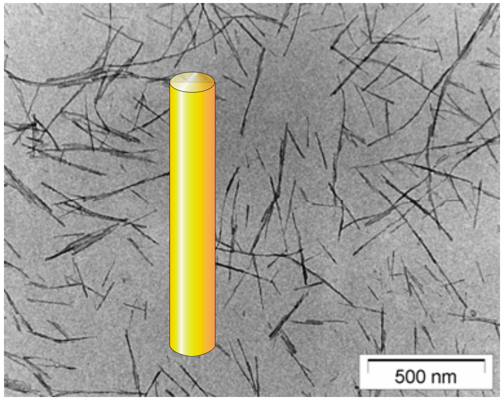
The Program

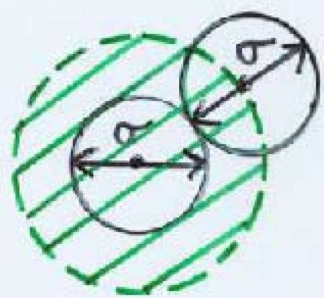
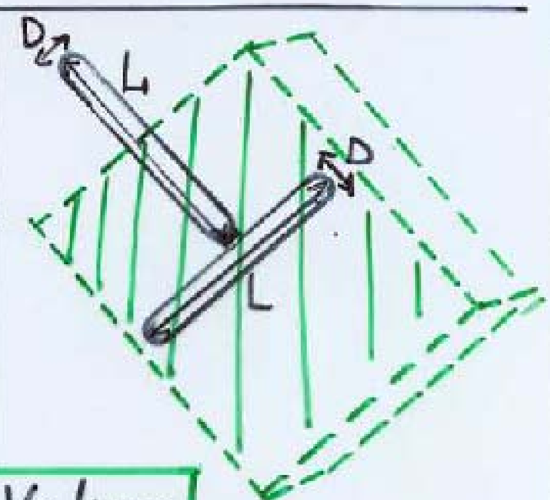
- Lecture 1: Phase transitions in atomic and molecular systems
- Lecture 2: Colloids as atoms
- Lecture 3: Hard spheres
- Lecture 4: Hard spheres + attraction
- Lecture 5: Rods
- Lecture 6: Platelets



WHY ARE DISPERSIONS OF COLLOIDAL RODS INTERESTING?

ANSWER **SHAPE MATTERS!**

THERMODYNAMICS ⇒ EXCLUDED VOLUME

SPHERES	RODS
	

Excluded Volume

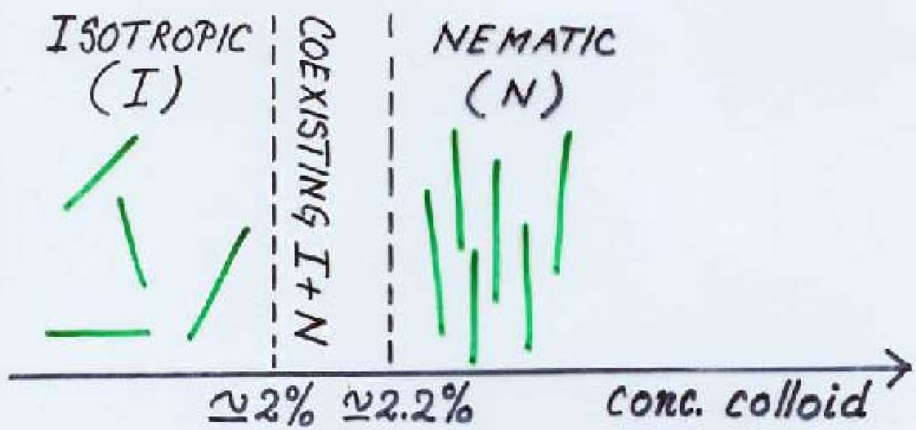
SPHERES	RODS
$4 \cdot \frac{\pi}{6} \sigma^3 \sim v_0$	$\frac{\pi}{4} L^2 D \sim \frac{L}{D} v_0$ (LARGE!)

Über freiwillige Strukturbildung in Solen.

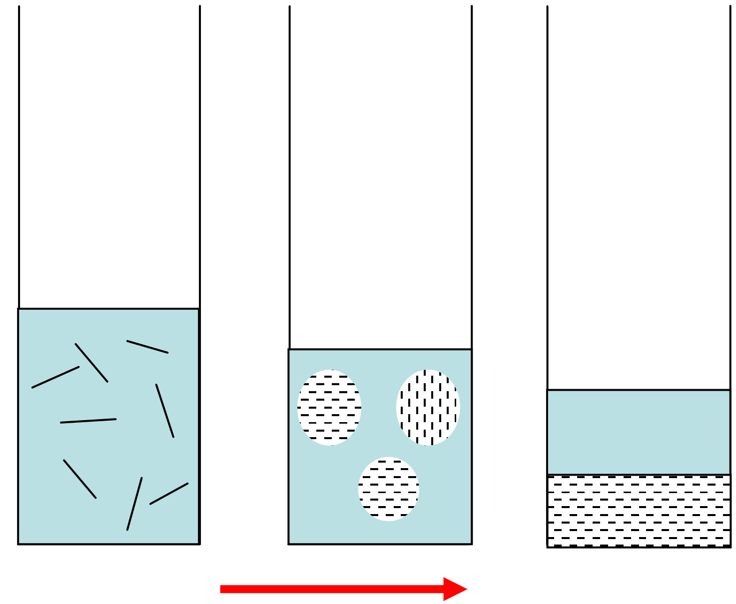
(Eine neue Art anisotrop-flüssiger Medien.)

