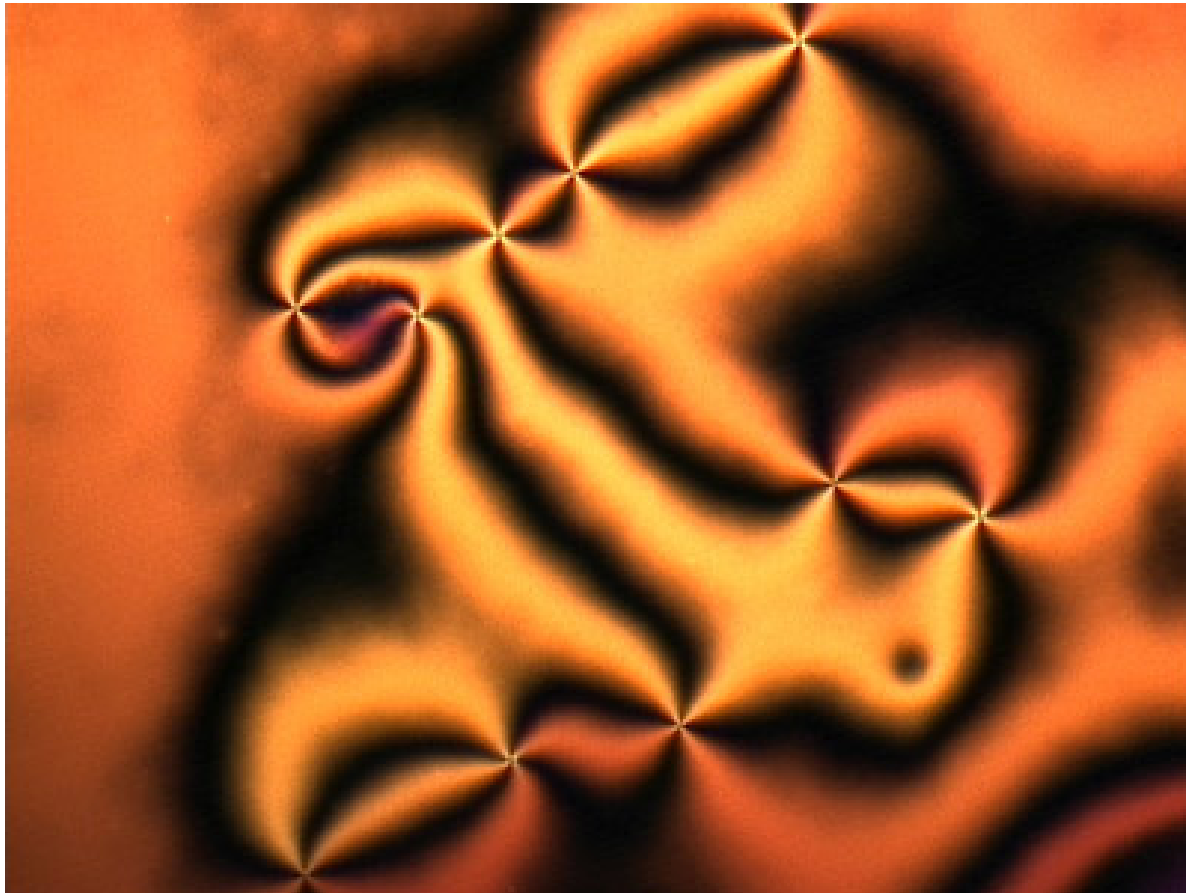


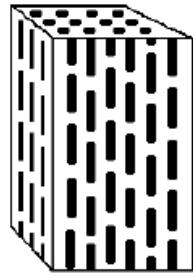
Day 3

<http://dept.kent.edu/spie/liquidcrystals/textures1.html#ch13>

Liquid crystal disclinations seen through cross-polars



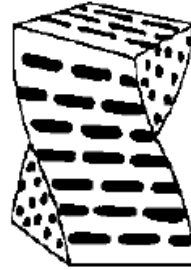
birefringence



Non-deformed
specimen



splay
distortion



twist
distortion



bend
distortion

$$f = \frac{1}{2} \left[k_{11} (\nabla \cdot n)^2 + k_{22} (n \cdot \nabla \times n)^2 + k_{33} (n \times \nabla \times n)^2 \right]$$

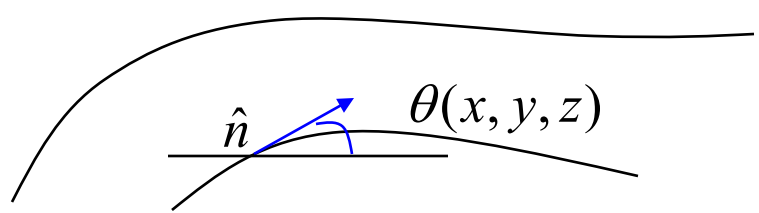
Free energy density due to spatial variation of nematic director.

Boundary Value Problems : nematic

For some volume of nematic, with specified boundary conditions the free energy in the volume is:

$$F = \int dx dy dz f(\hat{n}(\vec{r})).$$

In general, find $\hat{n}(\vec{r})$ that minimizes F . For any particular problem, choose coordinate system, make assumptions (guesses!) about the form of solution, generate f , and use Calculus of Variations to minimize F .



Example : Planar structures : $\hat{n} \parallel (x, y)$ plane

$$n_x = \cos \theta, \quad n_y = \sin \theta, \quad n_z = 0 \quad (\text{clearly } |\mathbf{n}| = 1)$$

$$\nabla \cdot \hat{n} = -\sin \theta \frac{\partial \theta}{\partial x} + \cos \theta \frac{\partial \theta}{\partial y}$$

$$\hat{n} \cdot \nabla \times \hat{n} = -\frac{\partial \theta}{\partial z}$$

$$\mathbf{n} \times \nabla \times \mathbf{n} = \hat{x} \left(\sin \theta \cos \theta \frac{\partial \theta}{\partial x} + \sin^2 \theta \frac{\partial \theta}{\partial y} \right) + \hat{y} \left(-\cos^2 \theta \frac{\partial \theta}{\partial x} - \sin \theta \cos \theta \frac{\partial \theta}{\partial y} \right)$$

Assume $K_{11} = K_{22} = K$ then

$$F = \int dx dy dz \left[\frac{1}{2} K \left(\left(\frac{\partial \theta}{\partial x} \right)^2 + \left(\frac{\partial \theta}{\partial y} \right)^2 \right) + \frac{1}{2} K_{22} \left(\frac{\partial \theta}{\partial z} \right)^2 \right]$$

$$\text{rescale } z = \sqrt{\frac{K_{22}}{K}} \xi$$

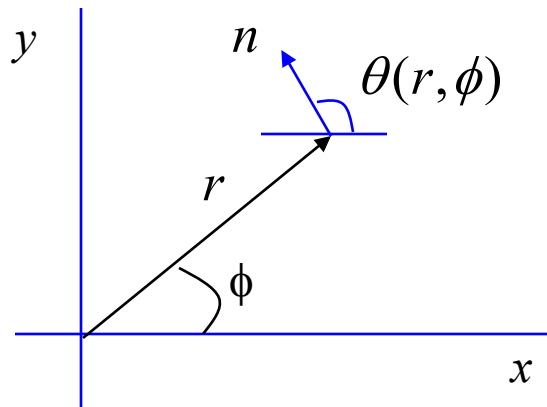
$$F = \frac{1}{2} \sqrt{K K_{22}} \int dx dy d\xi (\nabla \theta)^2 \rightarrow \nabla^2 \theta = 0 \quad \text{electrostatic!}$$

Euler Lagrange eqn

Energy of wedge planar line in isotropic elasticity

$$K = K_{11} = K_{22} = K_{33}$$

$$f = \frac{1}{2} K (\nabla \theta(x, y))^2 \quad \text{Euler - Lagrange} \longrightarrow \nabla^2 \theta(x, y) = 0$$

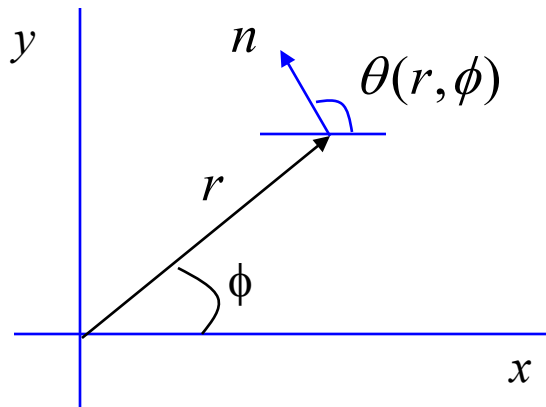


Cylindrical coordinates:

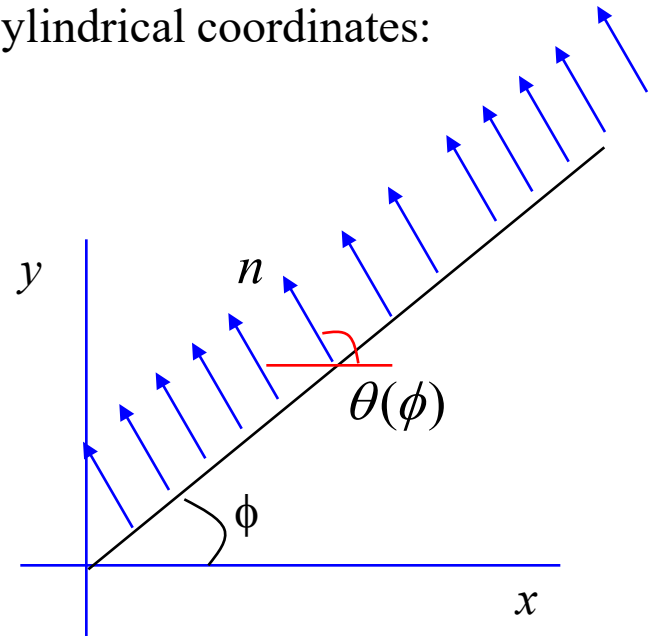
$$\nabla^2 \theta = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \theta}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 \theta}{\partial \phi^2} = 0$$

a solution to
$$\nabla^2 \theta = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \theta}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 \theta}{\partial \phi^2} = 0$$

$$\theta(r, \phi) = m \phi + \text{constant}$$



Cylindrical coordinates:

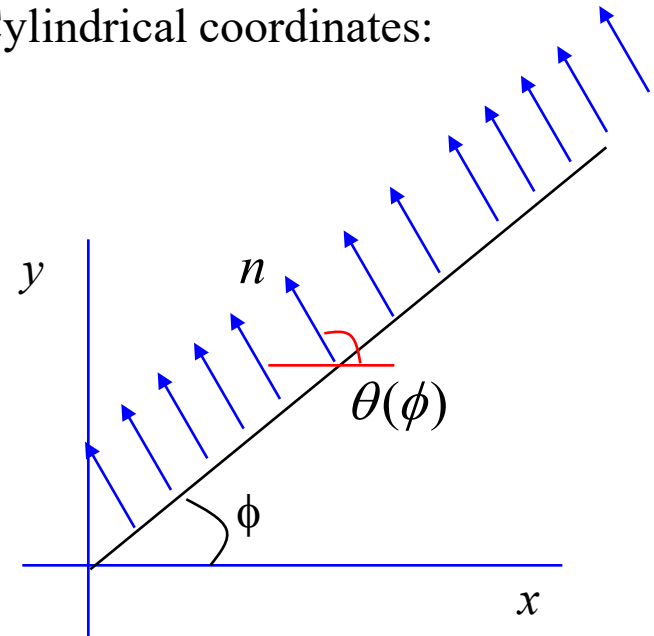


$$\theta(r, \phi) = m \phi + \text{constant}$$

$$f = \frac{1}{2} K (\nabla \theta)^2 = \frac{1}{2} K \left(\frac{\partial \theta}{\partial r} \hat{r} + \frac{1}{r} \frac{\partial \theta}{\partial \phi} \hat{\phi} \right)^2$$

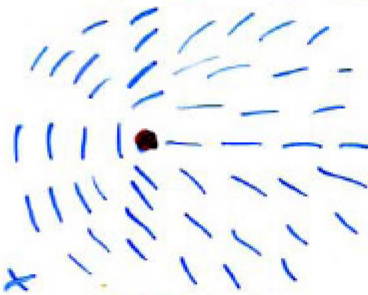
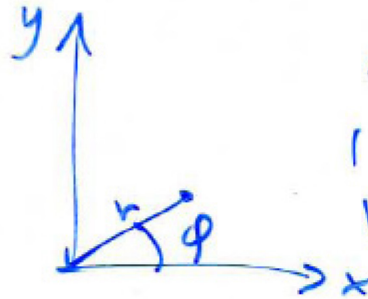
$$f = \frac{1}{2} K \left(\frac{1}{r} \frac{\partial \theta}{\partial \phi} \right)^2 = \frac{1}{2} K \frac{m^2}{r^2}$$

Cylindrical coordinates:

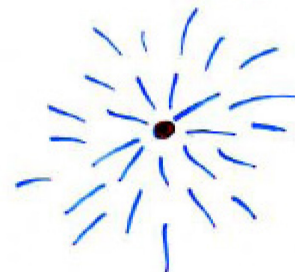


Topology constrains m to be integer, or half-integer.

