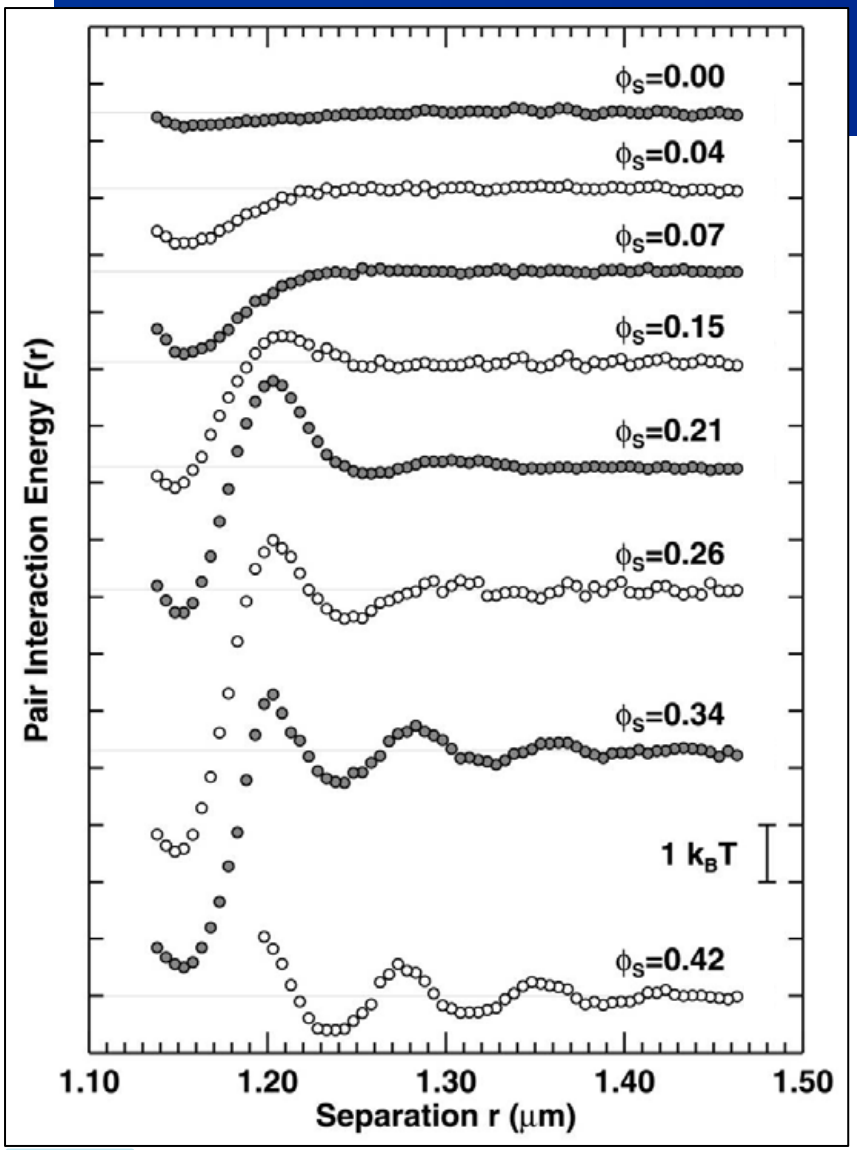
Φ_s from Viscometry

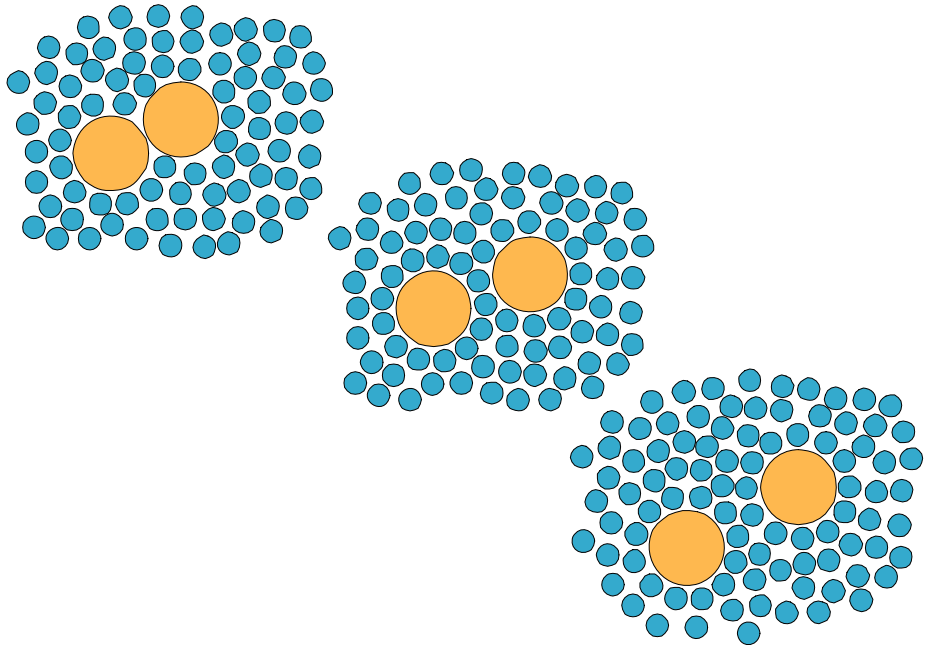
$L_{D\text{-}H} \approx 3$ nm



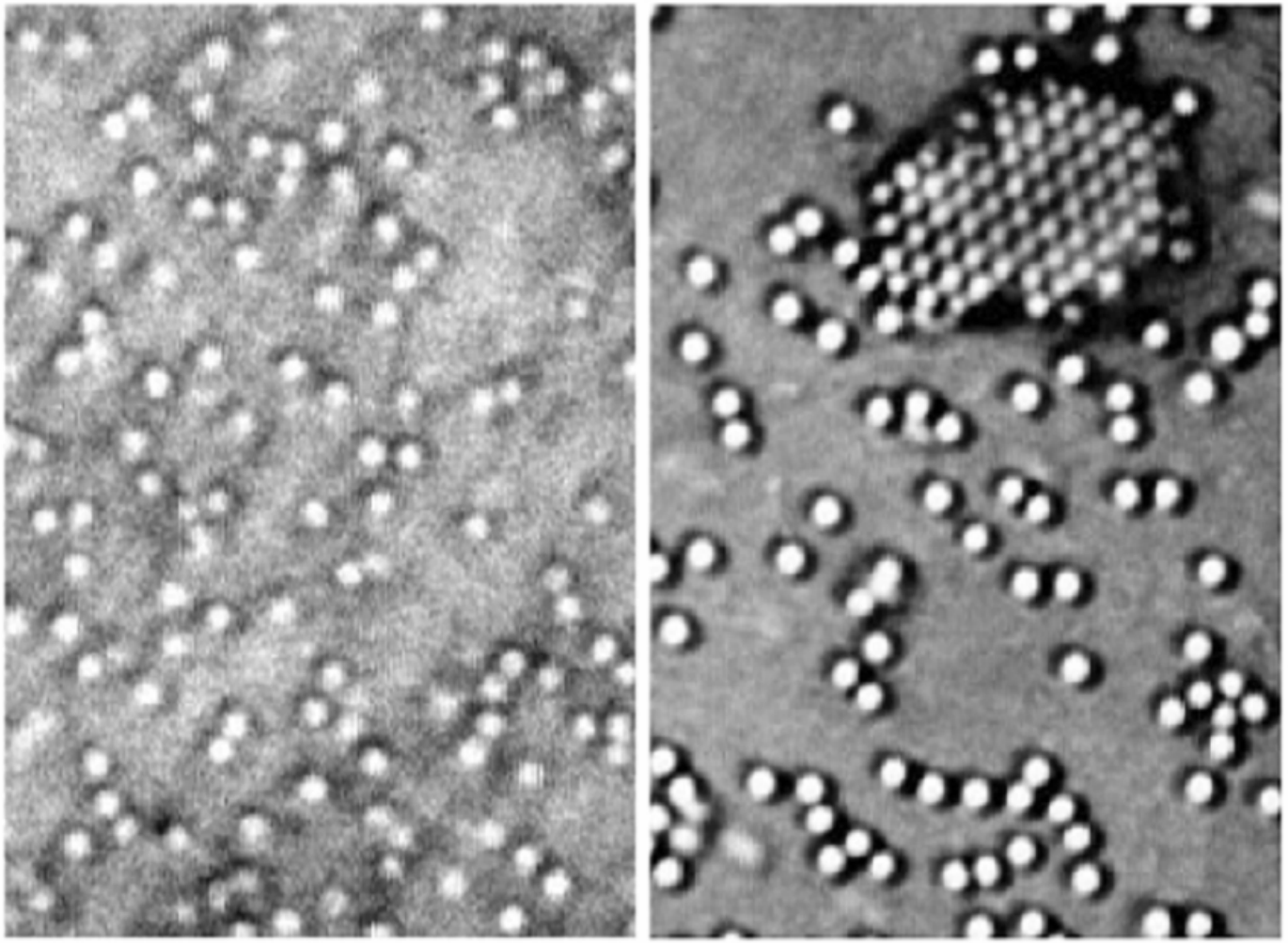
Crocker, Matteo, Dinsmore, Yodh,
Physical Review Letters v. 82, 4352 (1999)