Von H. Zocher. (1925)

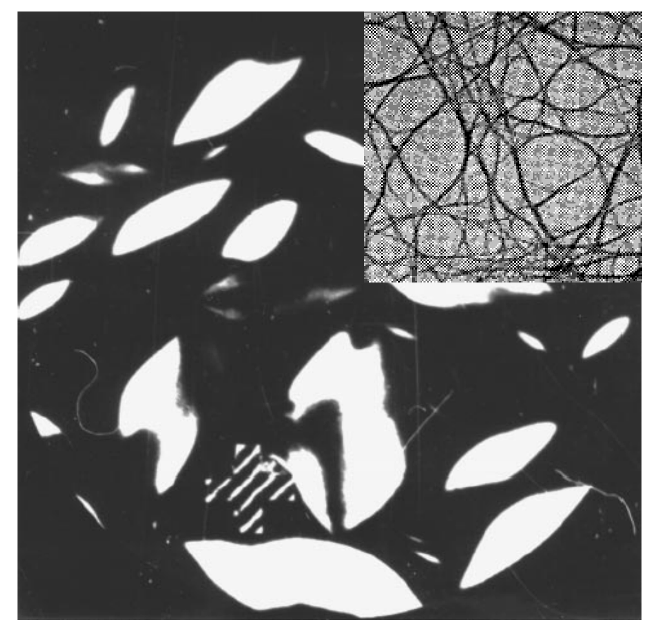
In alten Vanadinpentoxyd- und Eisenhydroxydsolen geeigneter Konzentrationen sammeln sich anisotrope Kolloidteilchen in höherer Konzentration unter Parallelorientierung. Die Brown'sche Molekularbewegung ist in diesen Gebieten noch als lebhafte Schwingung um Gleichgewichtslagen vorhanden. Kräftiges Durchmischen bringt die Strukturen völlig zum Verschwinden. Im Laufe der Zeit bilden sie sich stets wieder aus, solange nicht Koagulation im engeren Sinne eintritt.



- Inorganic Colloids — V_2O_5, β-FeOOH (1920s)
- Viruses — TMV (1930s)
- Stiff Polymers — PBG, DNA (1950s)
- (Cylindrical Micelles)

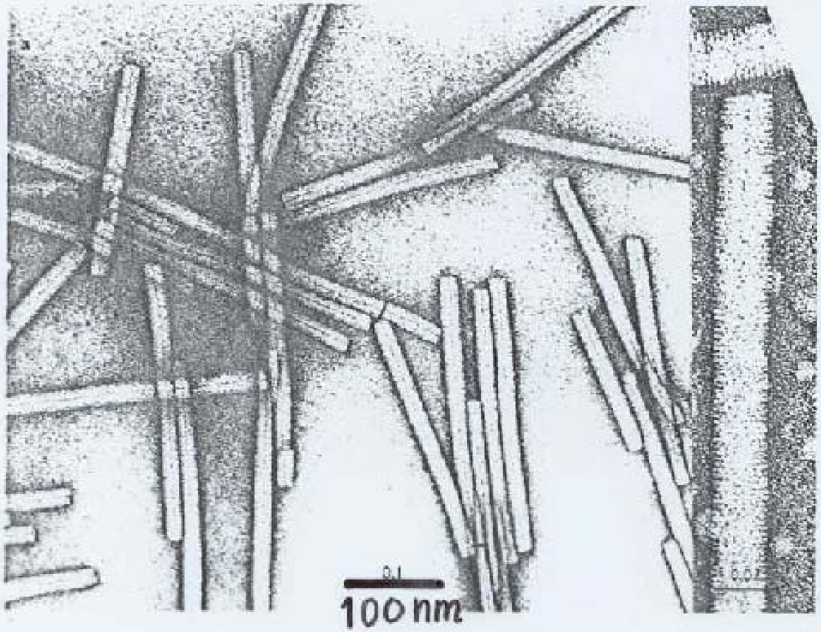


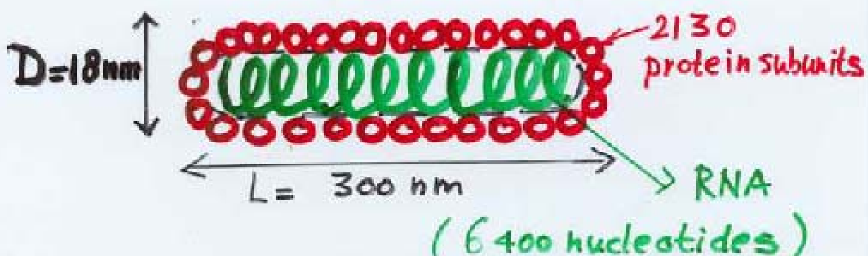
Increase concentration



TOBACCO MOSAIC VIRUS $L = 300\,nm$ 8

$D = 18\,nm$

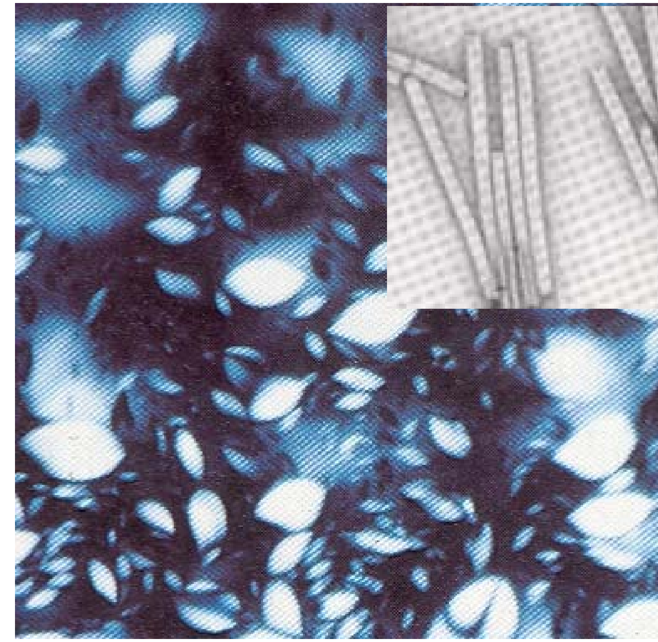


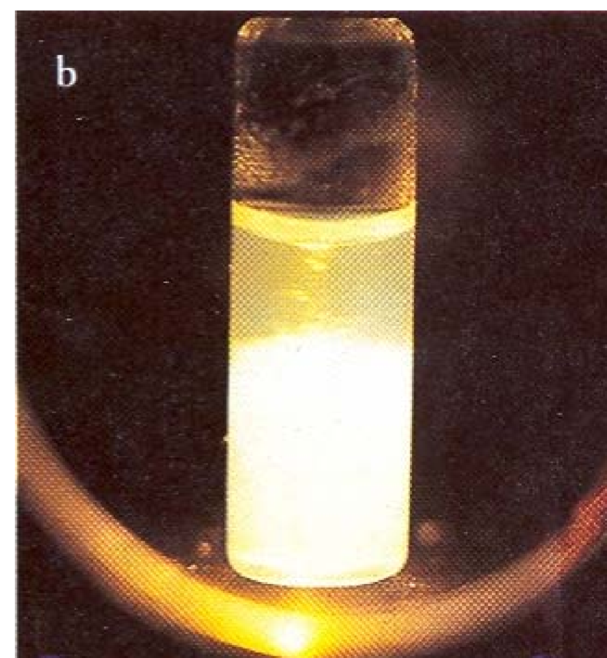


pH=7 -2e/nm

F.C. Bawden, N.W. Pirie, J.D. Bernal, I. Fankuchen

LIQUID CRYSTALLINE SUBSTANCES FROM VIRUS INFECTED PLANTS. NATURE, 138, 1051 (1938)