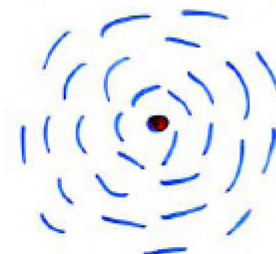
Disclinations (2D) Polar coordinates (r, ϕ) ; $\theta = (\pm)m\phi + \theta_0$



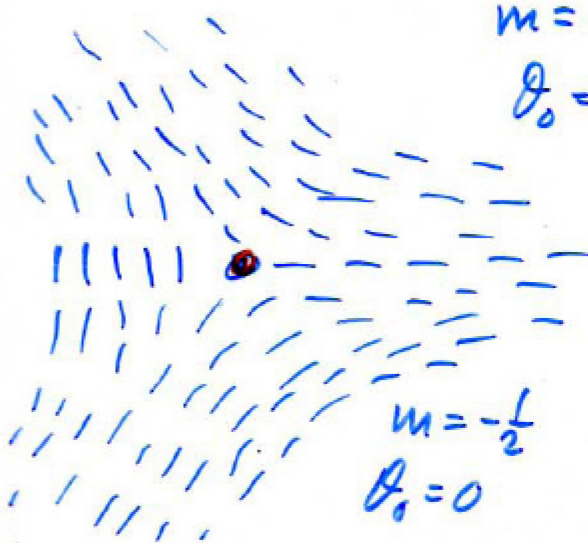
$m = +\frac{1}{2}$
 $\theta_0 = 0$



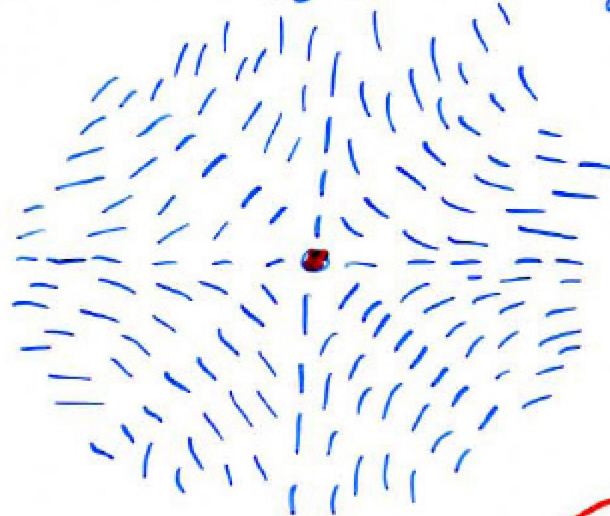
$m = +1$
 $\theta_0 = 0$



$m = +1$
 $\theta_0 = \frac{\pi}{2}$



$m = -\frac{1}{2}$
 $\theta_0 = 0$



$m = -1$
 $\theta_0 = 0$

[Invariant in z]

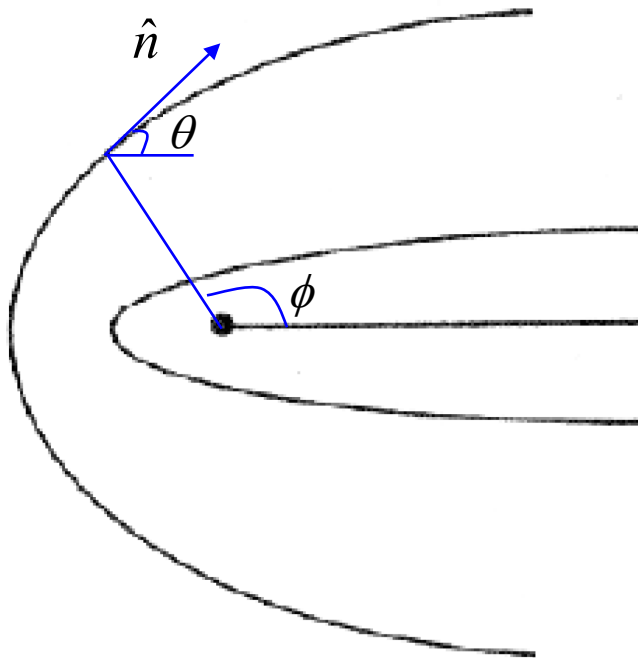
$$\frac{F}{\text{length}} = \int_{\epsilon}^R 2\pi r dr \frac{1}{2} k \left(\frac{m}{r} \right)^2 = \pi k m^2 \ln \frac{R}{\epsilon} + E_{\text{core}}$$

Energy / length

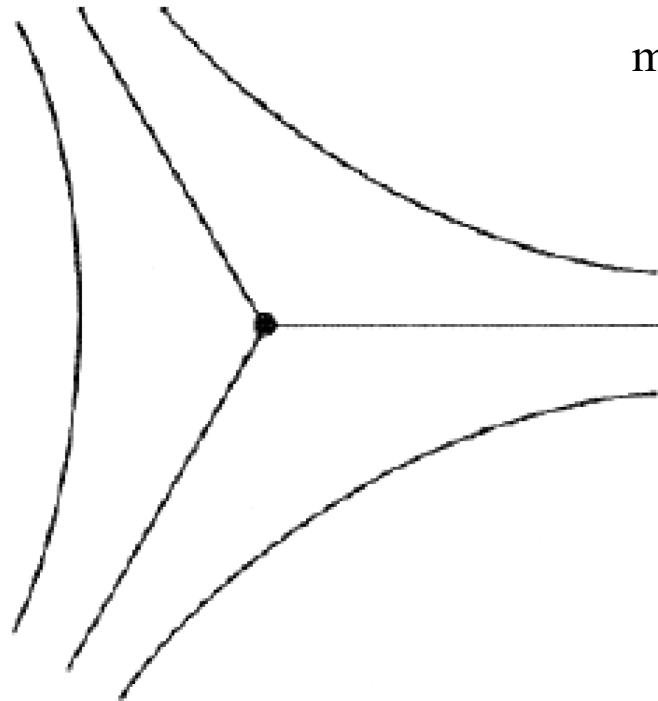
cutoff distance
"core" size

2D disclinations in nematic

$$\theta = \pm m \varphi + \theta_o$$



$m = +1/2$



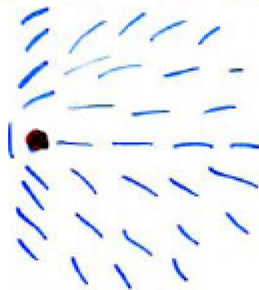
$m = -1/2$

Topology constrains m to be integer, or half-integer.

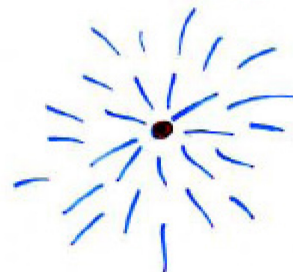
Disclinations (2D) Polar coordinates (r, ϕ) ; $\theta = (\pm)m\phi + \theta_0$

Planar lines of low topological rank are favored.

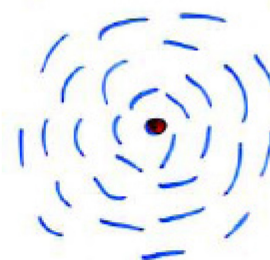
Only ± 1 and $\pm 1/2$ are observed.



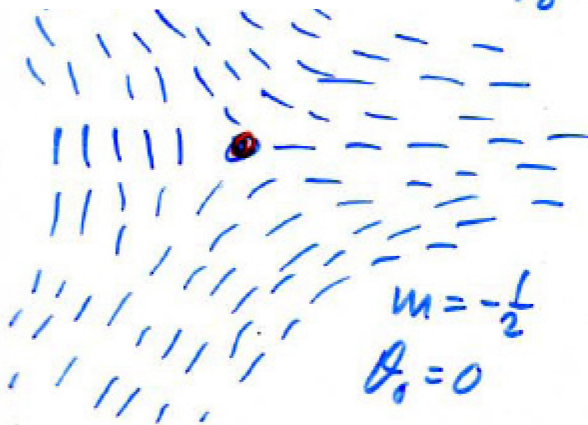
$m = +\frac{1}{2}$
 $\theta_0 = 0$



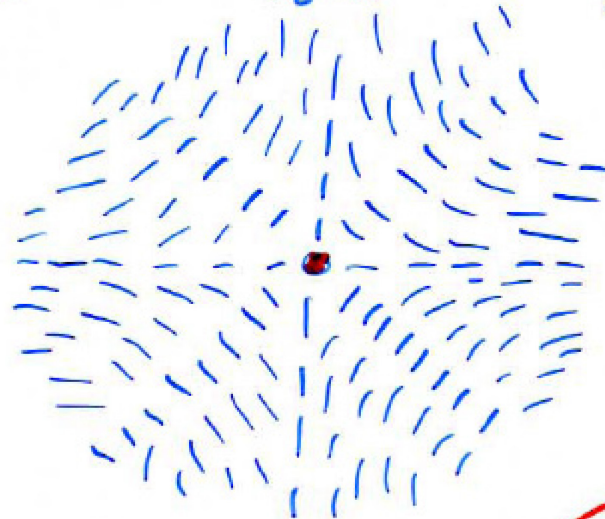
$m = +1$
 $\theta_0 = 0$



$m = +1$
 $\theta_0 = \frac{\pi}{2}$



$m = -\frac{1}{2}$
 $\theta_0 = 0$



$m = -1$
 $\theta_0 = 0$

[Invariant in z]

$$\frac{F}{\text{length}} = \int_{\epsilon}^R 2\pi r dr \frac{1}{2} k \left(\frac{m}{r} \right)^2 = \pi k m^2 \ln \frac{R}{\epsilon} + E_{\text{core}}$$

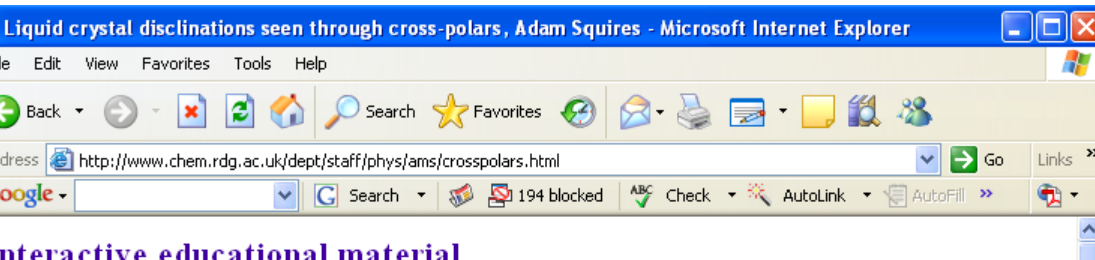
Energy / length

cutoff distance
"core" size

<http://www.chem.rdg.ac.uk/dept/staff/phys/ams/crosspolars.html>

Liquid crystal disclinations seen through cross-polars

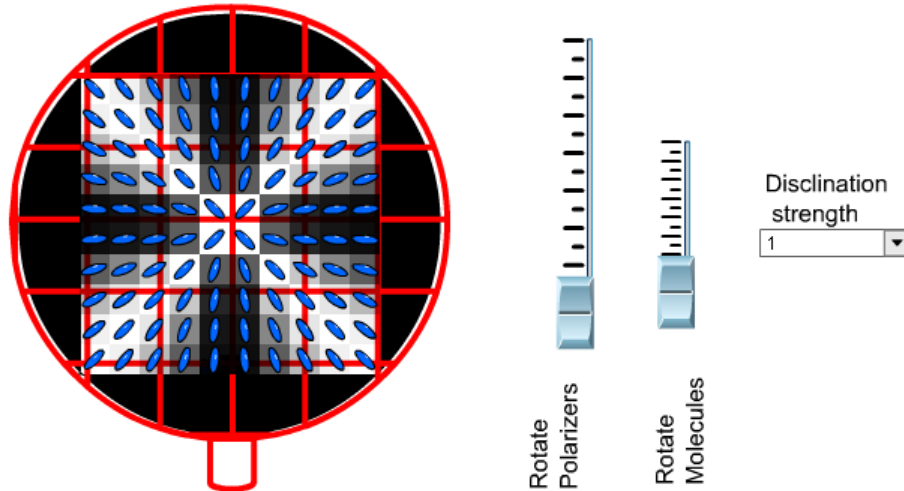
<http://dept.kent.edu/spie/liquidcrystals/textures1.html#ch13>



Interactive educational material

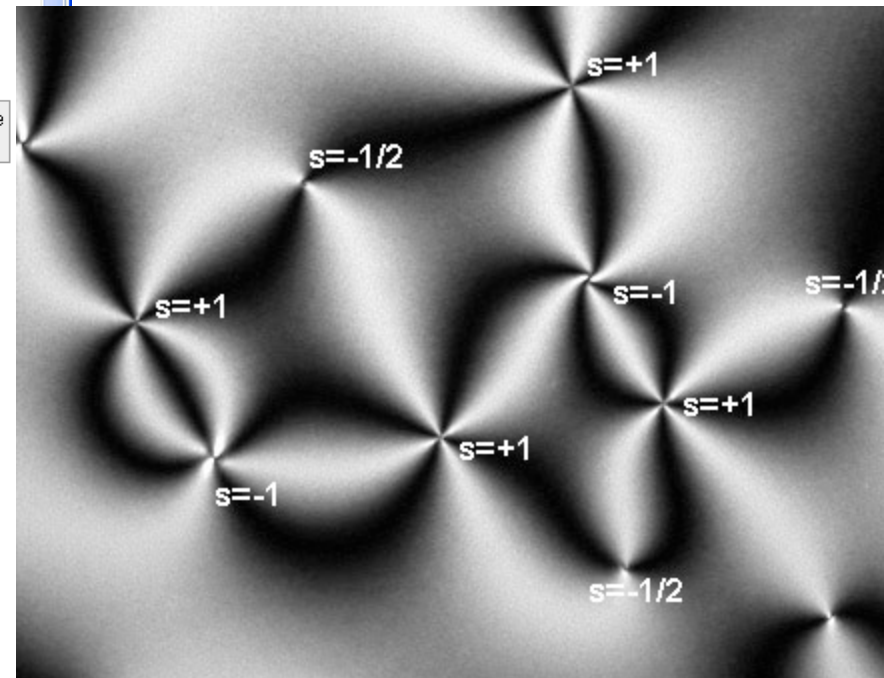
Liquid crystal disclinations seen through cross-polars

This interactive cartoon illustrates how the appearance of a liquid crystal disclination depends on the relative orientations of the molecules and the polarising filters.



Set the disclination strength to +1, and drag both sliders to their bottom position. This shows the familiar "maltese cross" pattern from structures with circular (or spherical) symmetry. You should convince yourself that areas where the molecules are aligned parallel / perpendicular to the polarisers appear darkest, whereas areas where the molecules are at 45 degrees to the polarisers are the brightest.

Rotate the polarisers through 360 degrees by dragging the appropriate slider upwards. The dark/light pattern should also rotate through 360 degrees, in the same direction. This is why the disclination is called "Strength +1". Rotate the molecules through 90 degrees using the other slider. You should see a continuum of defect structures, ranging from



The character of the disclinations changes when elastic anisotropy is considered.

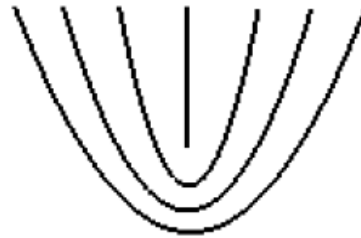
Important for liquid crystalline polymers and colloidal liquid crystals.

$s = +\frac{1}{2}$
defect

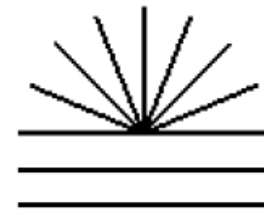


Archway

$$k_{11} > k_{33}$$



$$k_{11} = k_{33}$$



Sunrise

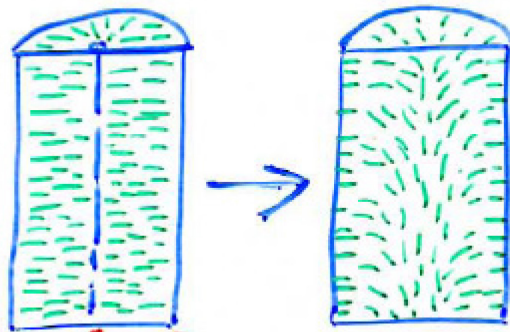
$$k_{11} < k_{33}$$

3D structures ($\hat{n}$ no longer planar)

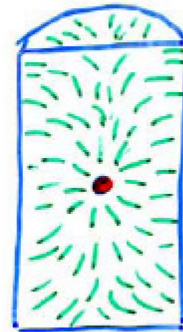
7

* point disclinations are possible

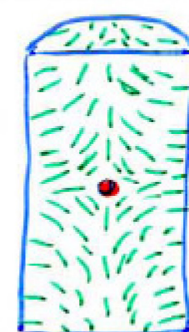
* Integer index ($m=1$) disclinations disappear!