Concentrated Suspensions

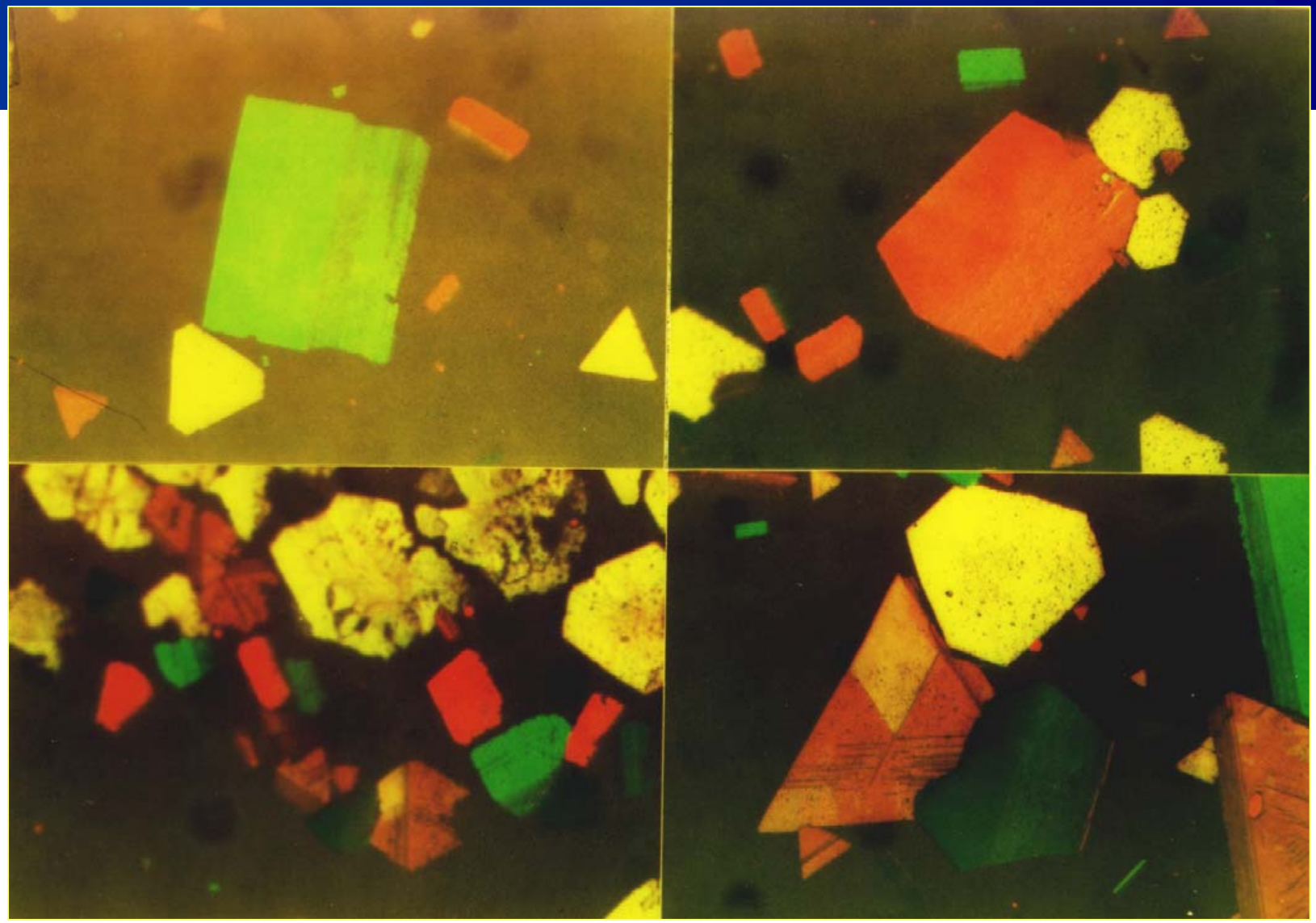




Fluid Phase Crystalline Phase

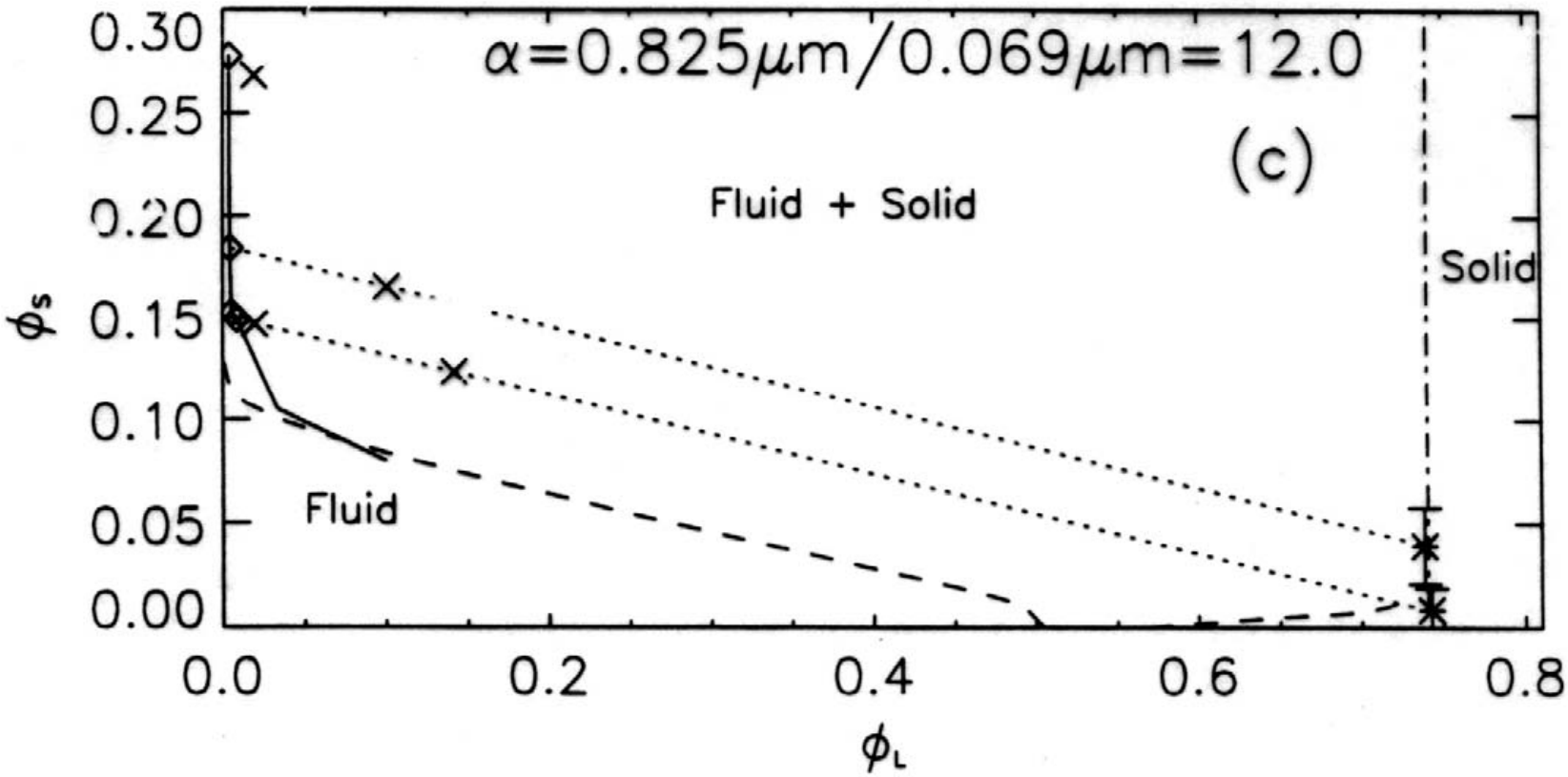


Increasing Φ_s



500μm

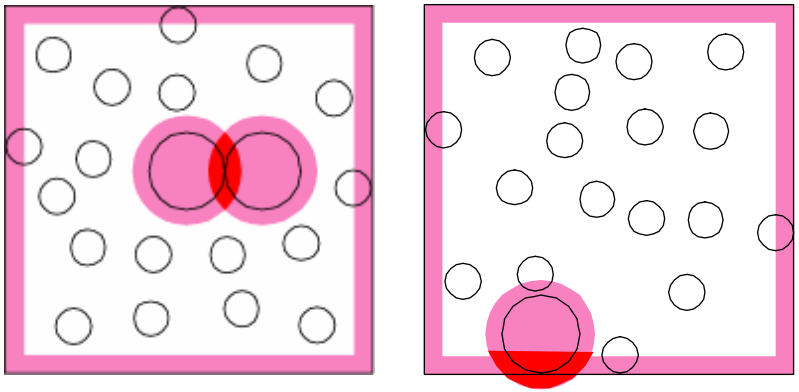
Phase Diagram



Dinsmore, A.D., Yodh, A.G., and Pine, D.J., Physical Review E 52, 4045-4057 (1995).

Entropic Effect Near a Wall

Depletion Forces at Surface: (HARD SPHERES)



→ **Moving large sphere to wall decreases the Free energy even more!**

$$\text{Force}_{\substack{\text{sphere}\\\text{-wall}}} \approx 2 \times \text{Force}_{\substack{\text{sphere}\\\text{-sphere}}}$$