Lars Onsager (1903-1976)

Nobelprijs Scheikunde 1968

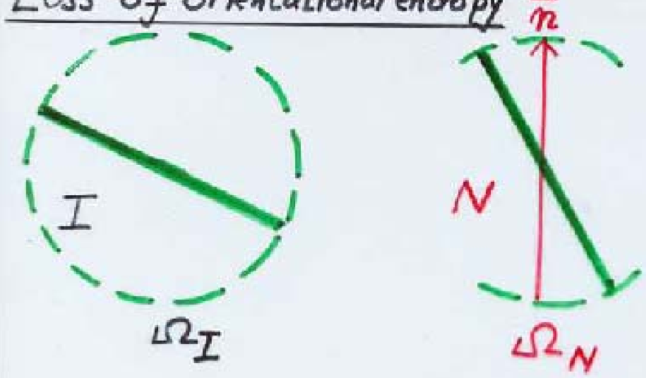
1. **Anisotropic Solutions of Colloids.** LARS ONSAGER, *Yale University*.—The solutions of certain colloids comprised of highly asymmetrical particles—plates or rods—are known to form anisotropic phases at remarkably low concentrations. For tobacco mosaic virus (rods), isotropic solutions containing 2–3 percent virus are in equilibrium with anisotropic phases containing 3–4.5 percent, respectively, according to the amount of electrolyte present. This phenomenon can be explained as a result of repulsive forces by the observation that the mutual co-volume of two swarms of parallel rods (or plates) is roughly proportional to the sine of the angle between their orientation, and larger than the volume of the particles by a factor which is proportional to the asymmetry. The case of rods is particularly simple in that the virial coefficients of order higher than 2 in Mayer's expansion are small, and a quantitative theory is possible. The computed ratio of concentrations at equilibrium is 1.34. The predicted osmotic pressure of the anisotropic phase is nearly proportional to the concentration, in fact, slightly greater than $3cRT/V$.

Physical Review (1942)

Onsager (1940's) Isotropic-Nematic phase transition in a dispersion of slender hard rods due to

Loss of orientational entropy vs. Gain of packing entropy

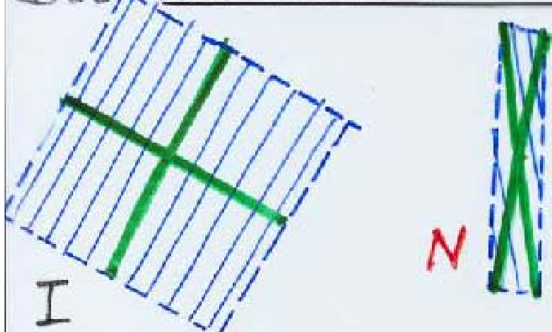
Loss of orientational entropy



$$\Delta S_{or} = k_B \ln \frac{\Omega_N}{\Omega_I} \sim -k_B$$

But, less excluded volume → gain in entropy

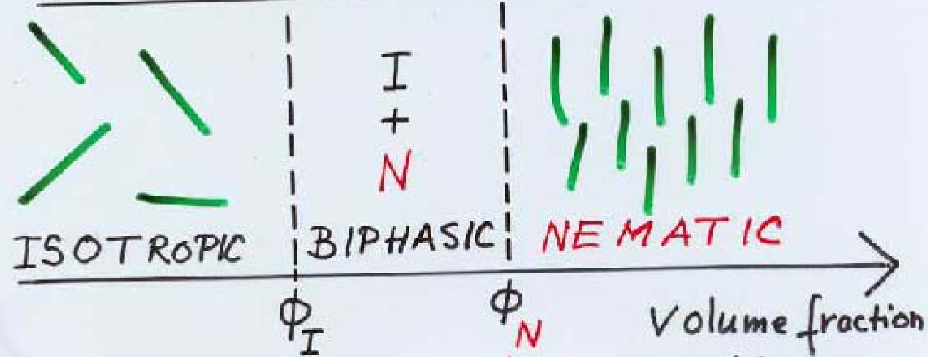
$$\Delta S_{excl\,vol} \sim k_B \rho L^2 D$$



$$I \to N : \Delta S_{or} + \Delta S_{excl.vol} = 0 \to \boxed{\rho^* \sim \frac{1}{L^2 D}}$$

(volume fraction: $\phi^* \sim \frac{D}{L}$)

Onsager's theory for the Isotropic-Nematic Liquid Crystal Phase Transition in a Dispersion of Hard Rods



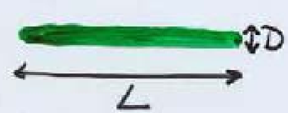
$$\phi = \frac{N}{V} \cdot \frac{\pi}{4} L D^2$$