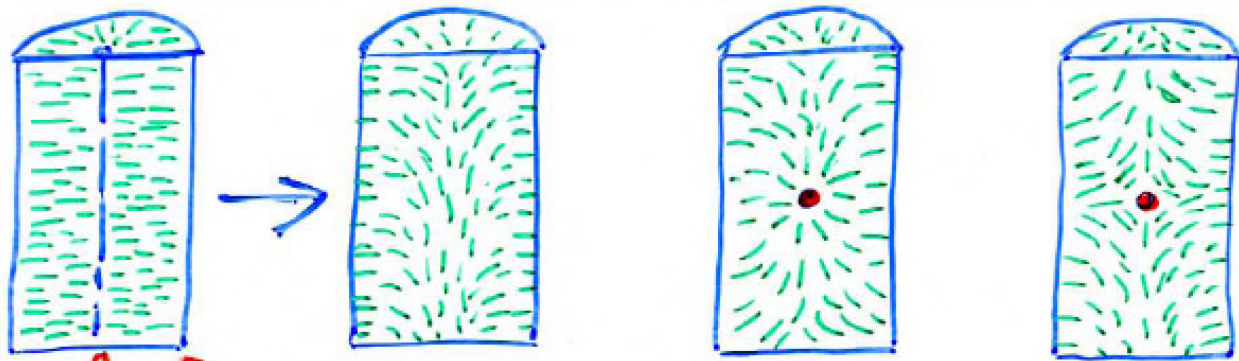
"escape" to the
third dimension



"hedgehog"



"negative
hedgehog"



"escape" to the
third dimension

"hedgehog"

"negative
hedgehog"

For the cylinder of radius r_0 , assume $n_r = \cos\theta$, $n_z = \sin\theta$
 $n_\phi = 0$:

$$\frac{F}{\text{length}} = \pi K \int_0^{r_0} \frac{dr}{r} \left[\cos^2\theta - 2r \sin\theta \cos\theta \frac{d\theta}{dr} + r^2 \left(\frac{d\theta}{dr} \right)^2 \right]$$

($K = K_{11} = K_{33}$) Euler Lagrange eqn: change to $x = \ln\left(\frac{r}{r_0}\right)$

$$\frac{d^2\theta}{dx^2} = -\sin\theta \cos\theta$$

Solution $\theta = 2 \tan^{-1}\left(\frac{r_0}{r}\right) - \frac{\pi}{2}$.

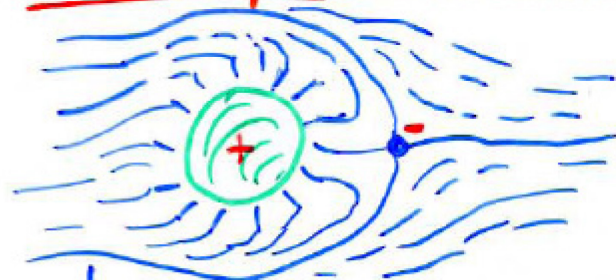
disclination

$$\pi K m^2 \ln \frac{R}{\epsilon}$$

$\frac{F}{\text{length}} = 3\pi K$ independent of r_0 . This is less than
the disclination energy, surely for $\ln \frac{r_0}{\epsilon} > 3$.

Nematic emulsions: A droplets of isotropic liquid⁸
suspended in a nematic:

Example: normal boundary conditions at interface



Pearl chain:

- + ⊕ + ⊕ + ⊕ + ⊕ + ⊕ + ⊕ + ⊕ + -

= hedgehog $\rightarrow$ needs a negative hedgehog nearby to cancel long range distortions.

Novel Colloidal Interactions in Anisotropic Fluids

Philippe Poulin, Holger Stark,* T. C. Lubensky, D. A. Weitz

SCIENCE • VOL. 275 • 21 MARCH 1997

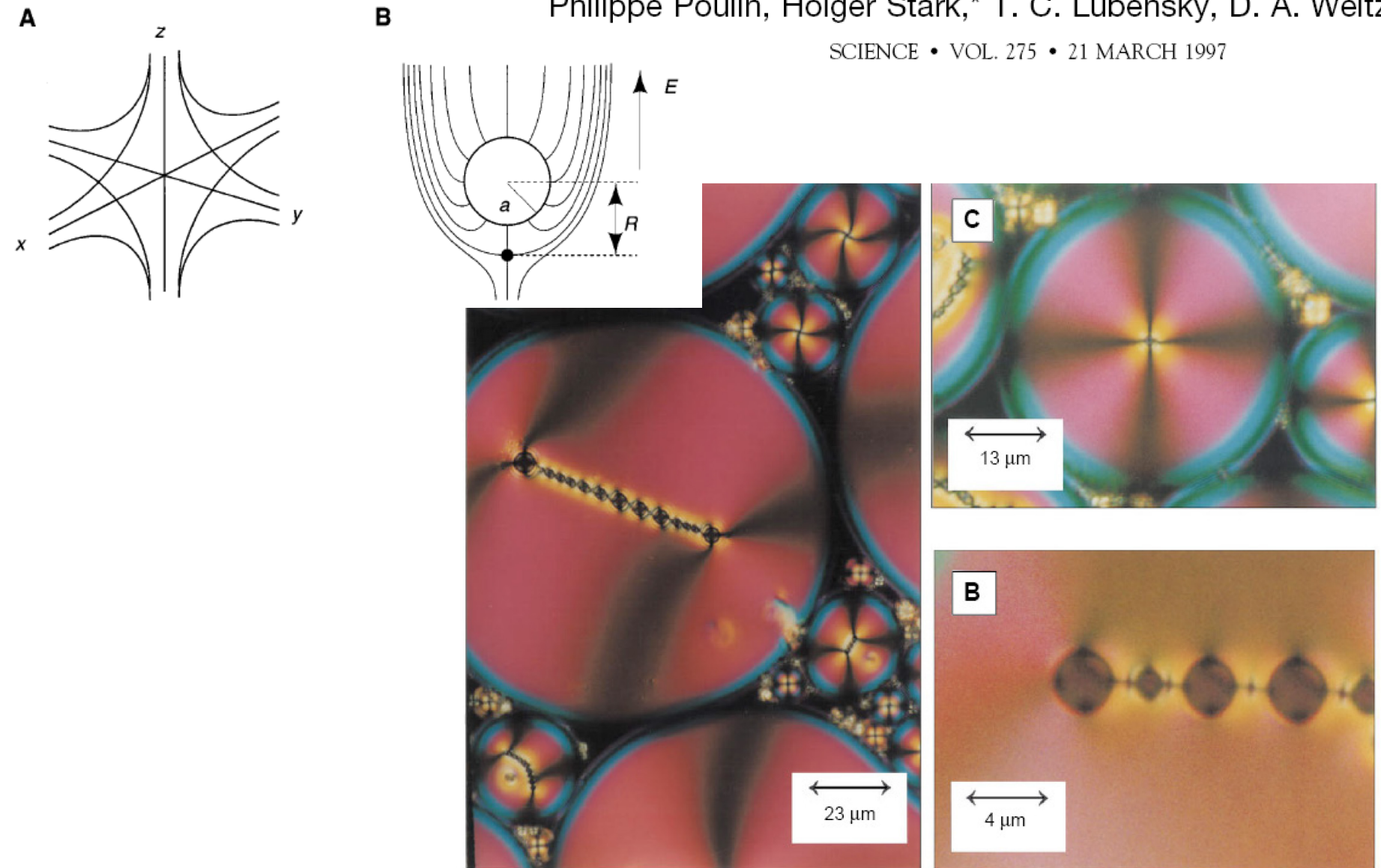
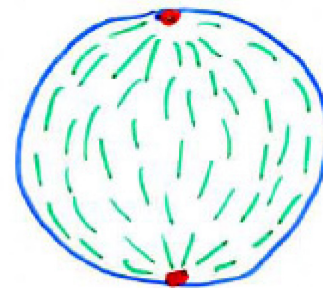
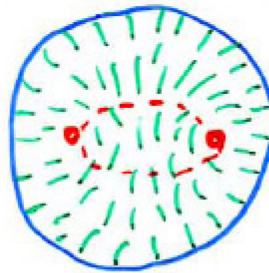
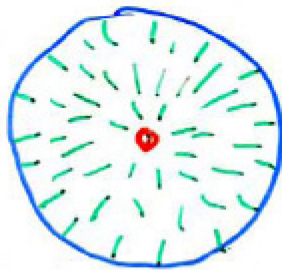


Fig. 1. (A) Microscope image of a nematic multiple emulsion taken under crossed polarizers. (B) A chain of water droplets under high magnification. (C) A nematic drop containing a single water droplet.

B. Droplets of nematic suspended in an isotropic matrix (solid or liquid): For $\perp$ or $\parallel$ boundary conditions, need disclinations in the structure of the droplet:



Field effects

① Anisotropy of susceptibility

Magnetic field: diamagnetic $\chi \sim 10^{-6}$ & negative.



π electrons in benzene rings are good at producing currents to oppose applied H .

Therefore rings tend to align parallel to H .

Electric field: Combination of electronic and dipolar effects:



large dipole dominates
response: $\hat{n} \parallel E$.

Magnetic free energy density:

$$f_H = \frac{1}{2} \chi_a H^2 \sin^2 \theta$$

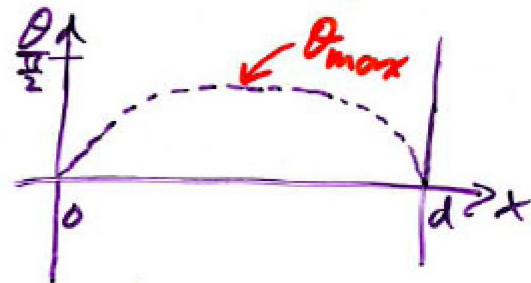
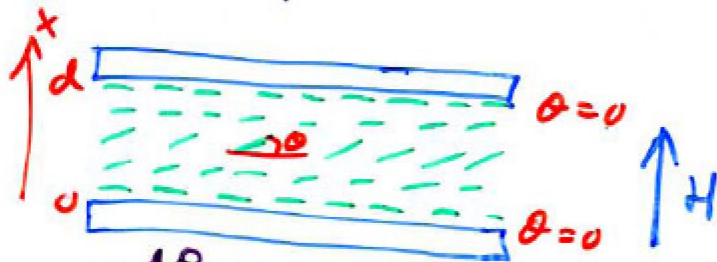


$$\chi_a = \chi_{||} - \chi_{\perp}$$

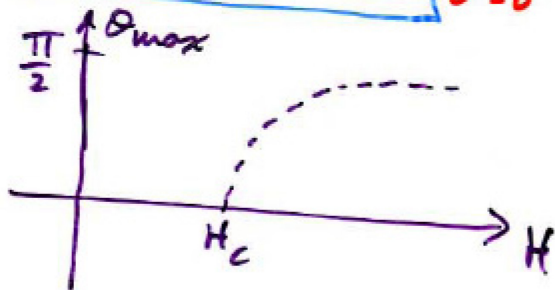
* Generally in a finite sample surface alignment and field alignment can compete. At low fields surface wins. At high field field wins, depending on sample dimensions.

Calculus of variations and Linear Stability Analysis. ^{CI}

Example: Frederike transition in splay-bend geometry



boundary condition:
 $\theta(0) = \theta(d) = 0$



$$\begin{aligned} \frac{F}{\text{area}} &= \int_0^d dx \left[\underbrace{\left(\frac{1}{2} k_{11} \cos^2 \theta + \frac{1}{2} k_{33} \sin^2 \theta \right)}_{A(\theta)} \left(\frac{d\theta}{dx} \right)^2 - \underbrace{\frac{1}{2} \chi_a H^2 \sin^2 \theta}_{C(\theta)} \right] \\ &= \int_0^d dx \left[A(\theta) \left(\frac{d\theta}{dx} \right)^2 + C(\theta) \right] \end{aligned}$$

Balance of torques

For $H > H_c$ Need to solve the F.L. equation. Simplify for

now: $K_{11} = K_{33} = K$; $-2\left(\frac{1}{2}K\right)\frac{d^2\theta}{dx^2} - \frac{1}{2}\chi_a H^2 (2\sin\theta\cos\theta) = 0$

$$\frac{d^2\theta}{dx^2} + \frac{1}{\xi_H^2} \sin\theta\cos\theta = 0, \quad \xi_H = \frac{1}{H} \sqrt{\frac{K}{\chi_a}}$$

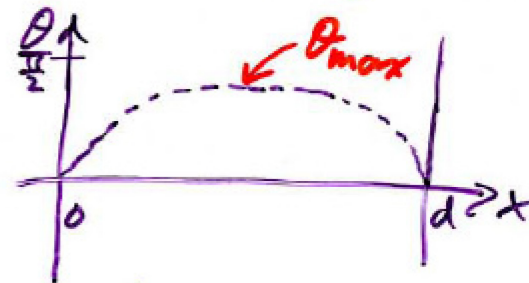
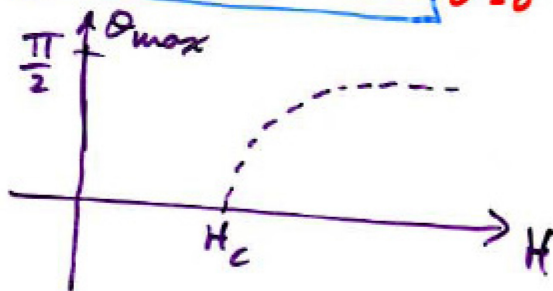
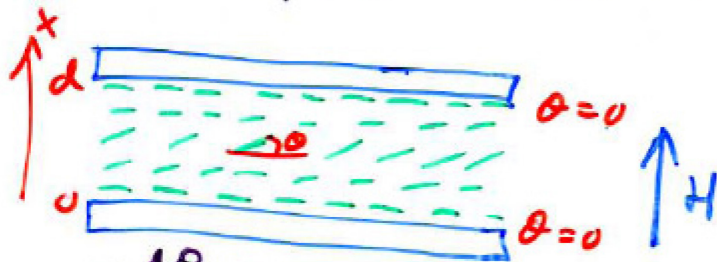
Solutions are elliptic integrals. Note: $\xi_{H_c} = \frac{d}{\pi}$