$$\approx 3\alpha\phi_S k_B T$$

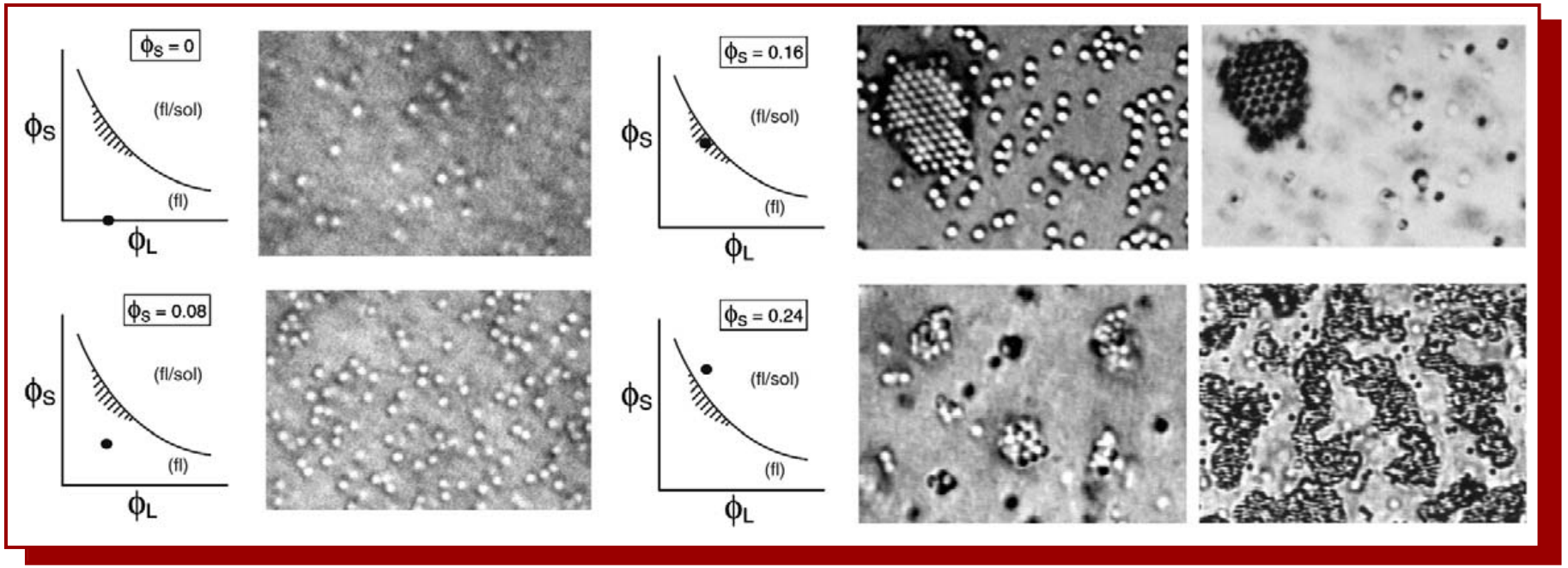
(a few $k_B T$ in strength)

$\alpha = \frac{a_L}{a_S}$

ϕ_S = volume fraction small particles

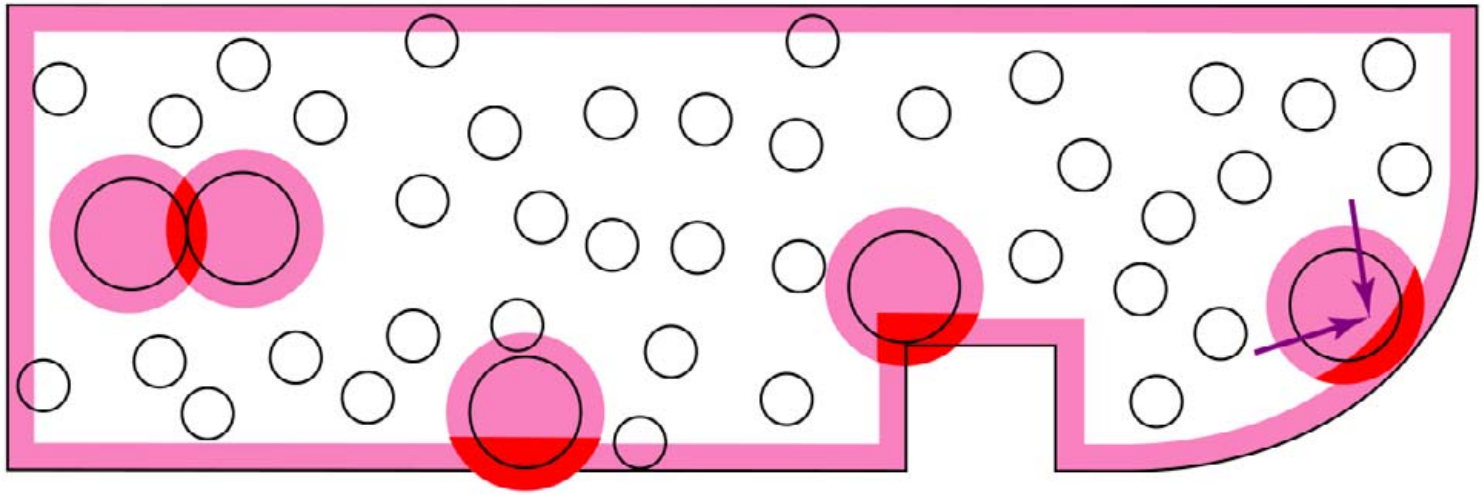
Kaplan, Rouke, Yodh, Pine, Physical Review Letters v.72, 582 (1994)

RANGE OF COMPOSITIONS WHERE "EQUILIBRIUM" COLLOIDAL EPITAXY IS POSSIBLE!



Dinsmore, A.D., Warren, P.B., Poon, W.C.K., Yodh, A.G., Europhys Lett 40, 337-342 (1997).
Dinsmore, A.D., Yodh, A.G., Pine, D.J., Phys Rev E 52, 4045-4057 (1995).