Coexistence Conditions

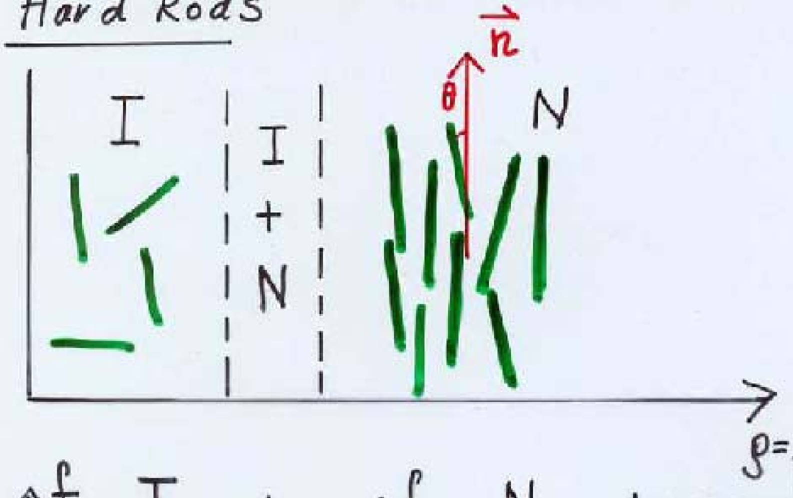
$$\mu_I = \mu_N$$

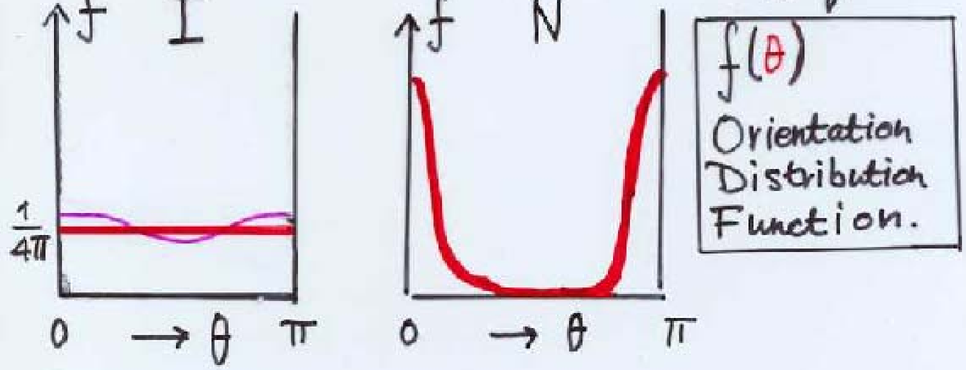
$$\Pi_I = \Pi_N$$

$$\boxed{\phi_I = 3.3\frac{D}{L} \qquad \phi_N = 4.2\frac{D}{L}}$$



Onsager theory for the Isotropic-Nematic Phase Transition in a Dispersion of Thin Hard Rods





Programme

1. Find $F[f]$
2. Minimize F w.r.t. $f \left(\frac{\delta F}{\delta f} = 0 \right)$
3. Solve coexistence conditions

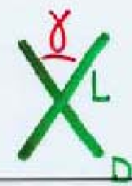
$$\Pi_I(\rho_I) = \Pi_N(\rho_N) \qquad \mu_I(\rho_I) = \mu_N(\rho_N)$$

Onsager theory I–N transition

Step 1 $F[f]$

$$\frac{F}{NkT} = \text{const} + \ln\rho + \int f(\theta)\ln[4\pi f(\theta)]\,d\Omega$$

(– orientational entropy)



$$+\rho L^2 D \iint f(\theta) f(\theta') \sin\gamma(\Omega,\Omega')\,d\Omega\,d\Omega'$$

$\frac{1}{2}$ x excluded volume of two rods $= B_2[f]$

Step 2 Minimize $F[f]$ w.r.t. f

$$I : \quad f(\theta) = \frac{1}{4\pi}$$

$$\boxed{\frac{F_I}{NkT} = \text{const.} + \ln c + c} \Rightarrow \quad \Pi_I = -\frac{\partial F_I}{\partial V}, \quad \mu_I = \frac{\partial F_I}{\partial N}$$

$$c = \rho \cdot \underbrace{\frac{\pi}{4} L^2 D}_{B_2}$$

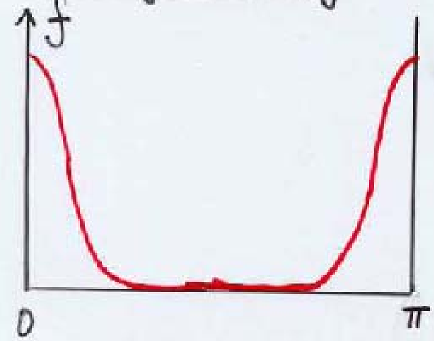
dimensionless number density

$$\rho = \frac{N}{V}$$

Onsager theory I – N transition

Step 2 Minimize $F[f]$ w.r.t. f

N. : Trial function: $f(\theta) \sim \exp\left(-\frac{1}{2}\alpha\theta^2\right)$



$$\langle \theta^2 \rangle = \frac{2}{\alpha}$$

$$(\alpha \gtrsim 10)$$

$$\frac{F_N}{NkT} = \text{const} + \ln c + [\ln(\alpha) - 1] + \frac{4c}{\sqrt{\pi\alpha}}$$

$$\frac{\partial F_N}{\partial \alpha} = 0 \rightarrow \alpha = \frac{4c^2}{\pi}$$

$$\boxed{\frac{F_N}{NkT} = \text{const} + 3\ln c + \ln\left(\frac{4}{\pi}\right) + 1}$$

$$\Longrightarrow \quad \Pi_N = -\frac{\partial F_N}{\partial V} \qquad \mu_N = \frac{\partial F_N}{\partial V}$$

Onsager theory I - N transition

Step 3 Solve coexistence conditions

- Equal osmotic pressure

$$\Pi_I = \Pi_N$$

$$\Rightarrow c_I + c_I^2 = 3\, c_N$$

- Equal chemical potential.

$$\mu_I = \mu_N$$

$$\Rightarrow \ln c_I + 2c_I = 3\ln c_N + \ln\left(\frac{4}{\pi}\right) + 3$$

$c_I = 3.45$

$c_N = 5.12$

$\alpha = 33.4$

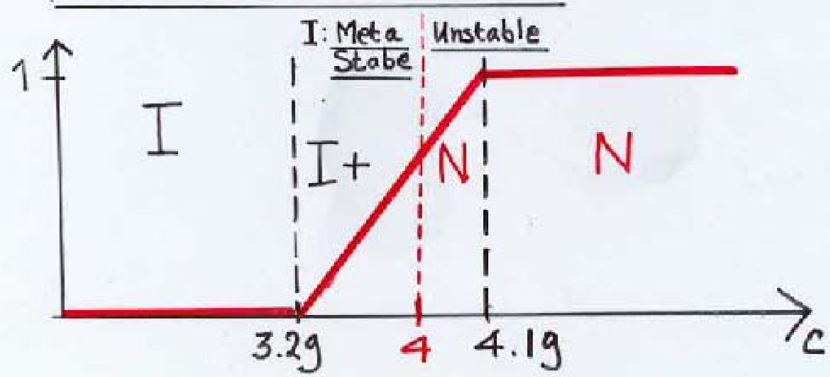
$S = \langle P_2(\cos\theta)\rangle = 09$

Accurate ("exact") solution

$c_I = 3.29$ → $\phi_I = 3.29\,\frac{D}{L}$

$c_N = 4.19$ → $\phi_N = 4.19\,\frac{D}{L}$

$S = \langle P_2(\cos\theta)\rangle = 0.79$



True Hard Rod Colloids do not exist, but (perhaps) good approximations can be prepared (!)(?)