Linear stability analysis

Calculus of variations and Linear Stability Analysis. ^{CI}

Example: Frederike transition in splay-beer geometry



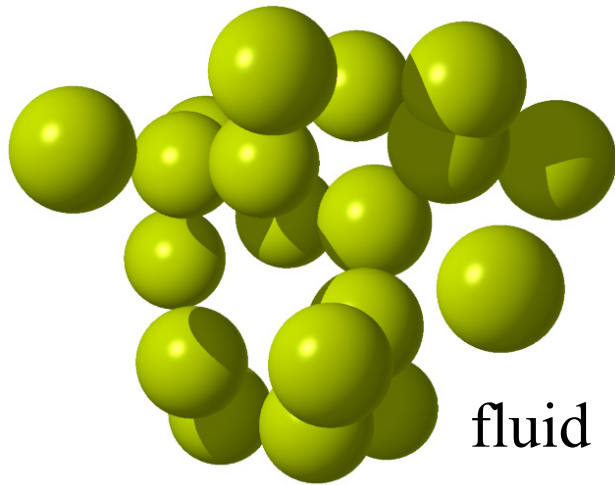
boundary condition:
 $\theta(0) = \theta(d) = 0$

$$\begin{aligned} \frac{F}{\text{area}} &= \int_0^d dx \left[\underbrace{\left(\frac{1}{2} k_{11} \cos^2 \theta + \frac{1}{2} k_{33} \sin^2 \theta \right)}_{A(\theta)} \left(\frac{d\theta}{dx} \right)^2 - \underbrace{\frac{1}{2} \chi_a H^2 \sin^2 \theta}_{C(\theta)} \right] \\ &= \int_0^d dx \left[A(\theta) \left(\frac{d\theta}{dx} \right)^2 + C(\theta) \right] \end{aligned}$$

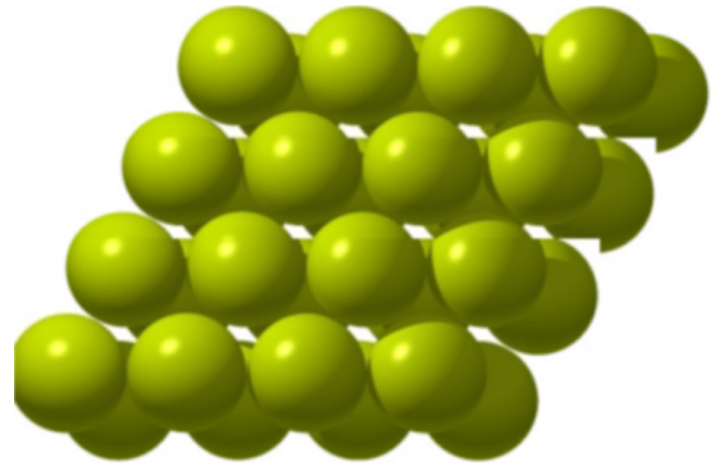


Entropy driven phase transitions

Hard core repulsion



hard spheres



49% volume fraction

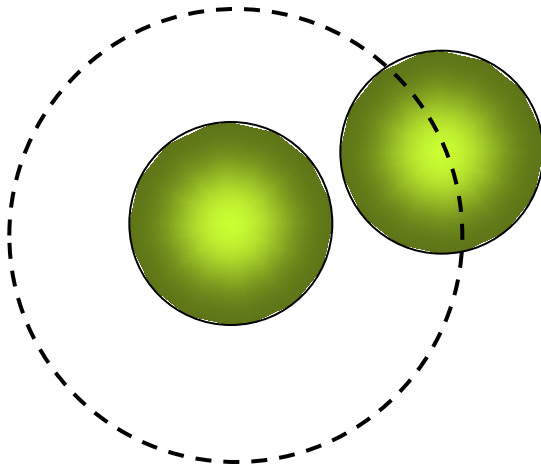
crystal

concentration

more configurations in crystal than fluid

Excluded volume

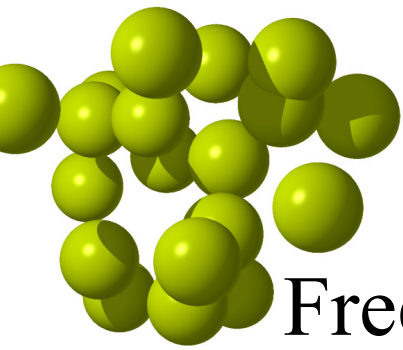
excluded volume of sphere $V_{ex} = 8V$



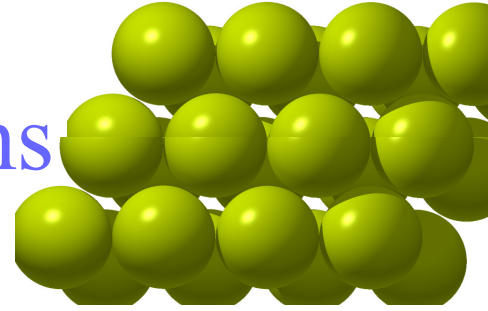
loss of translational entropy

volume fraction of phase transition

$$\phi \approx \frac{4/V_{ex}}{1/V} = 50\%$$



Hard particle suspensions



Free energy

$$F = U - TS$$

U energy **independent** of configuration

$$U = Nk_B T$$

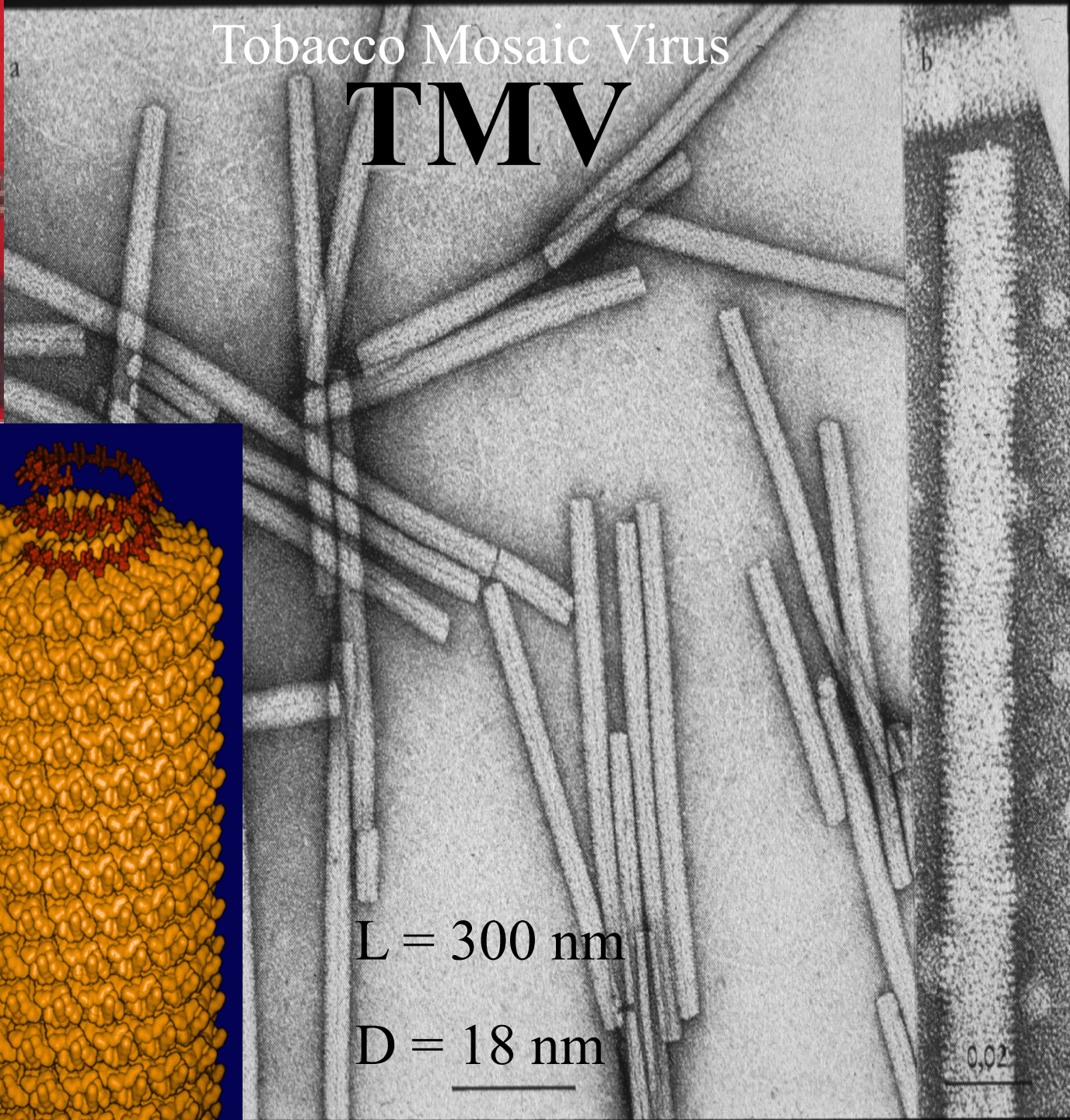
S entropy **dependent** of configuration

$$F_i = T(Nk_B - S_i)$$

free energy difference:

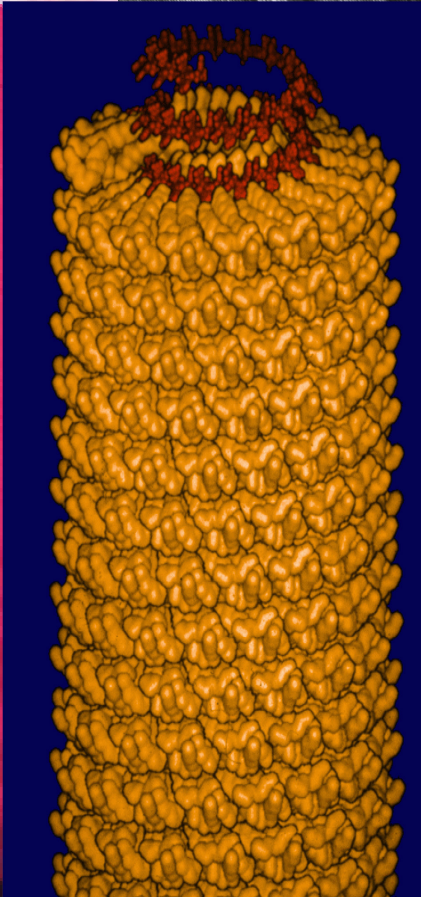
$$\Delta F_{ij} = -T\Delta S_{ij}$$

phase with largest entropy $S \uparrow$ and the phase transition is
lowest free energy $F \downarrow$ **athermal**



Tobacco Mosaic Virus

TMV



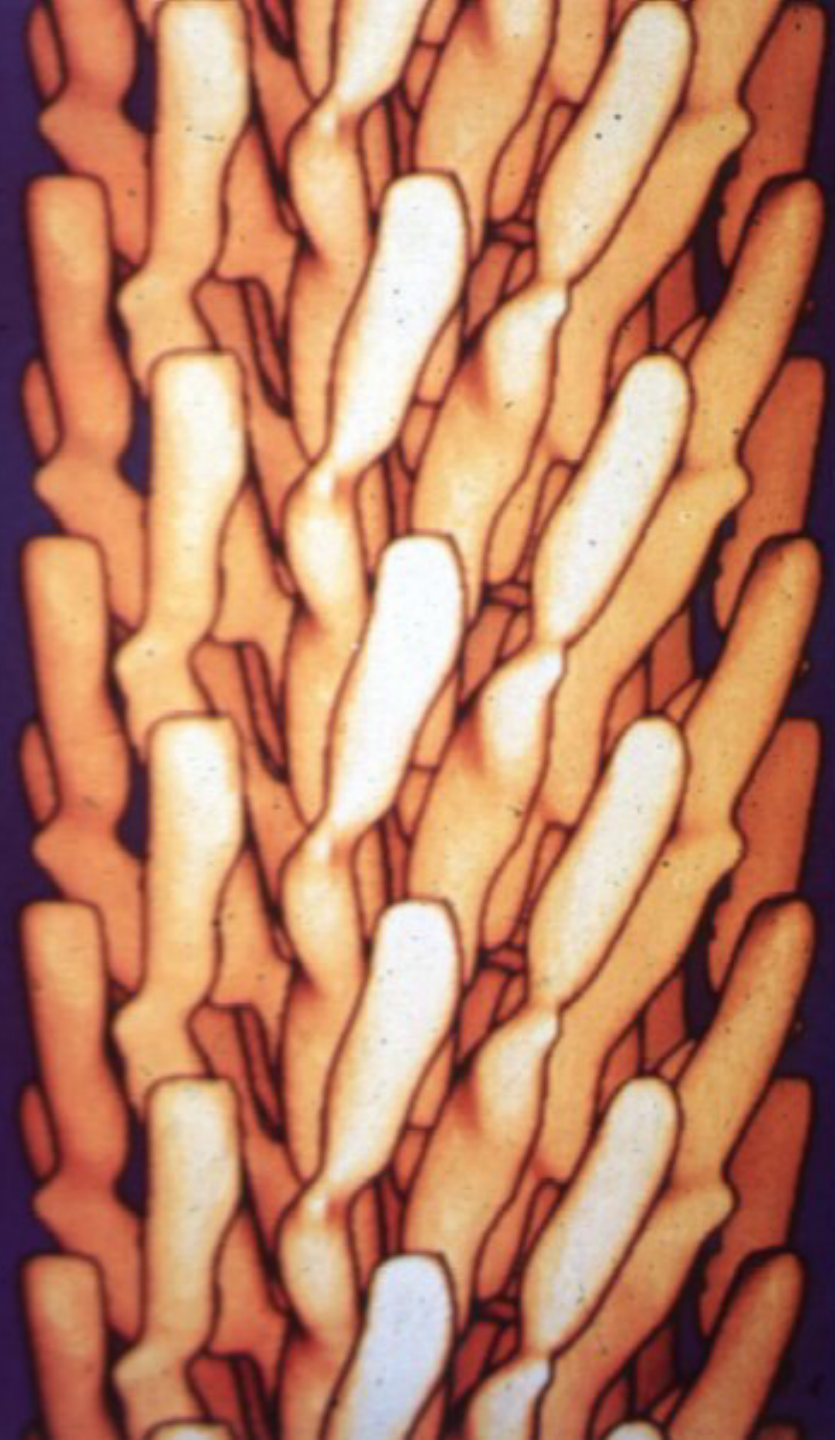
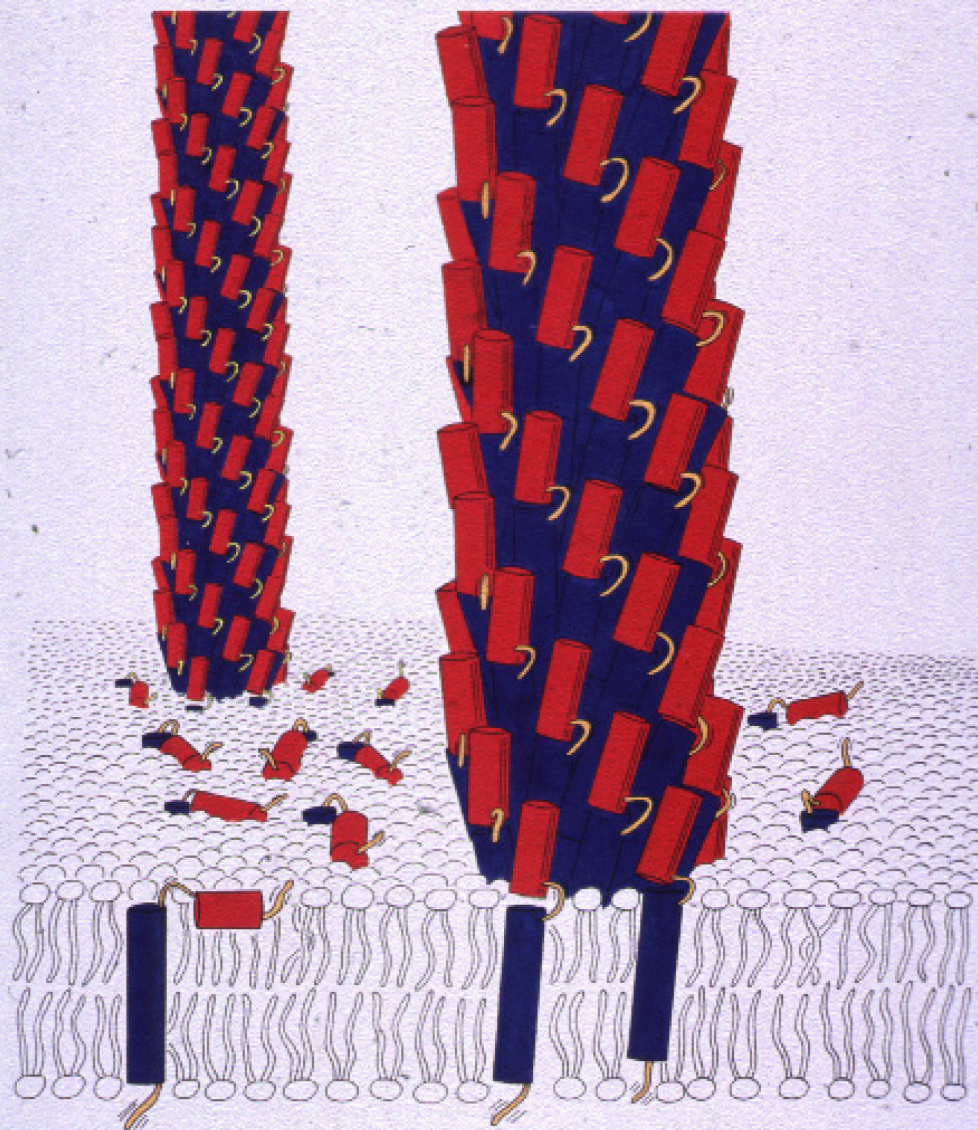
$L = 300 \text{ nm}$