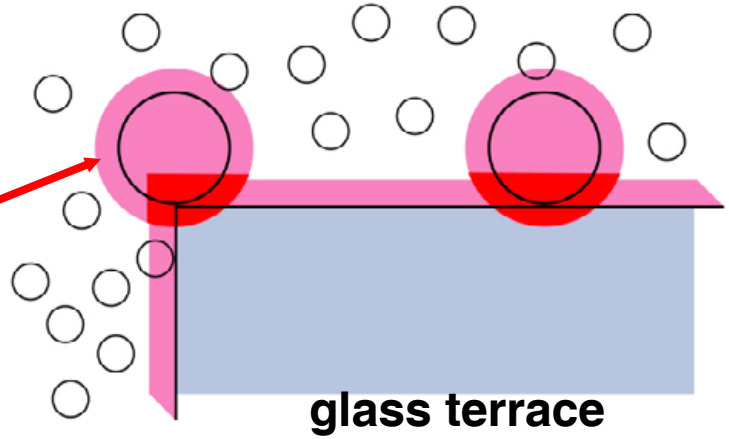
Entropic effects with Structure in the Walls

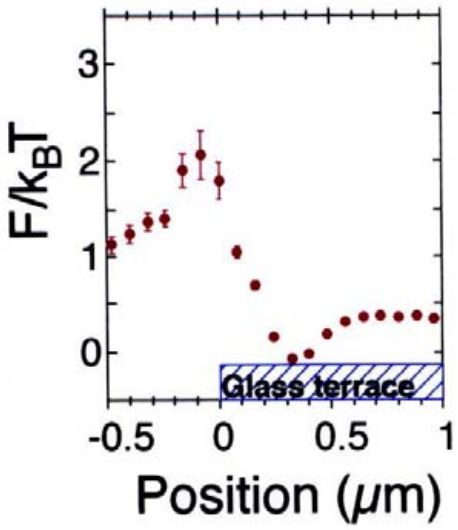


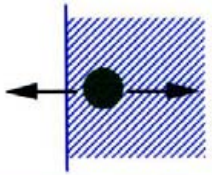
Dinsmore, A.D., Yodh, A.G., Pine, D.J., Nature 383, 239-242 (1996).
Dinsmore, A.D., Wong, D.T., Nelson, P., Yodh, A.G., Phys Rev Lett 80, 409-412 (1998).
Dinsmore, A.D., Yodh, A.G., Langmuir 15, 314-316 (1999).

Entropic repulsion from a step edge:

Less excluded-volume overlap here



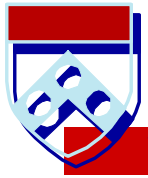




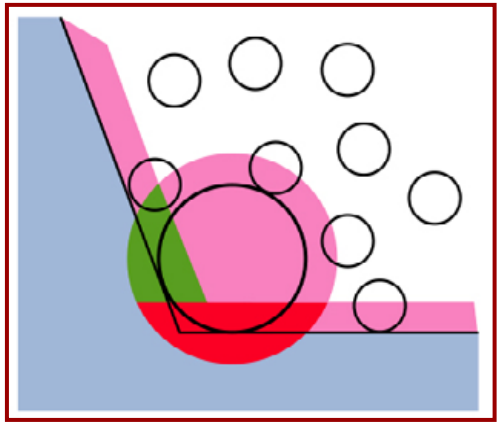
Free-energy barrier ≈ $2k_BT$ at edge of terrace

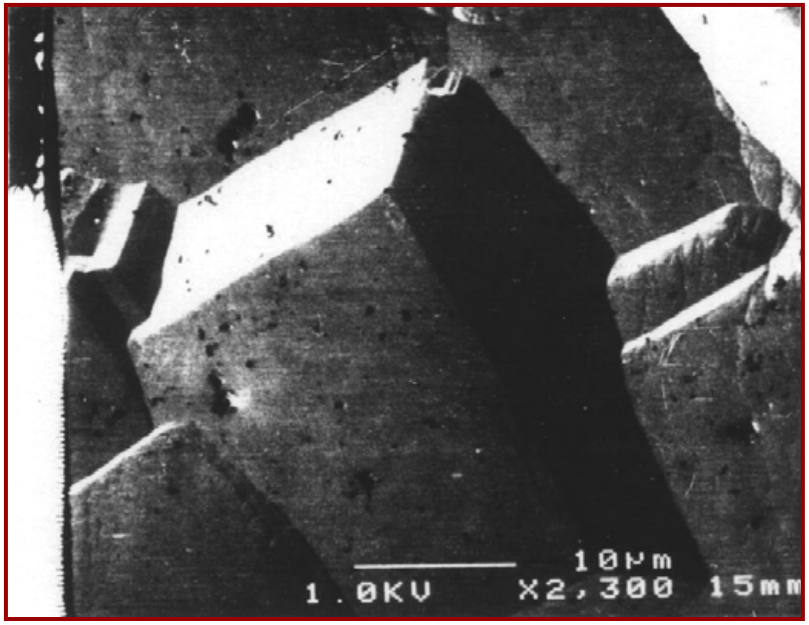
Maximum force = 0.04 pN

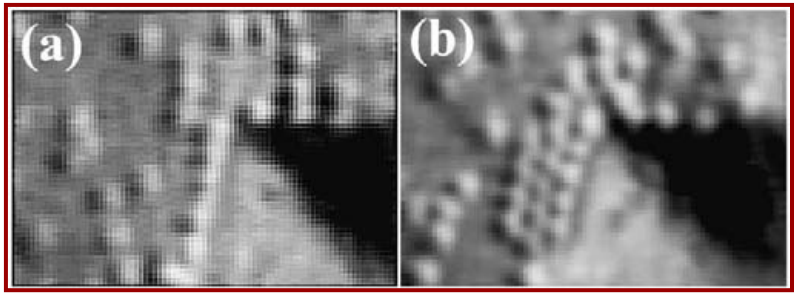
Dinsmore, Yodh, Pine, Nature v.3838, 239 (1996)



CORNERS



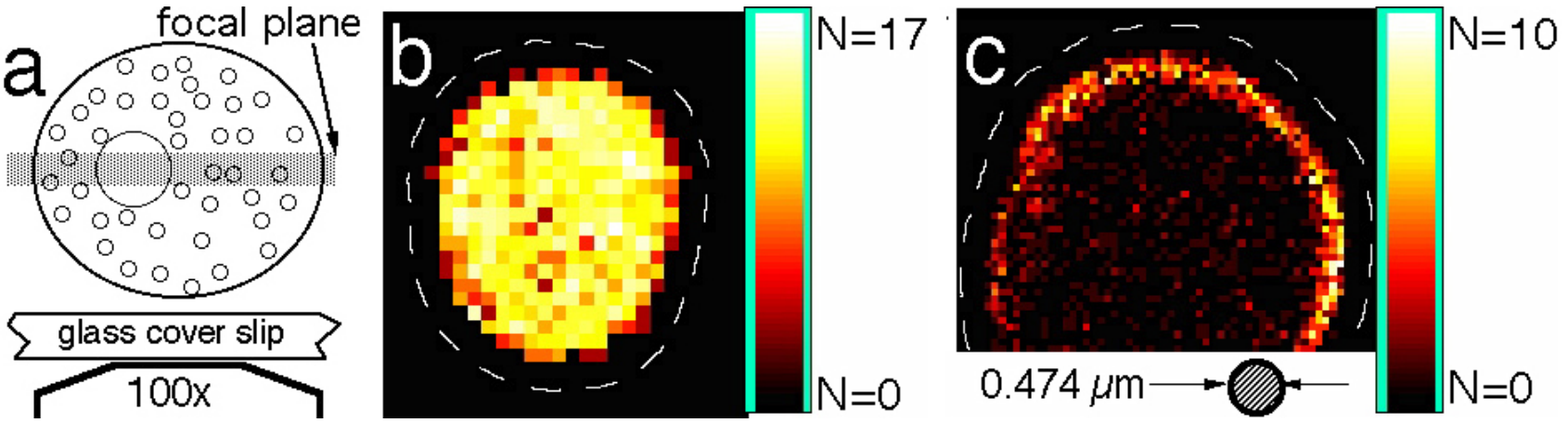




Dinsmore, Yodh, Langmuir v.15, 314 (1999)

VESICLES

(PARTICLES PUSHED TO WALLS AND REGIONS OF HIGH CURVATURE)