MODEL SYSTEM

Inorganic Colloidal Rods (γ-AlOOH)
Sterically Stabilized with Polymer
(Poly IsoButylene)
(Buining et al. Colloids and Surfaces 64, 47 (1992))

Dispersed in a good organic solvent
⟶ Steep Repulsion (!)(?)

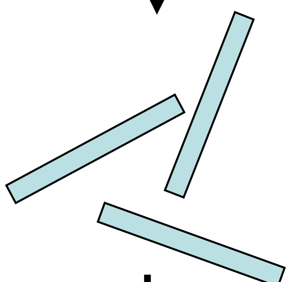
Rods at the van ‘t Hoff laboratory

Al-$(OR)_3$ in acidic aqueous solution

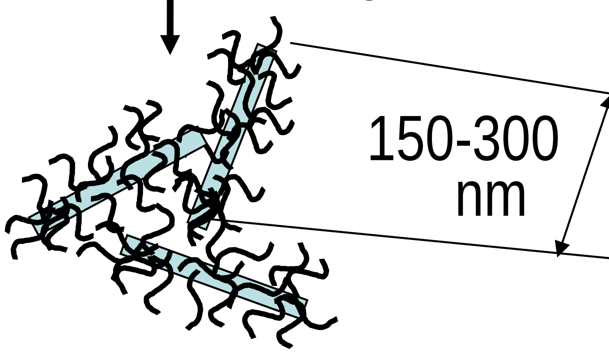
150 ^{0}C, 1 day

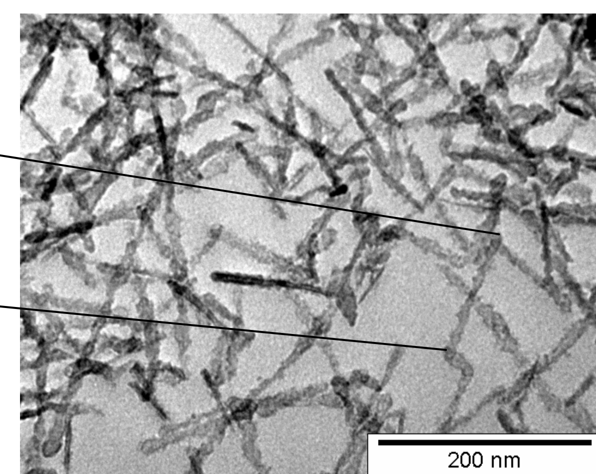
boehmite

AlOOH



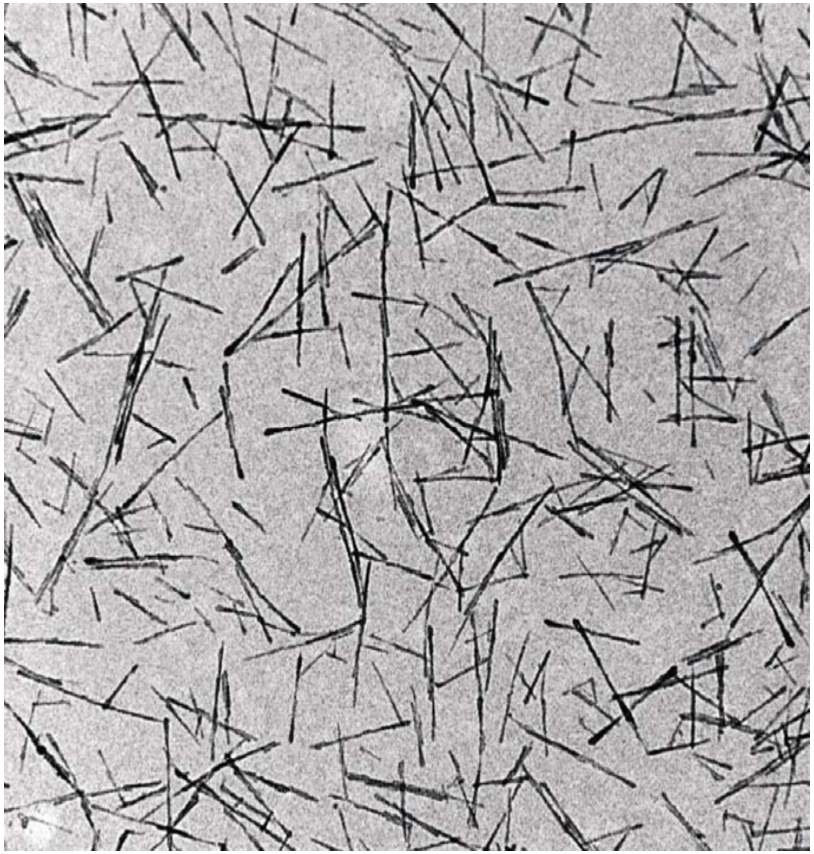
Coating PIB





P.A.Buining *et al.*, 1992

Isotropic-nematic phase equilibrium



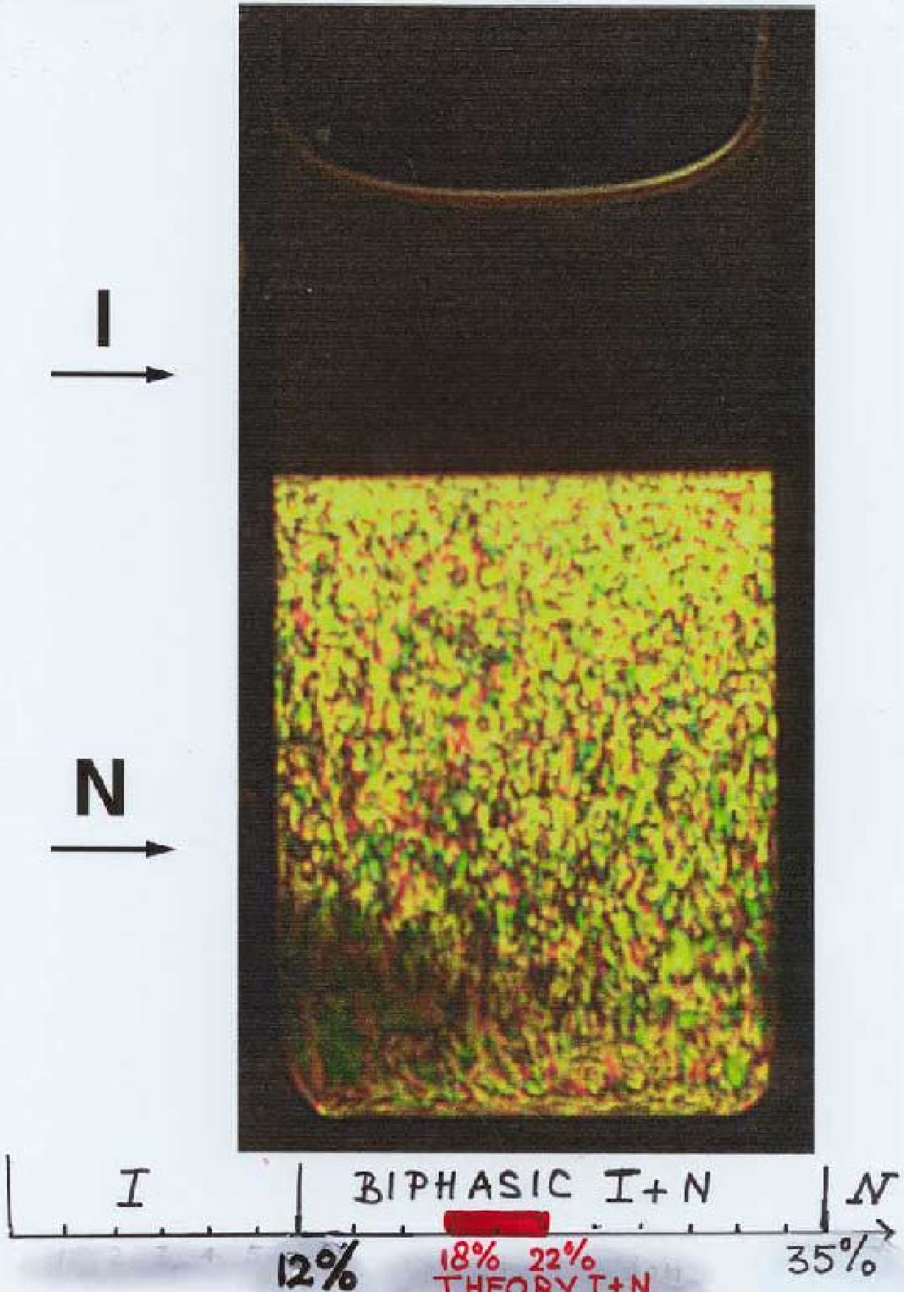
boehmiet (AlOOH)

dikte = 9 nm
lengte = 160 nm

volumefractie = 10%

BOEHMITE - PIB L=250nm D=18nm 16

in CYCLOHEXANE L/D=14



Theory of the Isotropic – Nematic – (Nematic) Phase Separation for a Solution of Bidisperse Rodlike Particles

G. J. Vroege + HNWL, J. Phys. Chem. 97, 3601 (93)

Step 1 $\qquad N_1 + N_2. \qquad x = \dfrac{N_2}{N_1 + N_2}$