$D = 18 \text{ nm}$

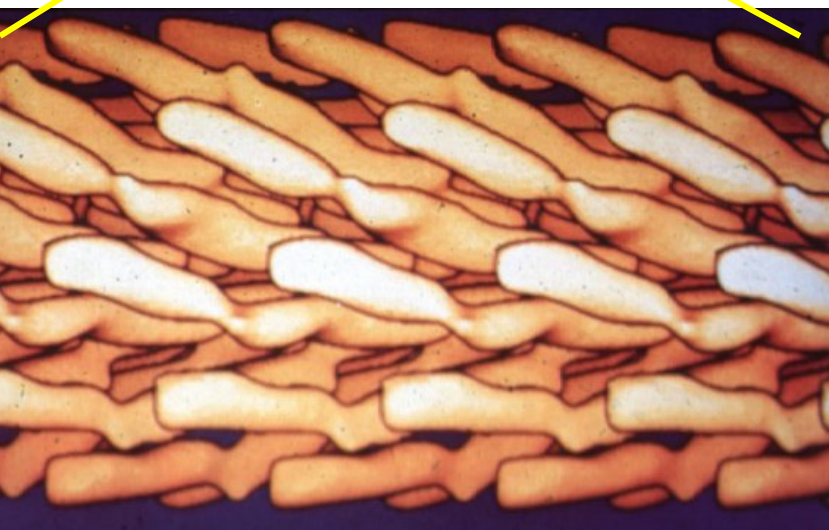
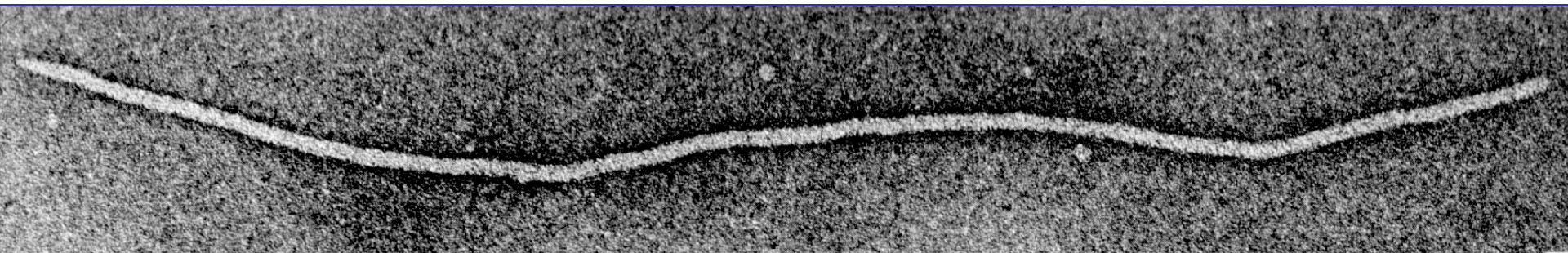
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SCIENCE

31 MAY 1991
VOL. 252 ■ PAGES 1221-1344

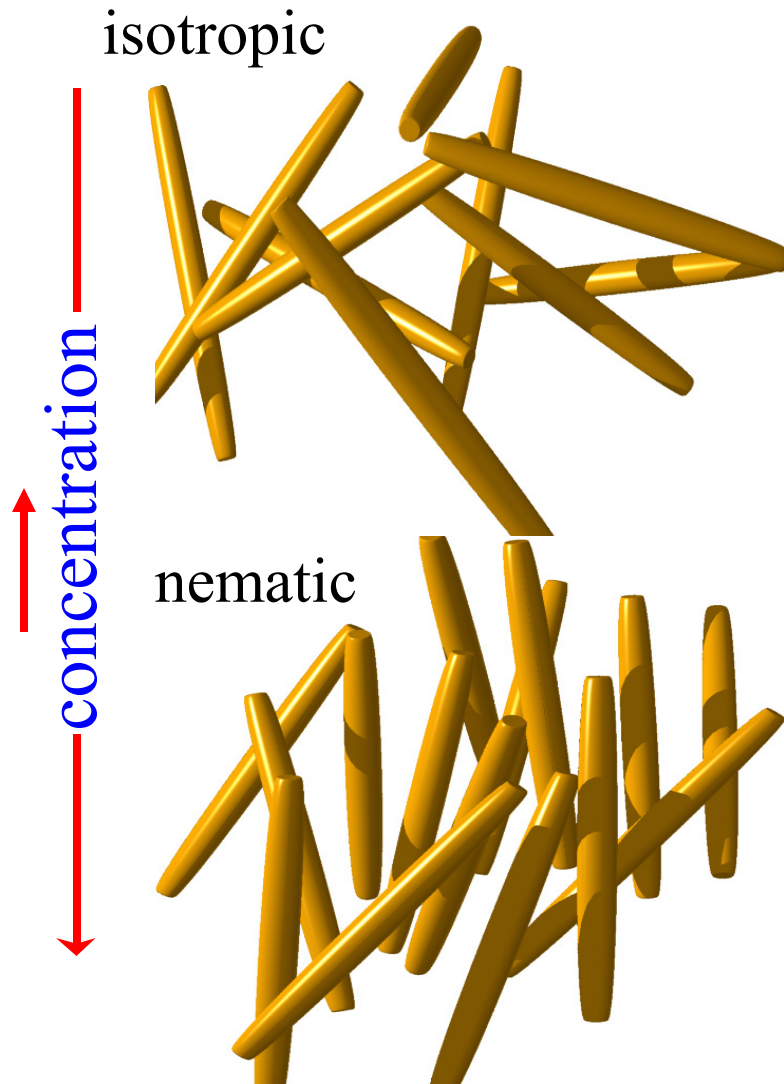


fd virus

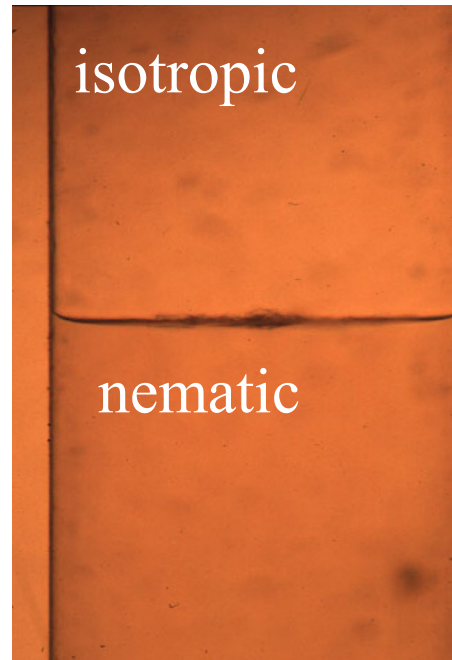


length	L	1000 nm
diameter	D	10 nm
persistence length	P	2000 nm
surface charge		10 e ⁻ /nm

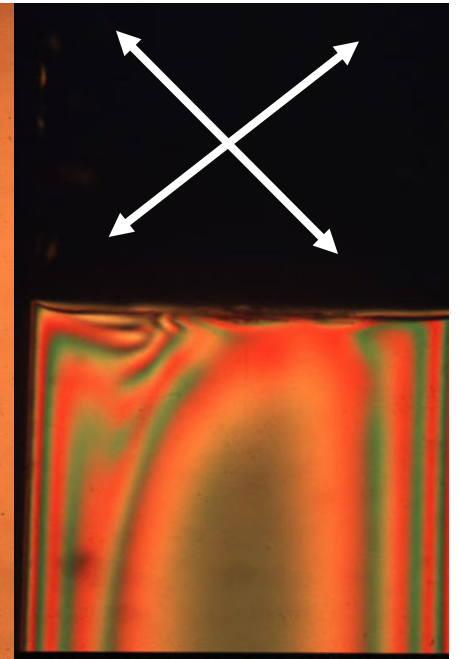
isotropic - nematic two phase coexistence



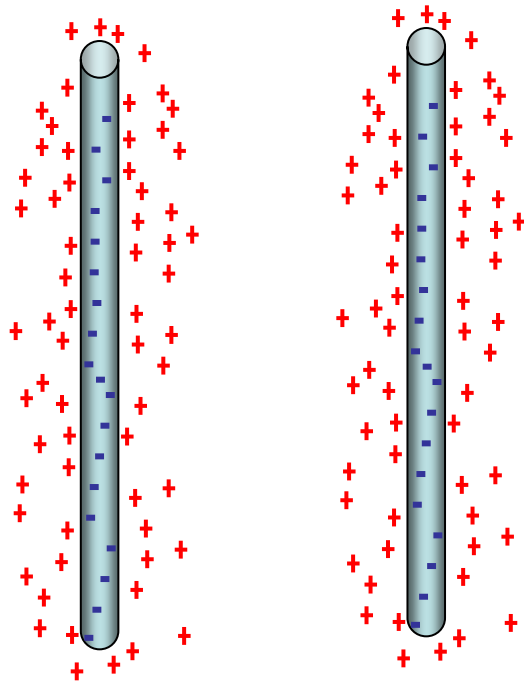
white light



crossed polarizers



Onsager, *Ann. NY Acad. Sci.* vol 51, 627 (1949)

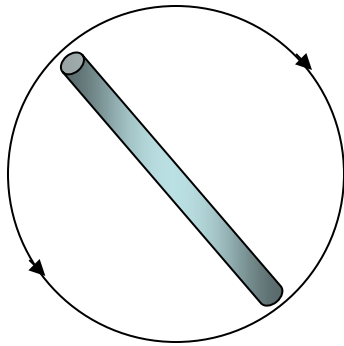


Introduction. The shapes of colloidal particles are often reasonably compact, so that no diameter greatly exceeds the cube root of the volume of the particle. On the other hand, we know many colloids whose particles are greatly extended into sheets (bentonite), rods (tobacco virus), or flexible chains (myosin, various linear polymers).

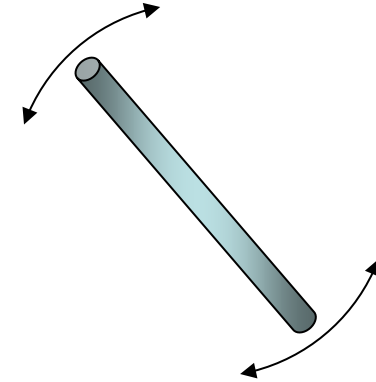
In some instances, at least, solutions of such highly anisometric particles are known to exhibit remarkably great deviations from Raoult's law, even to the extent that an anisotropic phase may separate from a solution in which the particles themselves occupy but one or two per cent of the total volume (tobacco virus, bentonite). We shall show in what follows how such results may arise from electrostatic repulsion between highly anisometric particles.