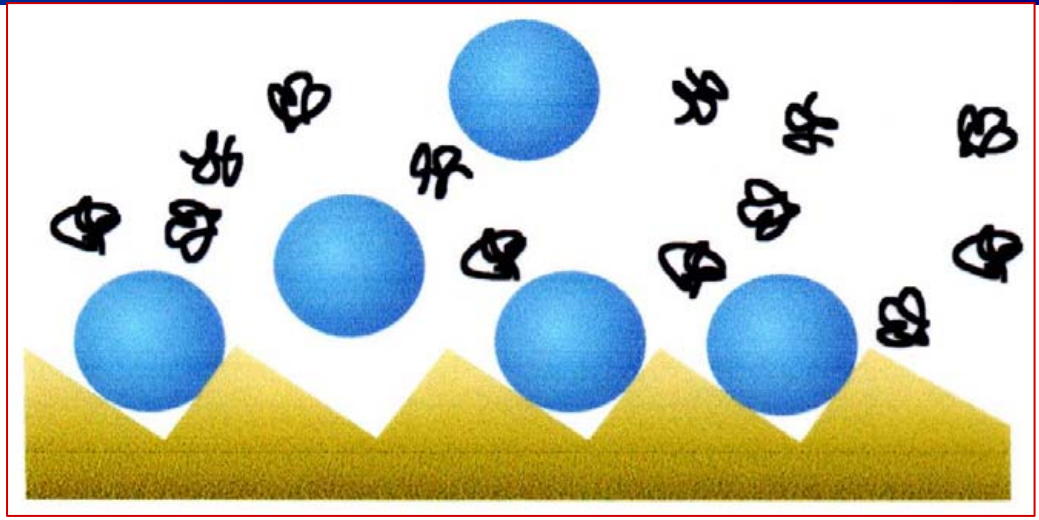


Large Particles Alone **Large and Small Particles**

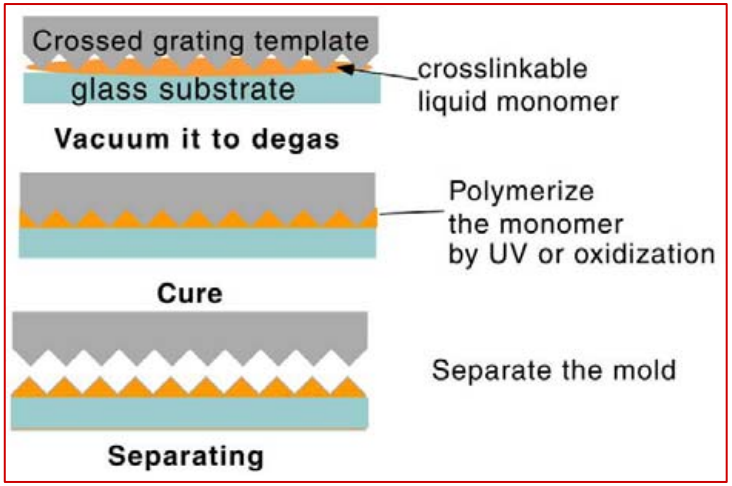
Dinsmore, A.D., Wong, D.T., Nelson, P., Yodh, A.G., Phys Rev Lett 80, 409-412 (1998).

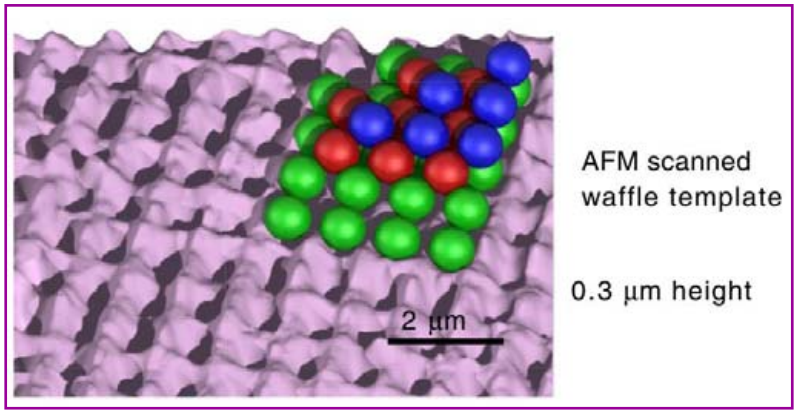
Controlled Colloidal Epitaxy

- **PMMA beads with Polymer, index matched for 3D confocal microscopy.**
- **Slight density mis-match for 3D growth (decalin)**



Lin, K-H, Crocker, J.C., Prasad, V., Schofield, A.,Lubensky, T.C., Weitz, D.A., Yodh, A.G., Physical Review Letters, 85 (2000)



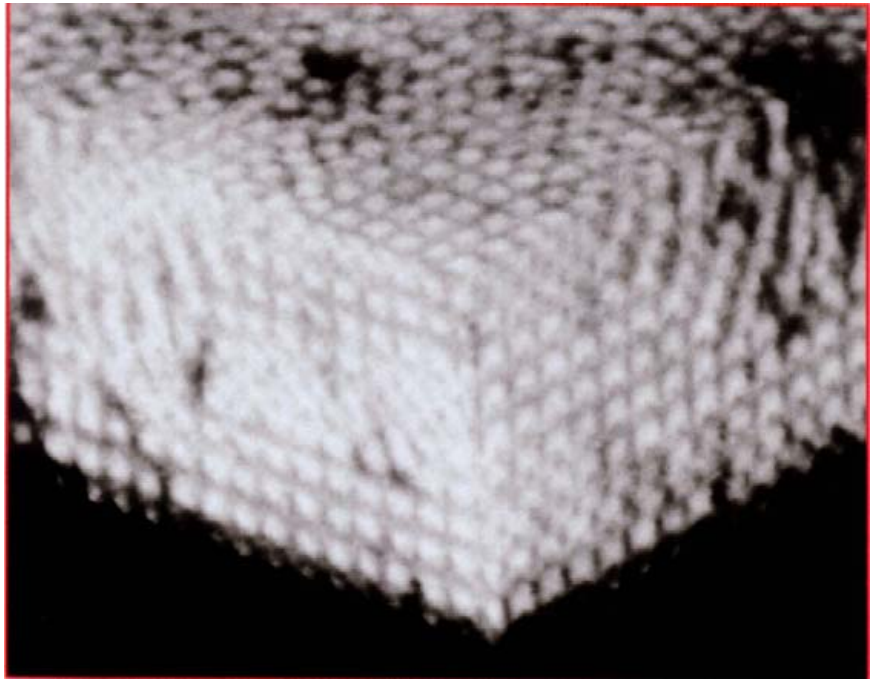


Steven Chou. J. Vac. Sci Tech: B 15 No.6 (1997).

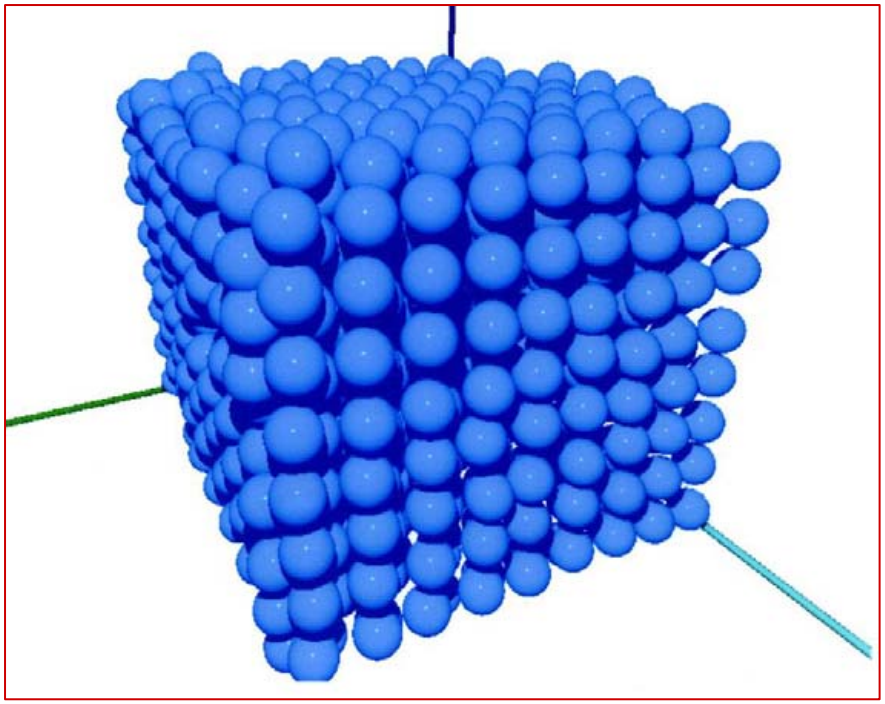
Xia, Y., et al, Science 273, 347-349 (1996).