$$\frac{F}{(N_1+N_2)kT} = cst$$

- ideal term → $+ \ln c$
- entropy of mixing → $+ (1-x)\ln(1-x) + x \ln x$
- orientation entropy → $+ (1-x)\langle \ln 4\pi f_1 \rangle + x \langle \ln 4\pi f_2 \rangle$
- excluded volume term → $+ \dfrac{N_1+N_2}{V}\Big[(1-x)^2 L_1^2 D \langle\langle |\sin\gamma| \rangle\rangle_{1,1}$

$$+ 2x(1-x) L_1 L_2 D \langle\langle |\sin\gamma| \rangle\rangle_{1,2}$$

$$+ x^2 L_2^2 D \langle\langle |\sin\gamma| \rangle\rangle_{2,2} \Big]$$

Theory of the Isotropic - Nematic - (Nematic) Phase Separation for a Solution of Bidisperse Rod like Particles - Cont'd

PROCEDURE

- Minimize the Free Energy with respect to the orientation distribution functions

- Solve the coexistence conditions

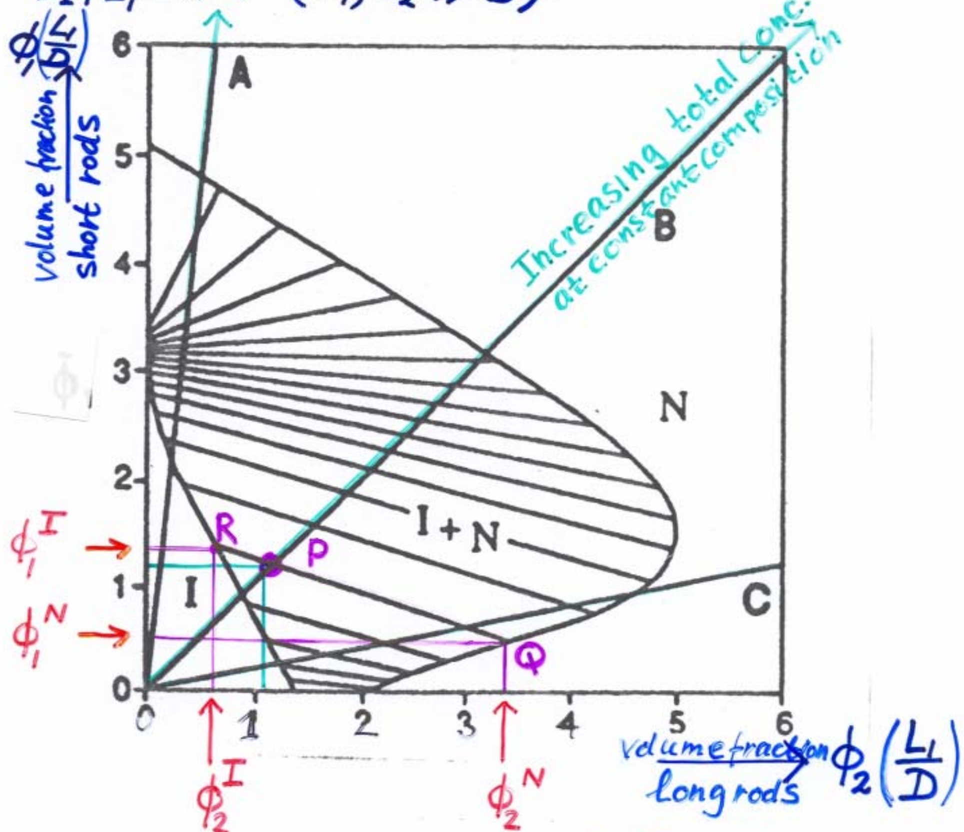
$$\mu_1' = \mu_1'' \quad \text{(equality chem. pot. comp. 1)}$$

$$\mu_2' = \mu_2'' \quad \text{(equality chem. pot. comp. 2)}$$

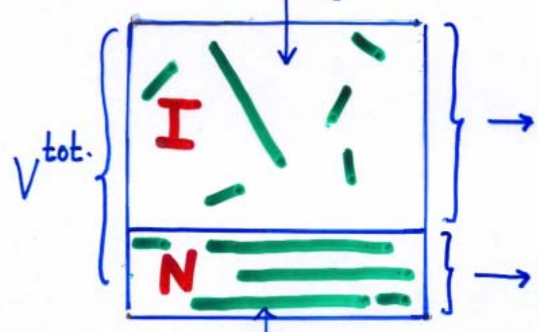
$$\Pi' = \Pi'' \quad \text{(equality osmotic pressure)}$$