Isotropic – Nematic Transition: Onsager Theory

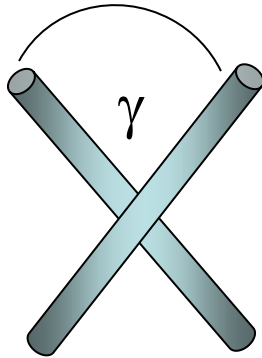
Isotropic



Nematic



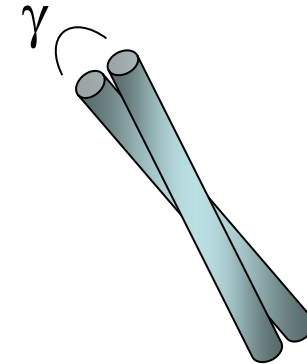
rotational entropy decreases



excluded volume entropy increases



$$b \sim 2D^2 L \sin \gamma$$

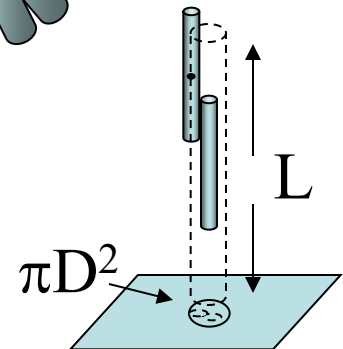


total entropy

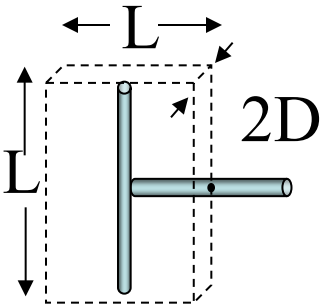


volume fraction at transition $\phi = cV_0 = 4 \frac{D}{L}$

$$c = \frac{1 \text{ rod}}{L^2 D} \text{ at transition}$$



excluded volume: $\pi D^2 L$



excluded volume: $2L^2 D$

Virial expansion – hard particle

Helmholtz
free energy

entropy of mixing

entropy of packing
excluded volume

$$\frac{\Delta F}{NkT} = \int f \ln(4\pi f) d\Omega - \frac{\rho}{2} \int f_1 f_2 \beta_m d\Omega_1 d\Omega_2$$

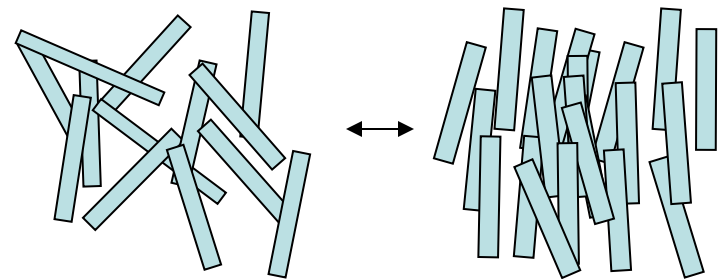
$$\beta_M(\Omega_1, \Omega_2) = \frac{1}{V} \int e^{-\beta U(\Omega_1, \Omega_2)} - 1 dr_1 dr_2$$

hard particle
excluded volume

$$\beta_M(\Omega_1, \Omega_2) = -2L^2 D |\sin \gamma|$$

orientational-positional
distribution function

$f(\Omega)$

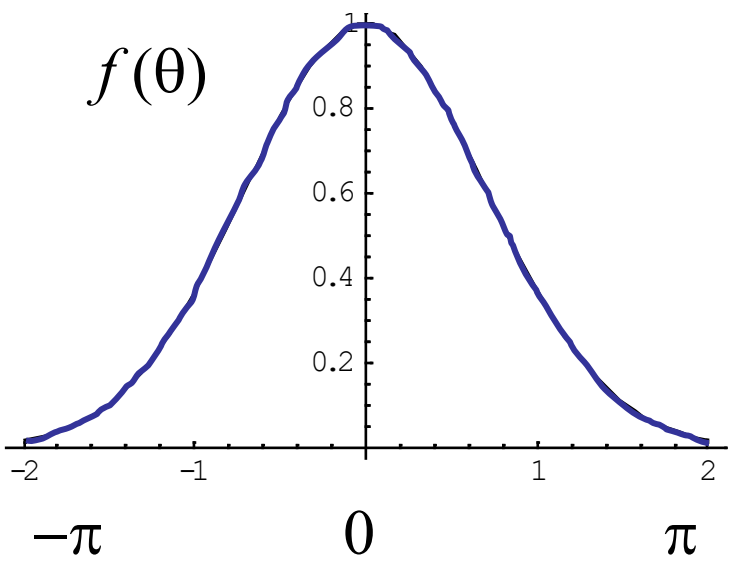
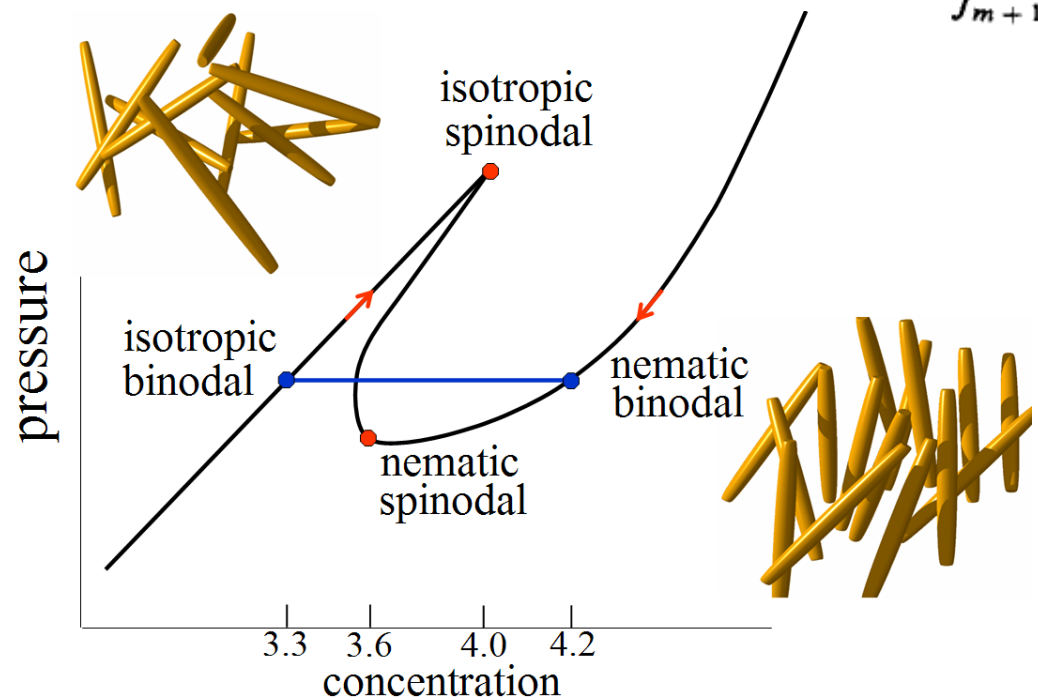


Bifurcation in Onsager's model of the isotropic-nematic transition

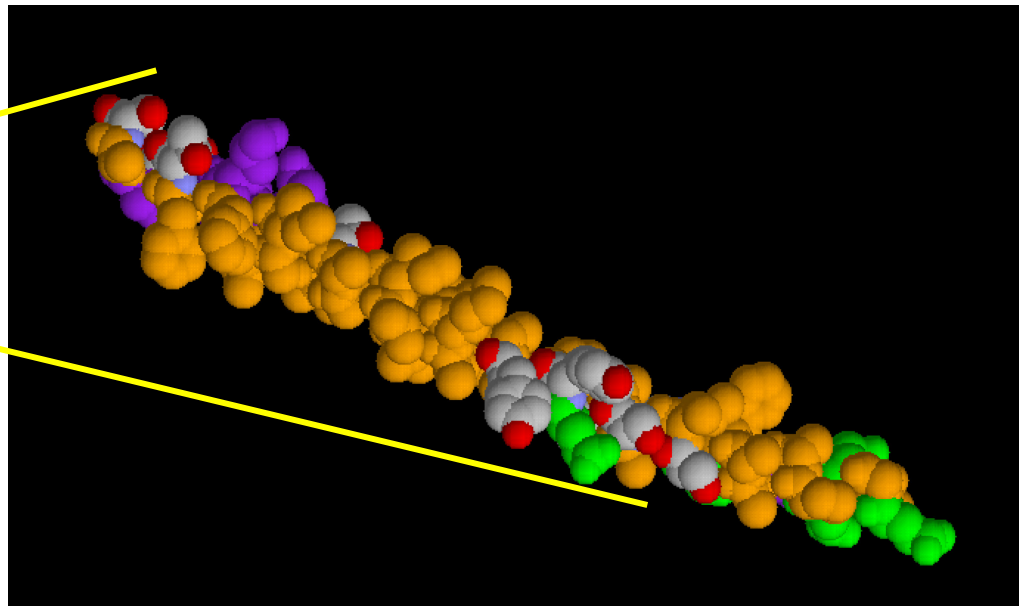
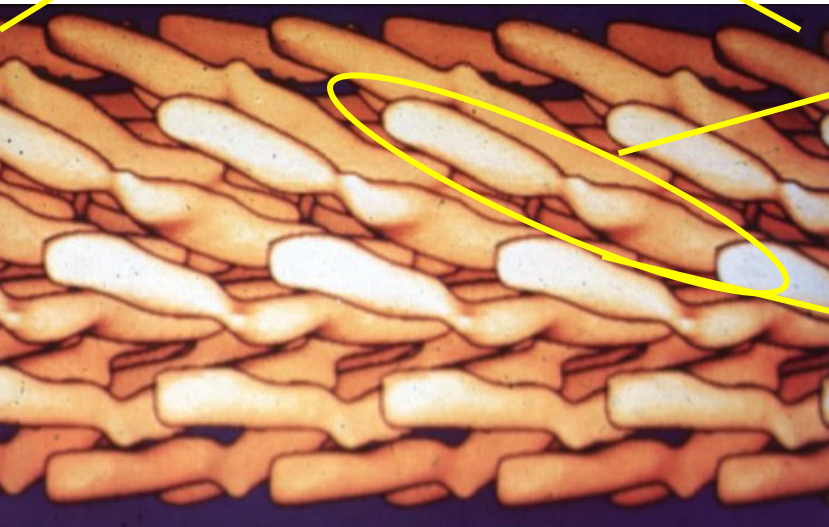
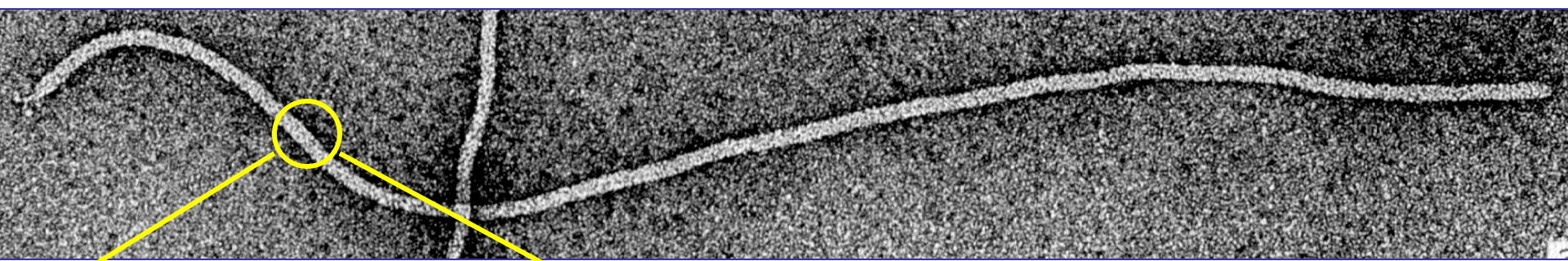
Richard F. Kayser, Jr. and Harold J. Raveché
National Bureau of Standards, Washington, D. C. 20234

$$\frac{\Delta F}{NkT} = \int f \ln(4\pi f) d\Omega - \frac{\rho}{2} \int f_1 f_2 \beta_m d\Omega_1 d\Omega_2$$

$$f_{m+1}(\theta) = \frac{\exp \left[- \frac{8q}{\pi} \int |\sin \gamma(\mathbf{a}, \mathbf{a}')| f_m(\mathbf{a}') d\mathbf{a}' \right]}{\int \exp \left[- \frac{8q}{\pi} \int |\sin \gamma(\mathbf{a}, \mathbf{a}')| f_m(\mathbf{a}') d\mathbf{a}' \right] d\mathbf{a}} \tag{12}$$



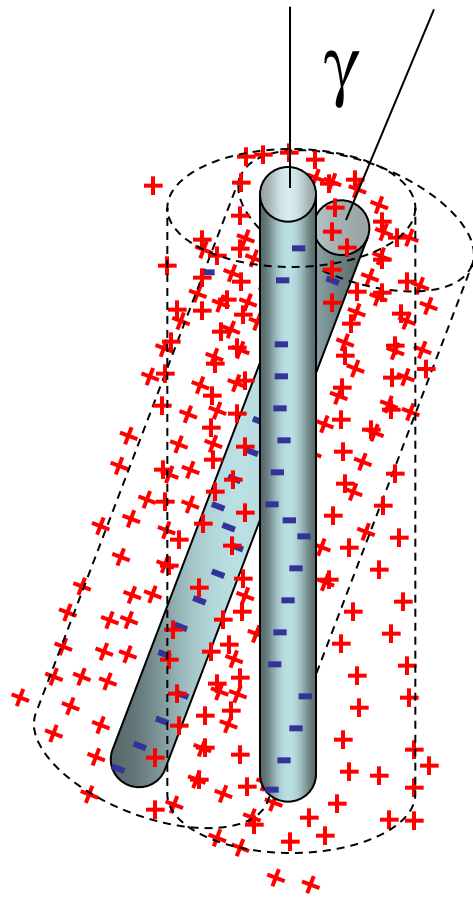
Viral Surface Charge



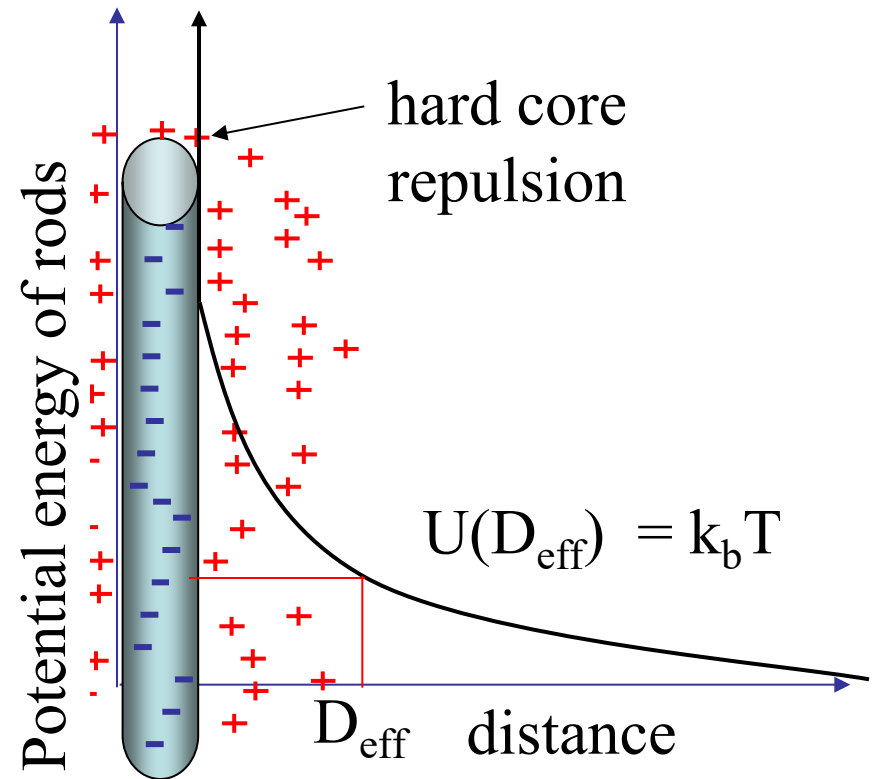
orange: hydrophobic, purple: positive, green: negative

electrostatics

screened Coulomb repulsion between charged rods



$$U(r) \propto \frac{e^{-\kappa r}}{r \sin(\gamma)}$$



Debye screening length $\kappa^{-1} = \frac{3 \text{ \AA}}{\sqrt{I}}$

Virial expansion – charged particle

Helmholtz
free energy

entropy of mixing

entropy of packing
excluded volume

$$\frac{\Delta F}{NkT} = \int f \ln(4\pi f) d\Omega - \frac{\rho}{2} \int f_1 f_2 \beta_m d\Omega_1 d\Omega_2$$

excluded volume

$$\beta_M(\Omega_1, \Omega_2) = \frac{1}{V} \int e^{-\beta U(\Omega_1, \Omega_2)} - 1 dr_1 dr_2$$