FCC Crystal

Confocal Image



Reconstruction

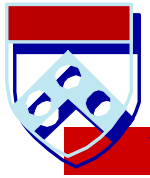


20 Layer Portion Within Larger Colloidal Crystal

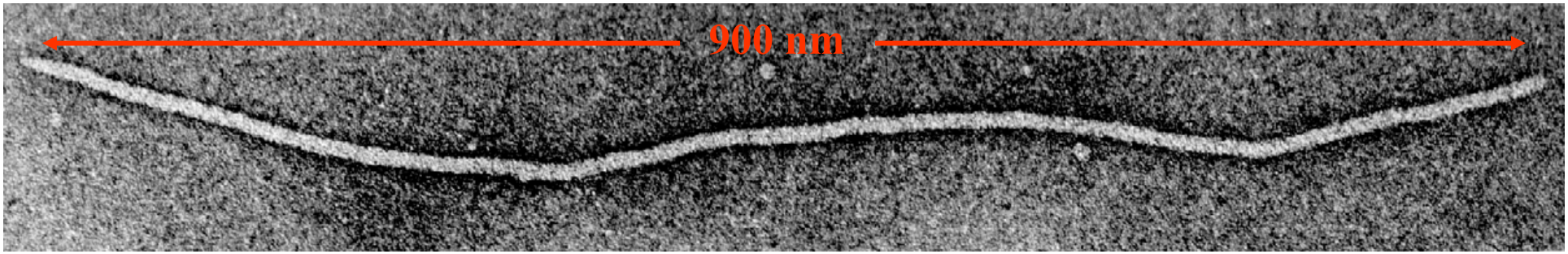
Lin, K-H, Crocker, J.C., Prasad, V., Schofield, A.,Lubensky, T.C., Weitz, D.A., Yodh, A.G., Physical Review Letters, 85 (2000)

BEYOND SPHERES

- Rods
- Rods & Polymers
- Rods & Polymer Gels
  (Carbon Nanotubes)



Rods: colloidal liquid crystals



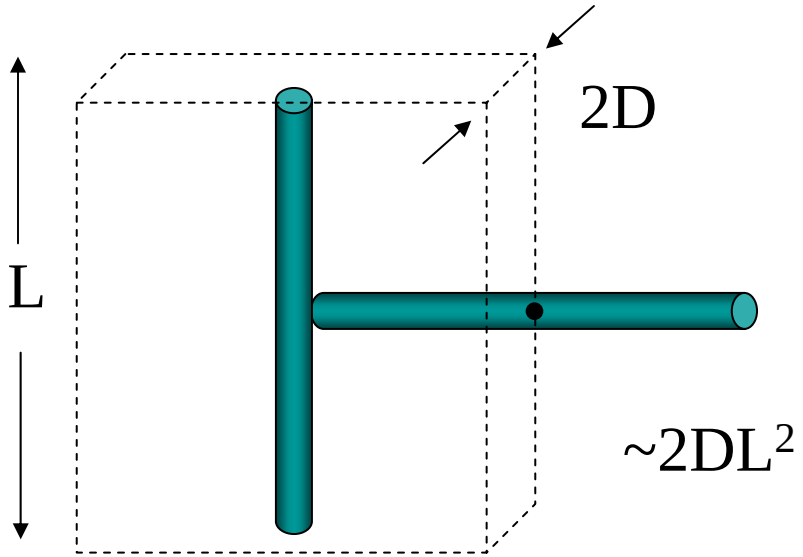
- *fd* virus : 900 nm length 7 nm diameter
- L/D=130
- higher monodispersity then chemical rod-like colloids
- semiflexible rods – persistence length 2.2 μm

hard core repulsion dominates interaction potential

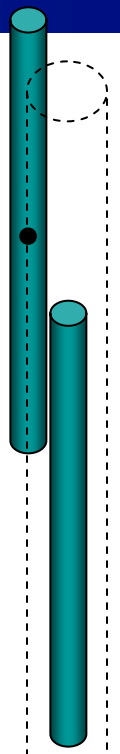
virus particles – often used to study liquid crystaline behavior

Experiment J. D. Bernal (1936), Onsager (1949)

Excluded Volume Depends on Rod Orientation



$\sim 2DL^2$

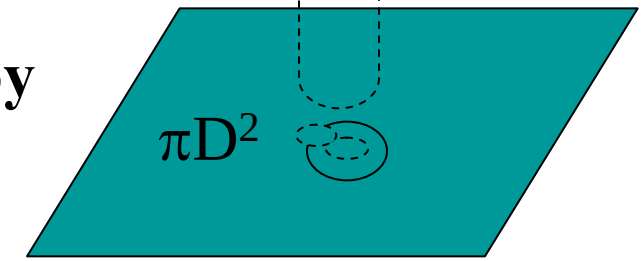


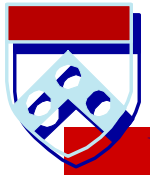
$\pi D^2\ 2L$

isotropic **nematic**

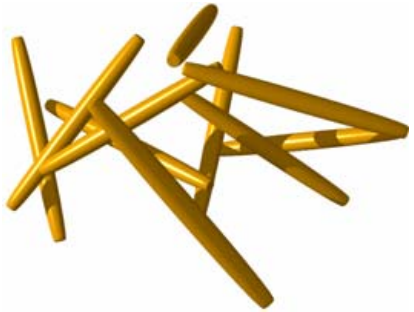
Ratio : $L/\pi D$

Orientational Entropy ↔ Packing Entropy





Concentration driven Isotropic-Nematic phase transition in hard rods



increasing concentration

isotropic phase

nematic phase

D - rod diameter

L – rod length

ϕ_{I-N} - rod concentration at I - N phase transition

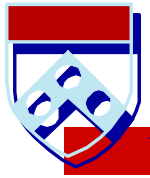
$$\phi_{I-N} = 4\frac{D}{L}$$

f(θ)–orientational distribution functions

order parameter S :

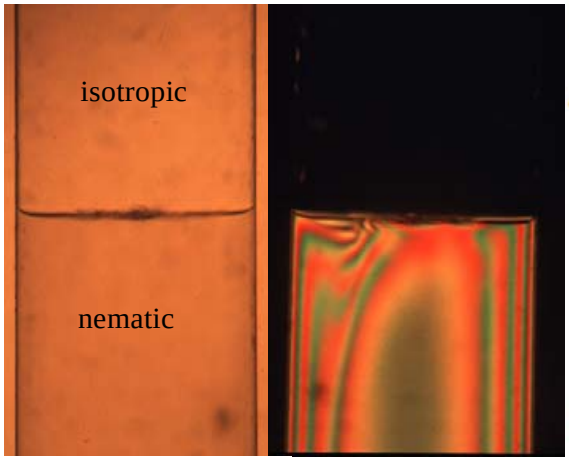
$$S = 2\pi\int \sin(\theta)(\frac{3}{2}\cos^2\theta - \frac{1}{2})\mathrm{f}(\theta)d\theta$$