PHASE DIAGRAM LONG (2) + SHORT RODS (1)

$L_2/L_1 = 2.5 \quad (L_1, L_2 \gg D)$



mainly short rods ($\phi_1^I > \phi_1^N$)



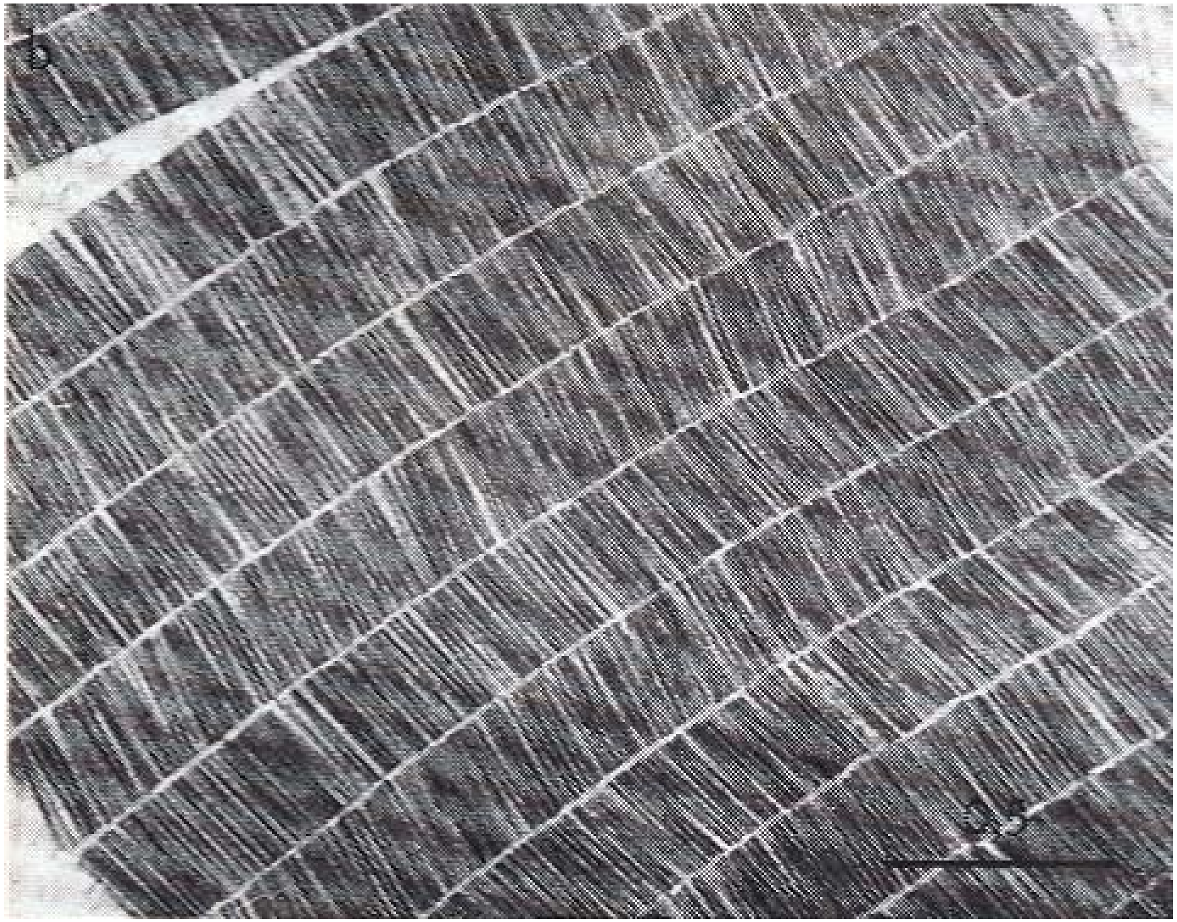
Lever rule

$$\frac{V^I}{V^{tot.}} = \frac{|PQ|}{|RQ|}$$

$$\frac{V^N}{V^{tot.}} = \frac{|RP|}{|RQ|}$$

mainly longrods ($\phi_2^N \gg \phi_1^N$)

Smectic phase in TMV dispersion



Oster 1951, Wetter 1985

Thermodynamic stability of a smectic phase in a system of *hard rods* ?

1985

The formation of a smectic *A* phase would be predominantly due to soft attractive forces and this is reflected e.g. in the shapes of coexistence lines of the phase diagram. Hence, no smectic *A* phase should ever be formed in systems of hard convex bodies.

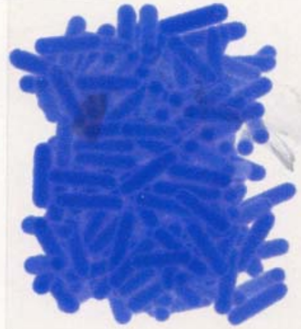
However……….