Mayer function

$$e^{-\frac{e^{-\kappa r}}{kT r \sin \gamma}} - 1$$

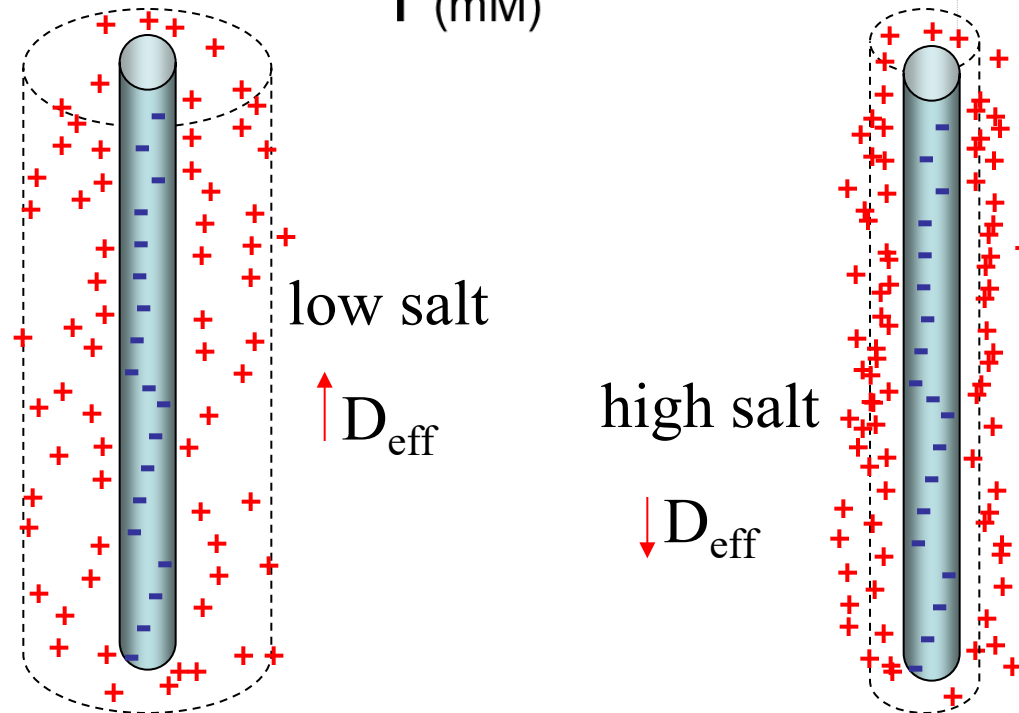
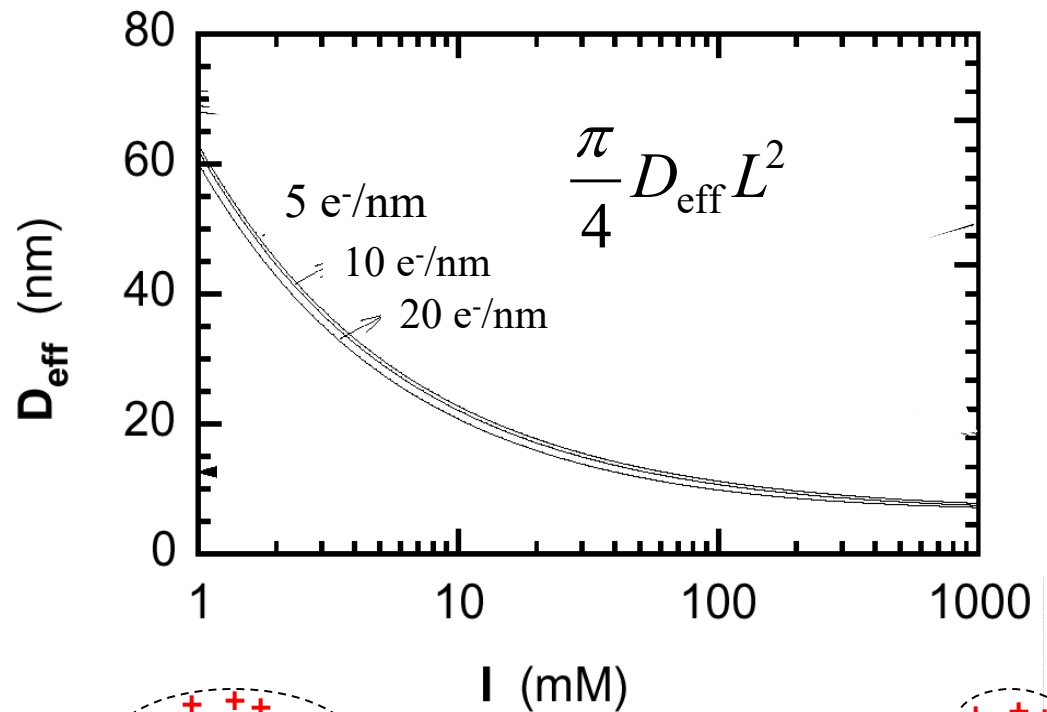
charged particle
excluded volume

$$\beta_M(\Omega_1, \Omega_2) = -2L^2 D_{\text{eff}} |\sin \gamma|$$

Effective diameter
in isotropic

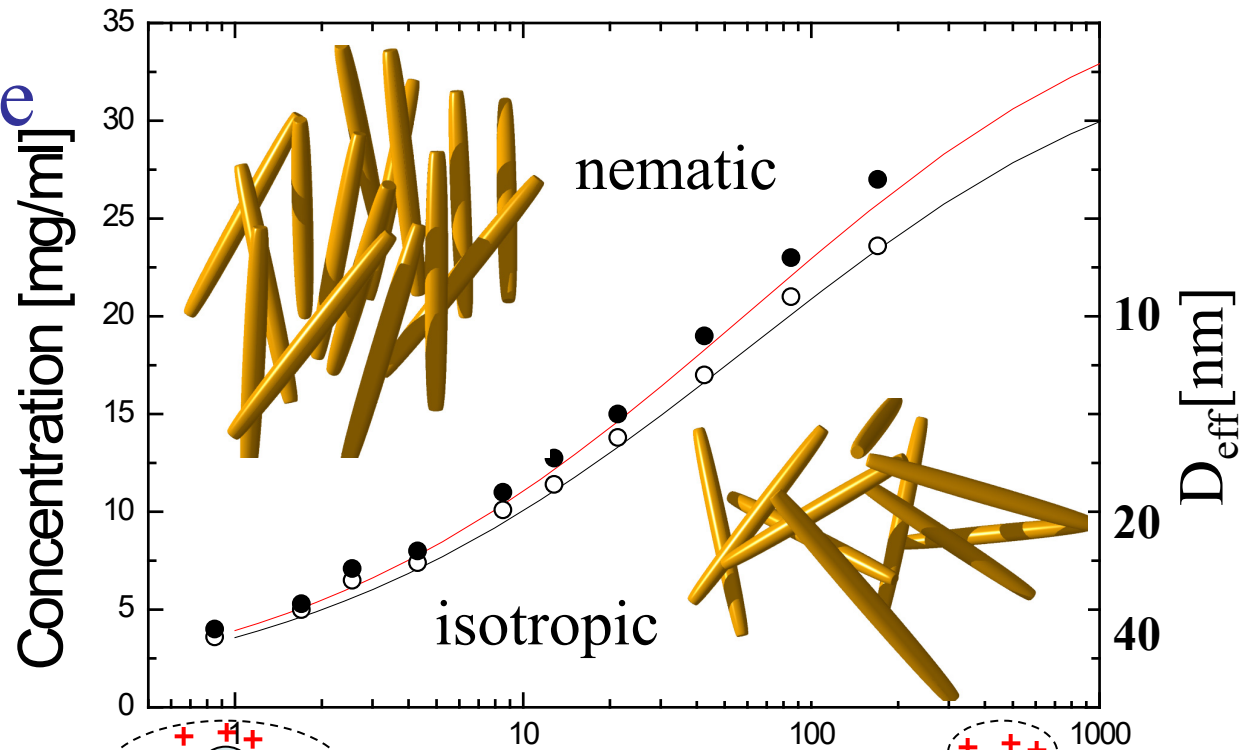
average over all
orientations

Manning condensation
is result of non-linear
Poisson-Boltzmann
equation.