Onsager, 1949

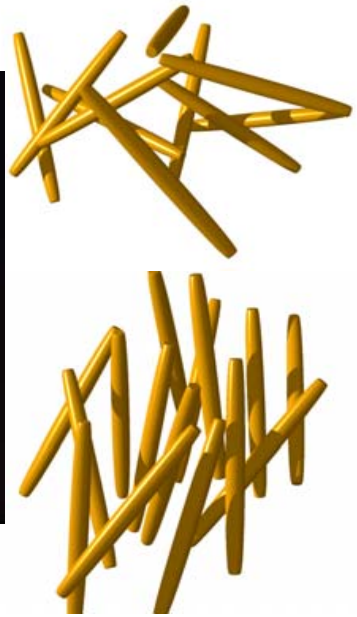


Phases of Lyotropic Rod Suspensions

isotropic-nematic (cholesteric) phase coexistance

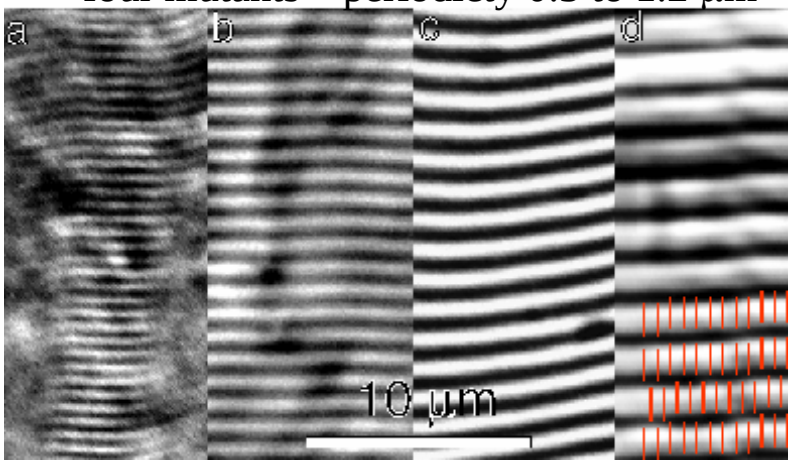


crossed polarizers



smectic phase

four mutants – periodicty 0.3 to 1.2 μm



fd virus – model system of monodisperse hard rods

phase diagram

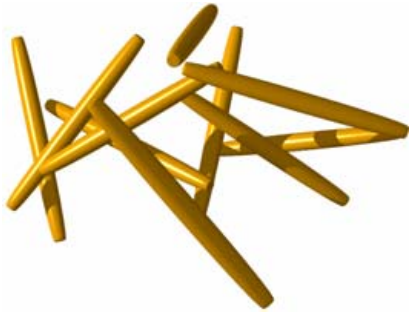
isotropic phase → nematic phase → smectic phase

(cholesteric)

concentration ↑ →

Tang and Fraden, Liq. Cryst, 1995
Dogic and Fraden, PRL 1997

Concentration driven Isotropic-Nematic phase transition in hard rods



increasing concentration

isotropic phase

nematic phase

D - rod diameter

L – rod length

ϕ_{I-N} - rod concentration at I - N phase transition

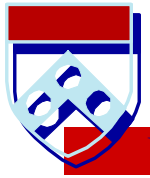
$$\phi_{I-N} = 4\frac{D}{L}$$

$\phi(\theta)$–orientational distribution functions

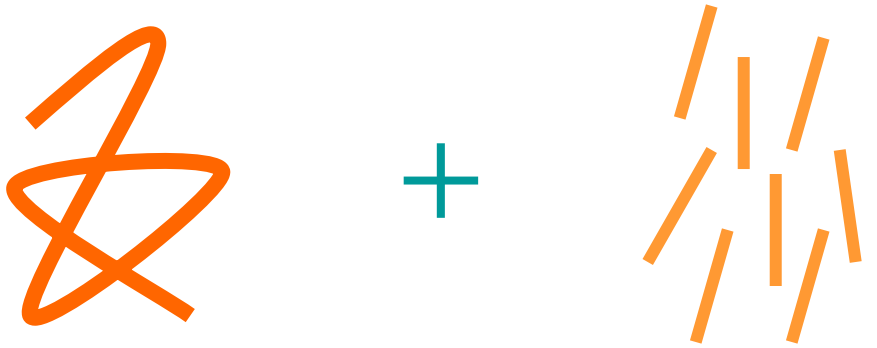
order parameter S :

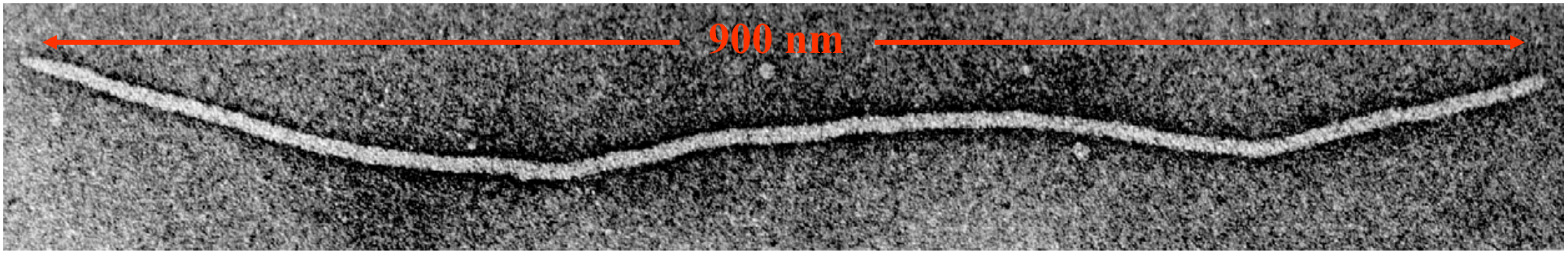
$$S = 2\pi\int \sin(\theta)(\frac{3}{2}\cos^2\theta - \frac{1}{2})\phi(\theta)d\theta$$