NATURE 332 822 (1988)

Thermodynamic stability of a smectic phase in a system of hard rods

D. Frenkel*, H. N. W. Lekkerkerker† & A. Stroobants†

* FOM Institute for Atomic and Molecular Physics, PO Box 41883, 1009 DB Amsterdam, The Netherlands
† Van 't Hoff Laboratory, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands



ISOTROPIC (I)

I + N $\phi = 0.41 - 0.47$

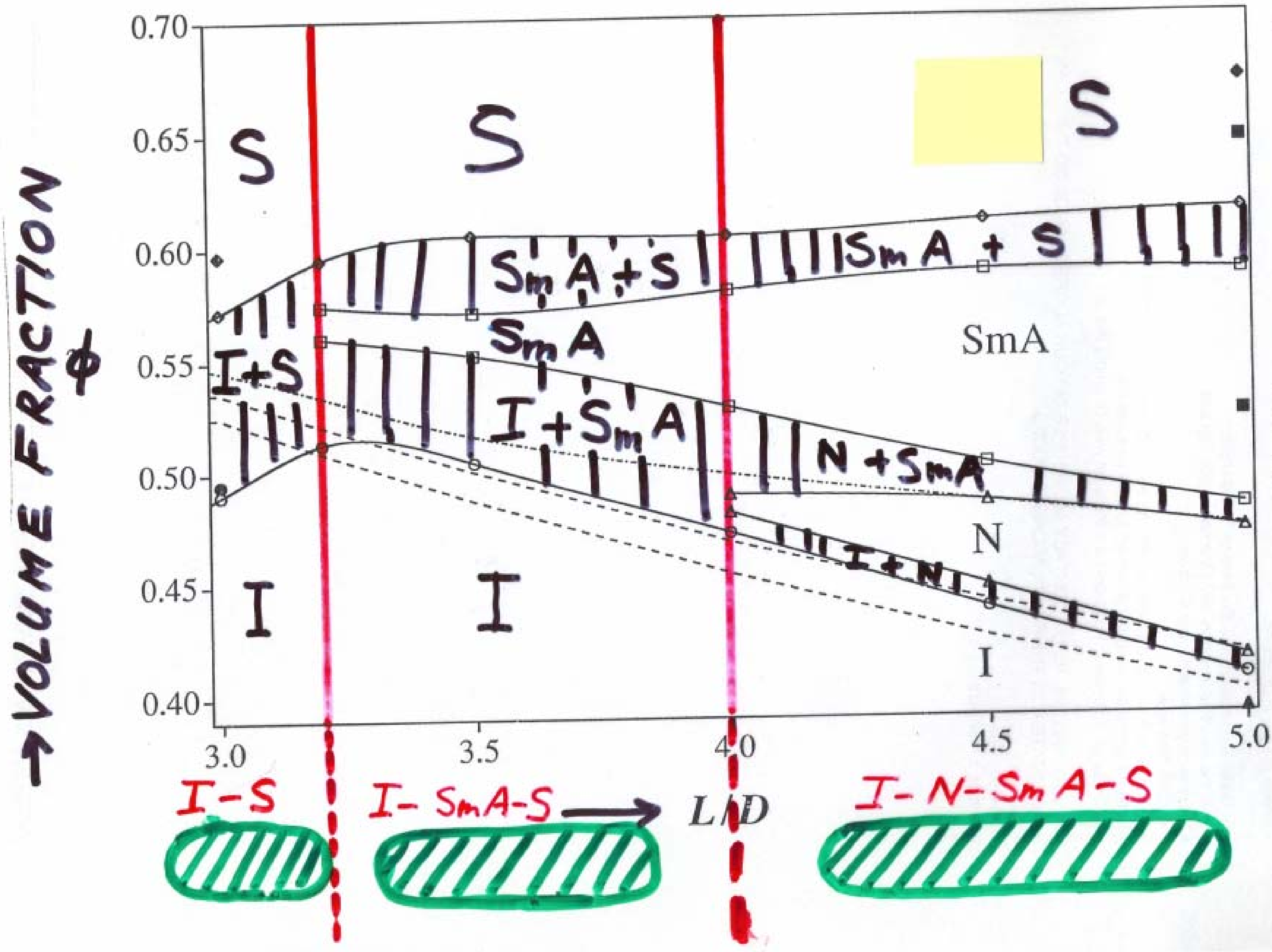
NEMATIC (N)

N + S $\phi = 0.49 - 0.58$

SMECTIC (S)

concentration rods $\left(\phi = \frac{N}{V}\frac{\pi}{4}D^2 L\right)$

PHASE DIAGRAM HARD SPHEROCYLINDERS



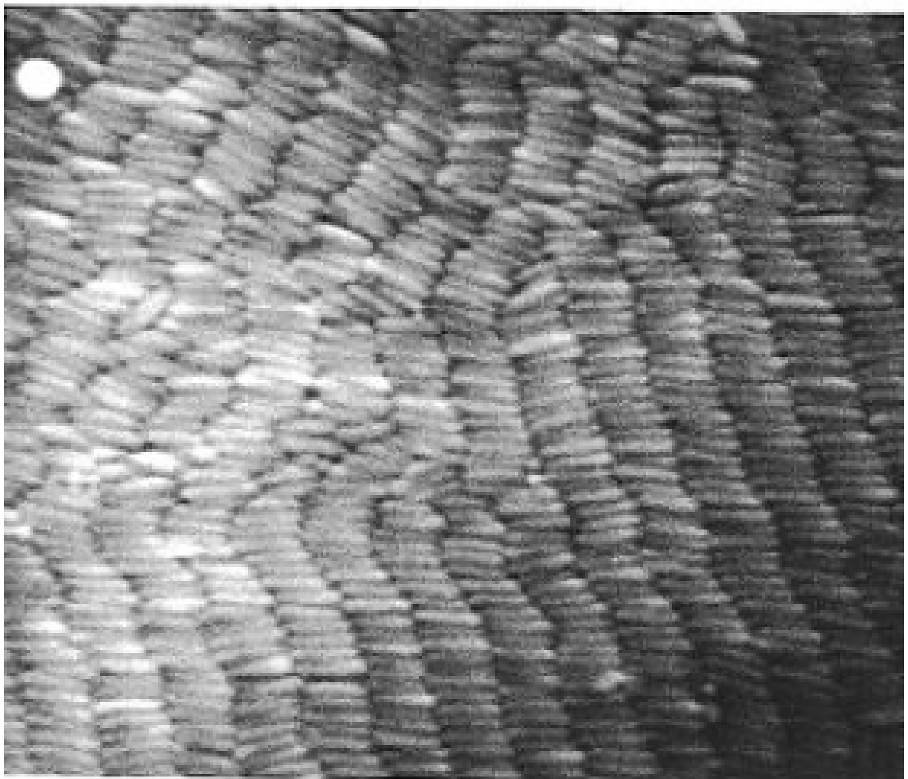
BOLHUIS + FRENKEL JCP 107 666 (1997)

McGrother Williamson Jackson JCP 104 6755 (1996)

Figure 21

Smectic Structures of Colloidal Crystals of β-FeOOH

Hideatsu Maeda and Yoshiko Maeda, Langmuir 1996, JCP 2004



The end of lecture 5