Onsager, 1949



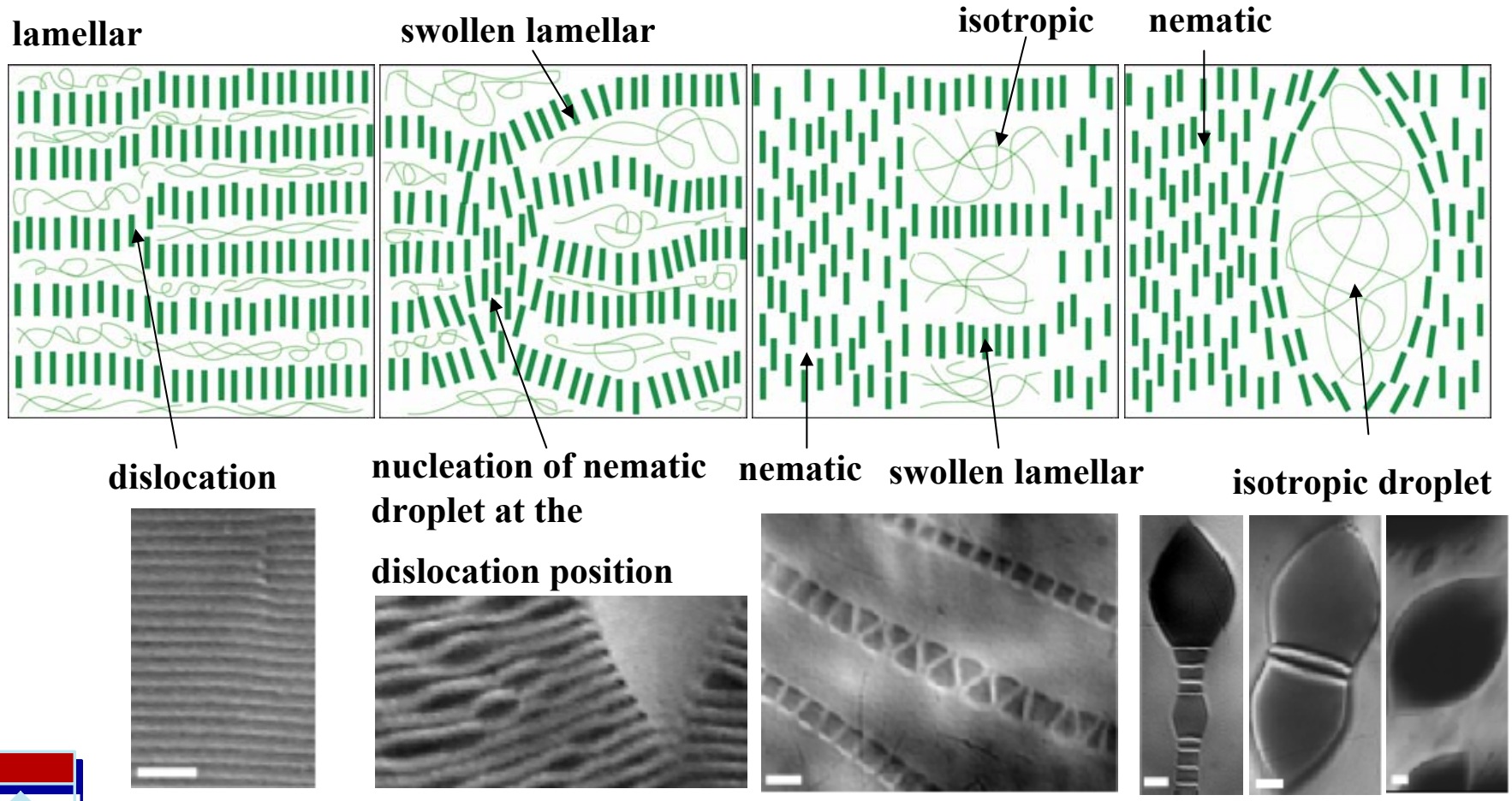
Polymers Plus Rods





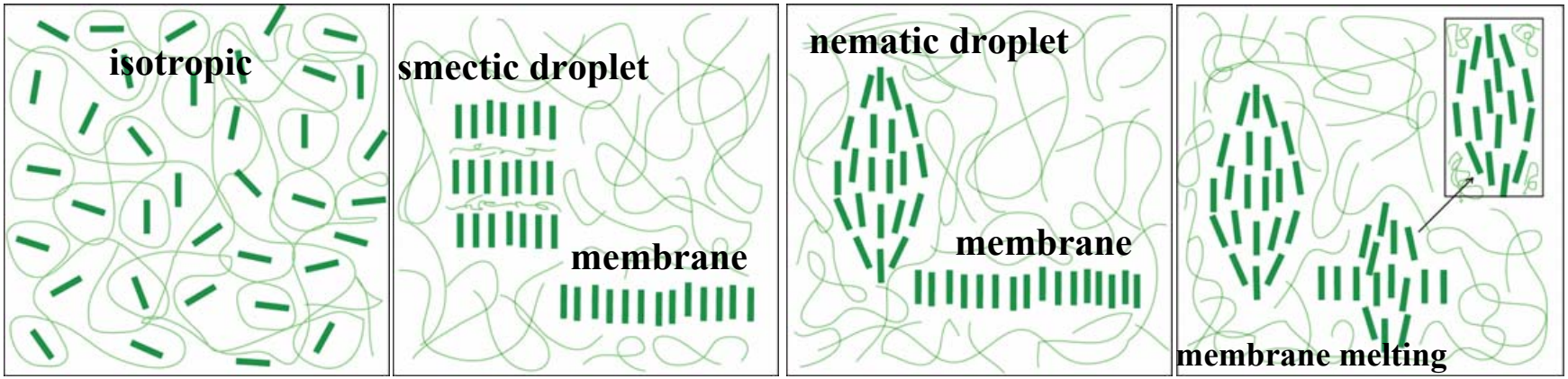
Behavior of fd/NIPA mixture:
Large [fd] and Low [NIPA]

50 mg/ml fd + 0.7 % NIPA in 20 mM trizma buffer solution, pH 8.15.

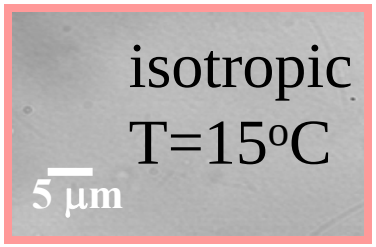


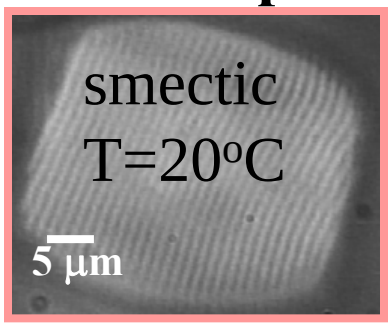
Behavior of fd/NIPA mixture: low [fd] and high [NIPA]

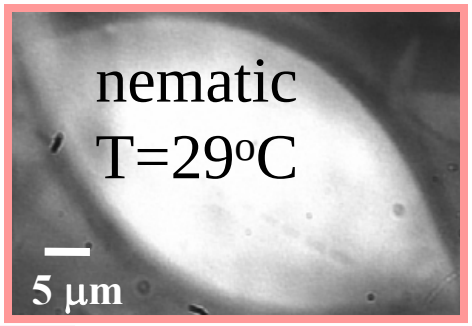
7mg/ml fd + 3.75% NIPA in 20 mM trizma buffer solution, pH 8.15.



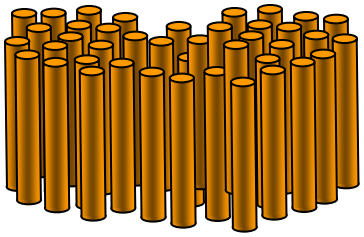
Temperature



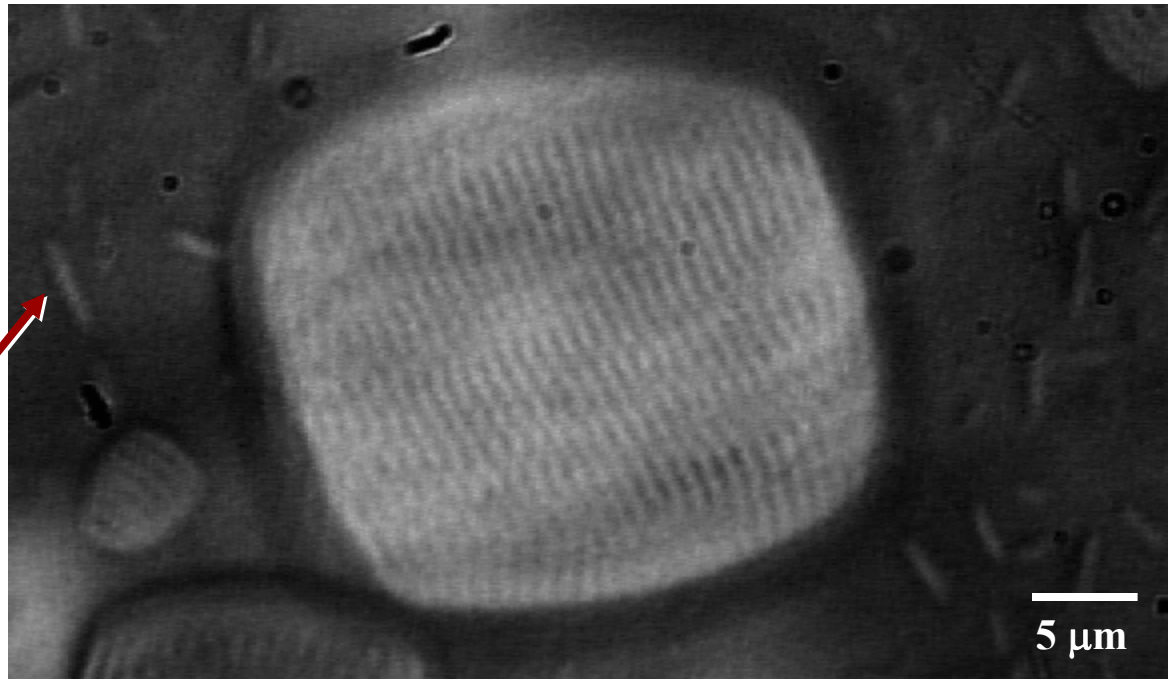




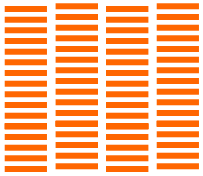
Melting of Lamellar Droplet



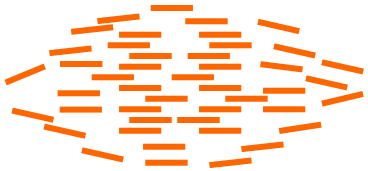
isolated 2D membrane

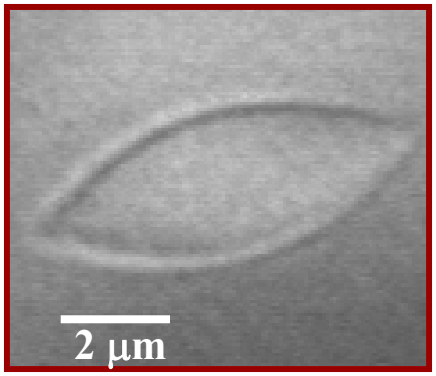


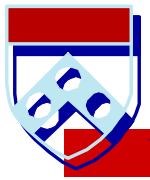
smectic droplets
(cylindrical shape)



nematic droplets
(elongated shape)





Summary

- Entropy is a pervasive effect in Condensed Matter Physics.
- In this talk we have used Model Systems to illustrate its effect.
- In practice Spheres & Rods can be small Molecules.