phase co-existence

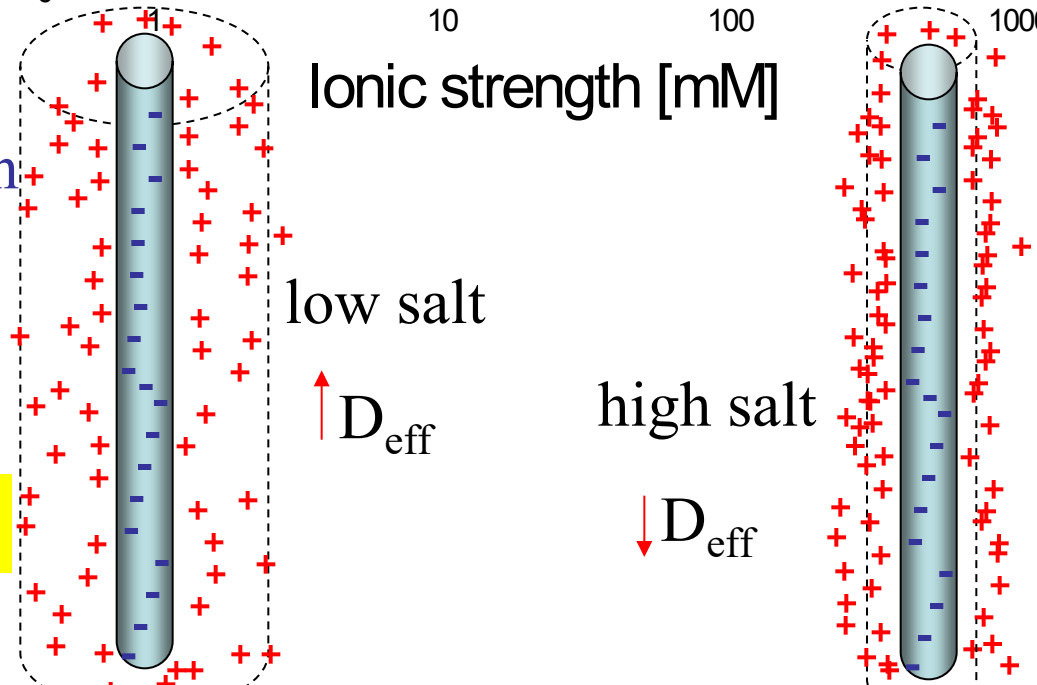
fd virus in buffer

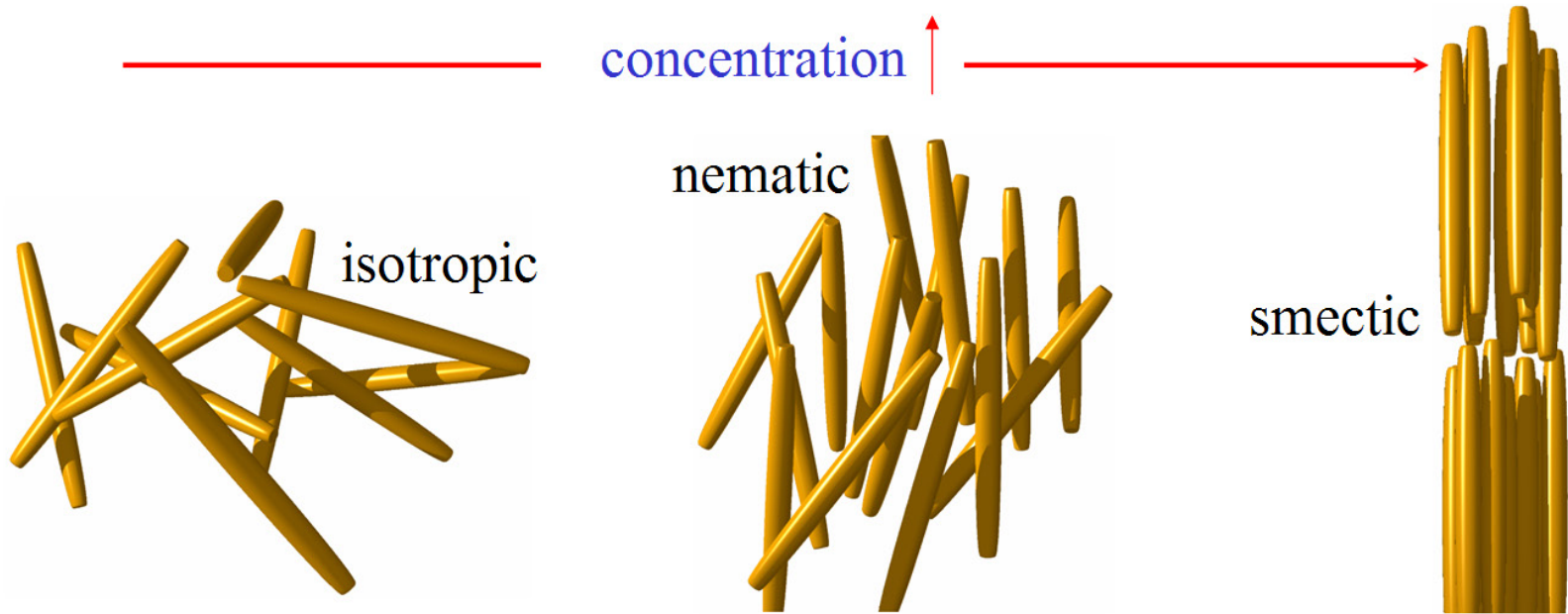


volume fraction at transition

$$\phi = 4 \frac{D_{eff}}{L} \propto c L D_{eff}^2$$

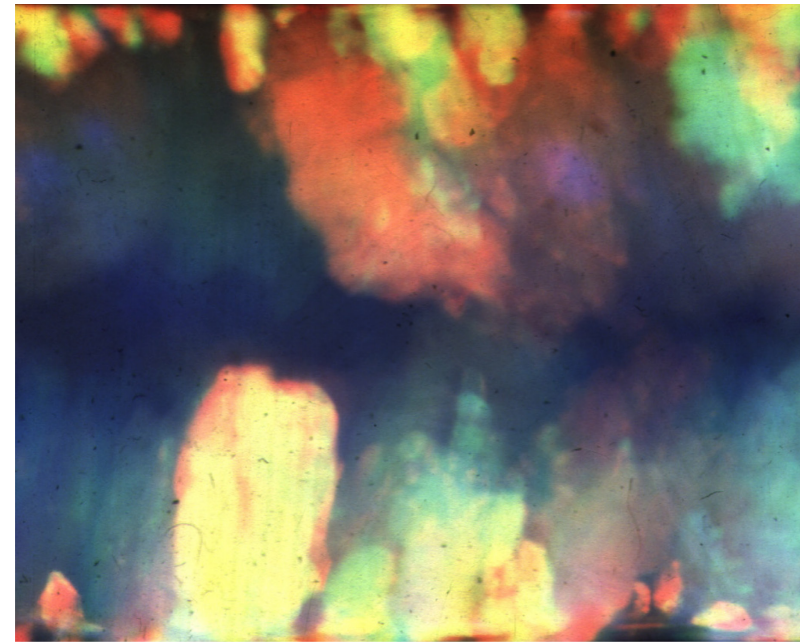
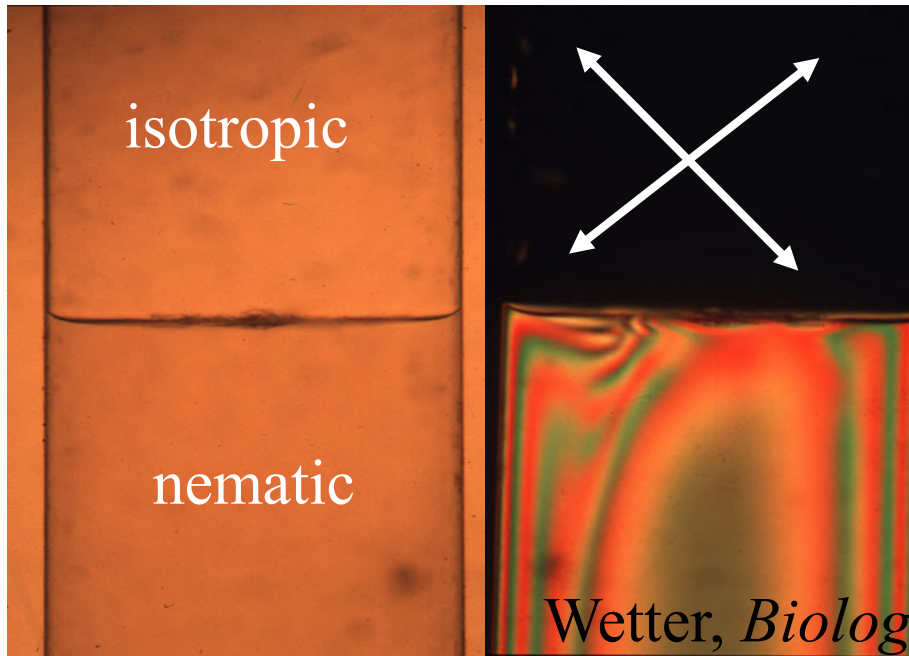
$$c_{fd} [\text{mg/ml}] = 222 / D_{eff} [\text{nm}]$$





white light

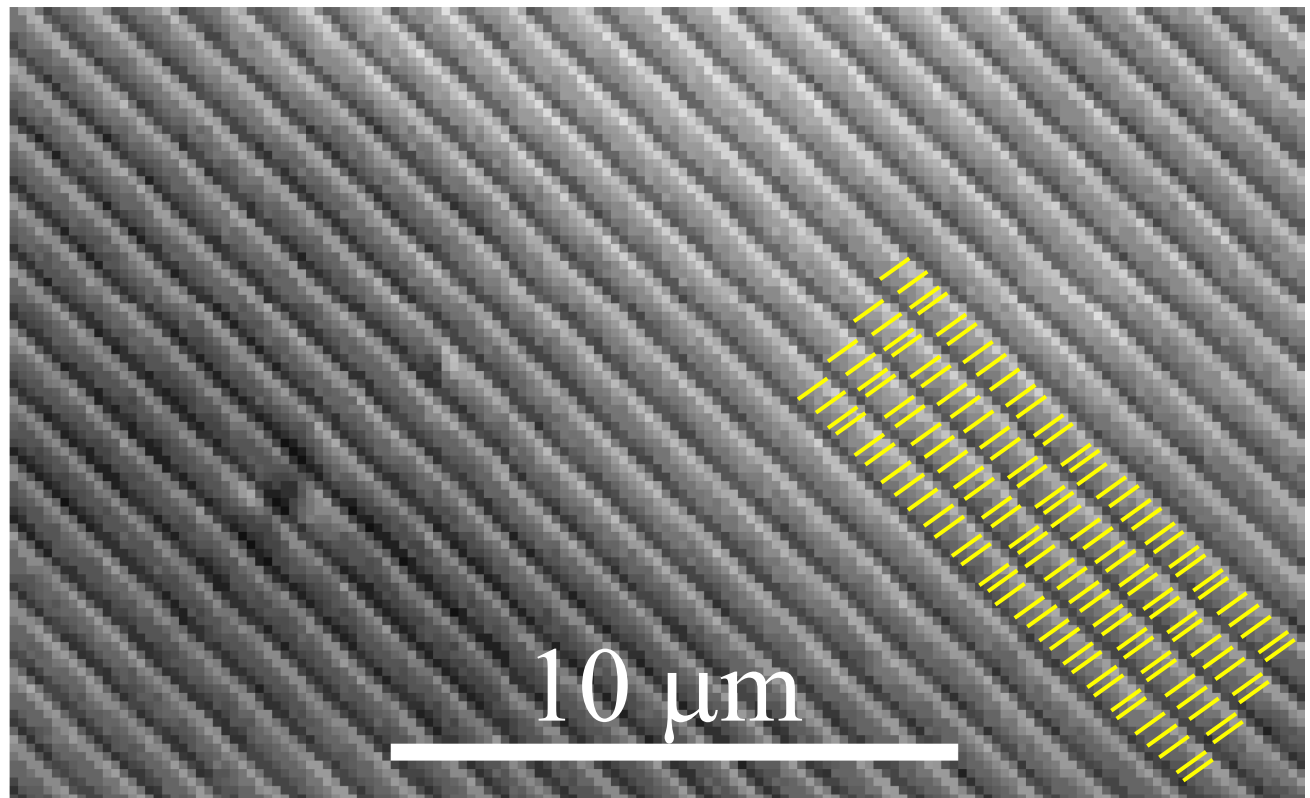
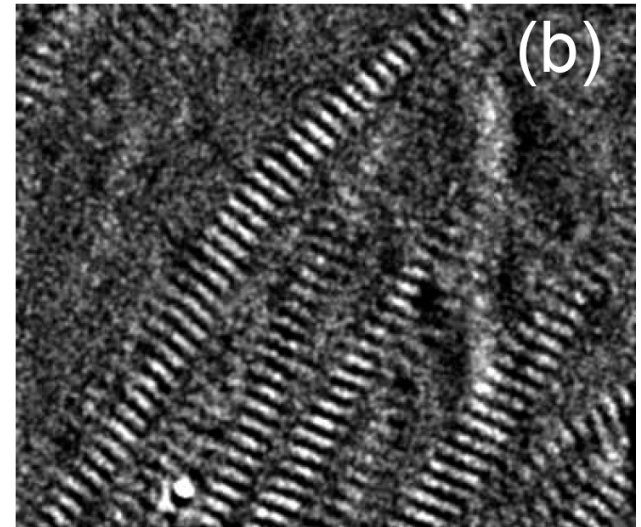
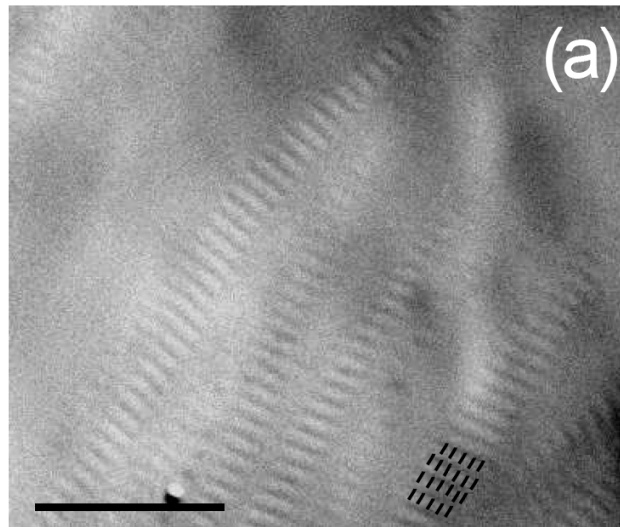
crossed polarizers

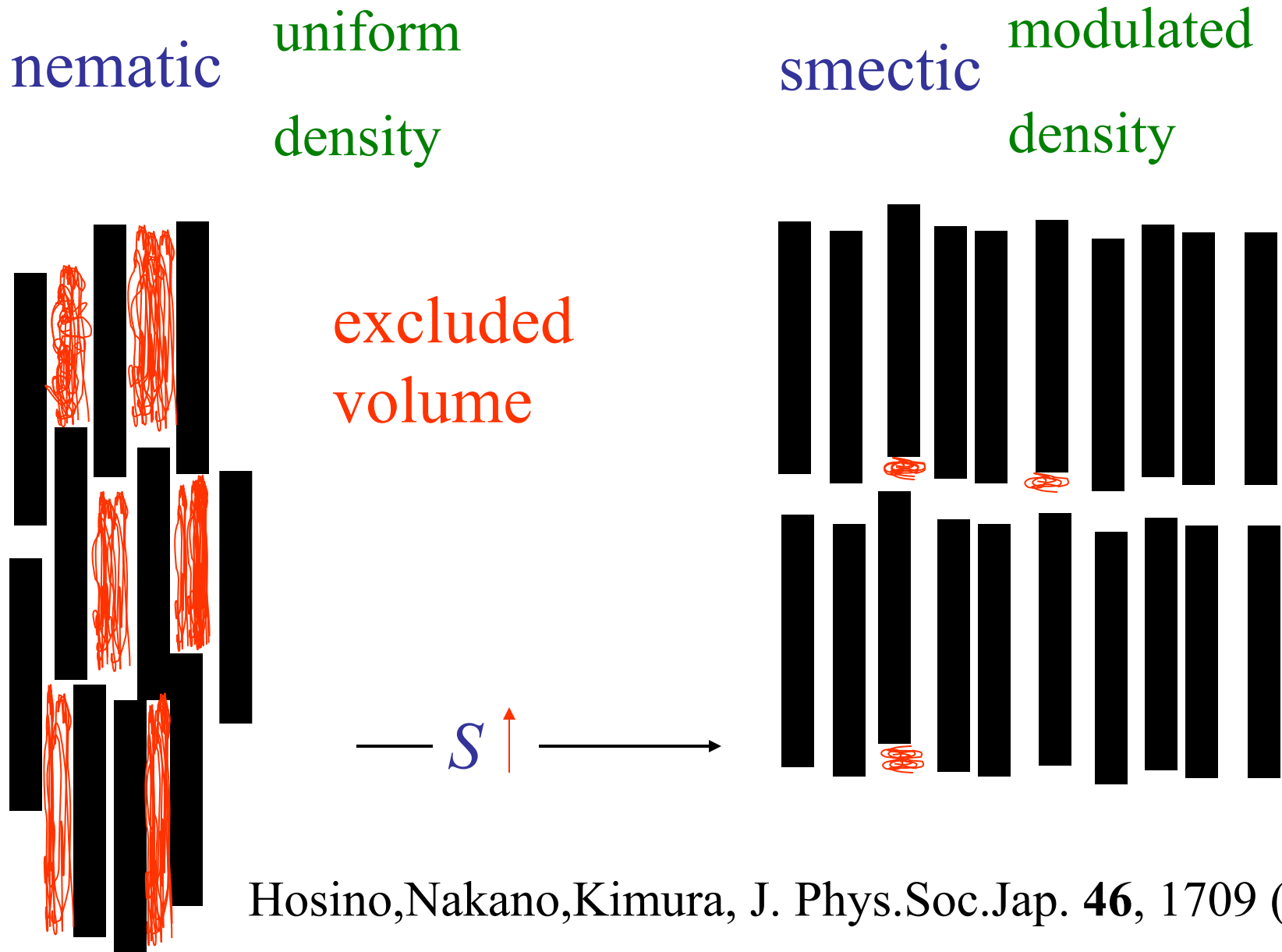


Wetter, *Biologie in unserer Zeit* 3, 81-89 (1985)

Smectic Phase
of *fd* virus

co-existence of
nematic and smectic





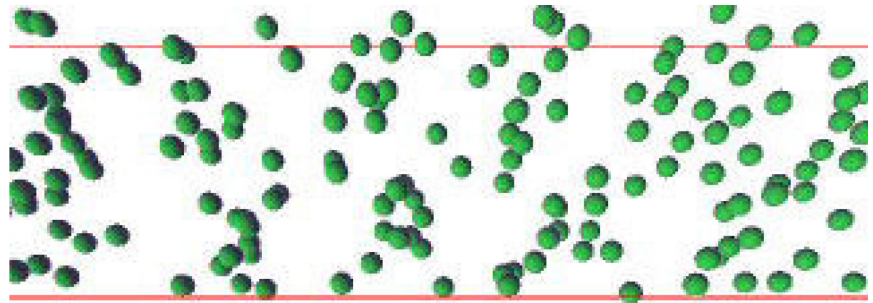
Hosino, Nakano, Kimura, J. Phys. Soc. Jap. **46**, 1709 (1979)

Frenkel, Lekkerkerker, Stroobants, Nature **332**, 822 (1988)

Monte Carlo Aligned Spherocylinders

Pressure jump: nematic $\longrightarrow$ smectic transition

Center of mass only

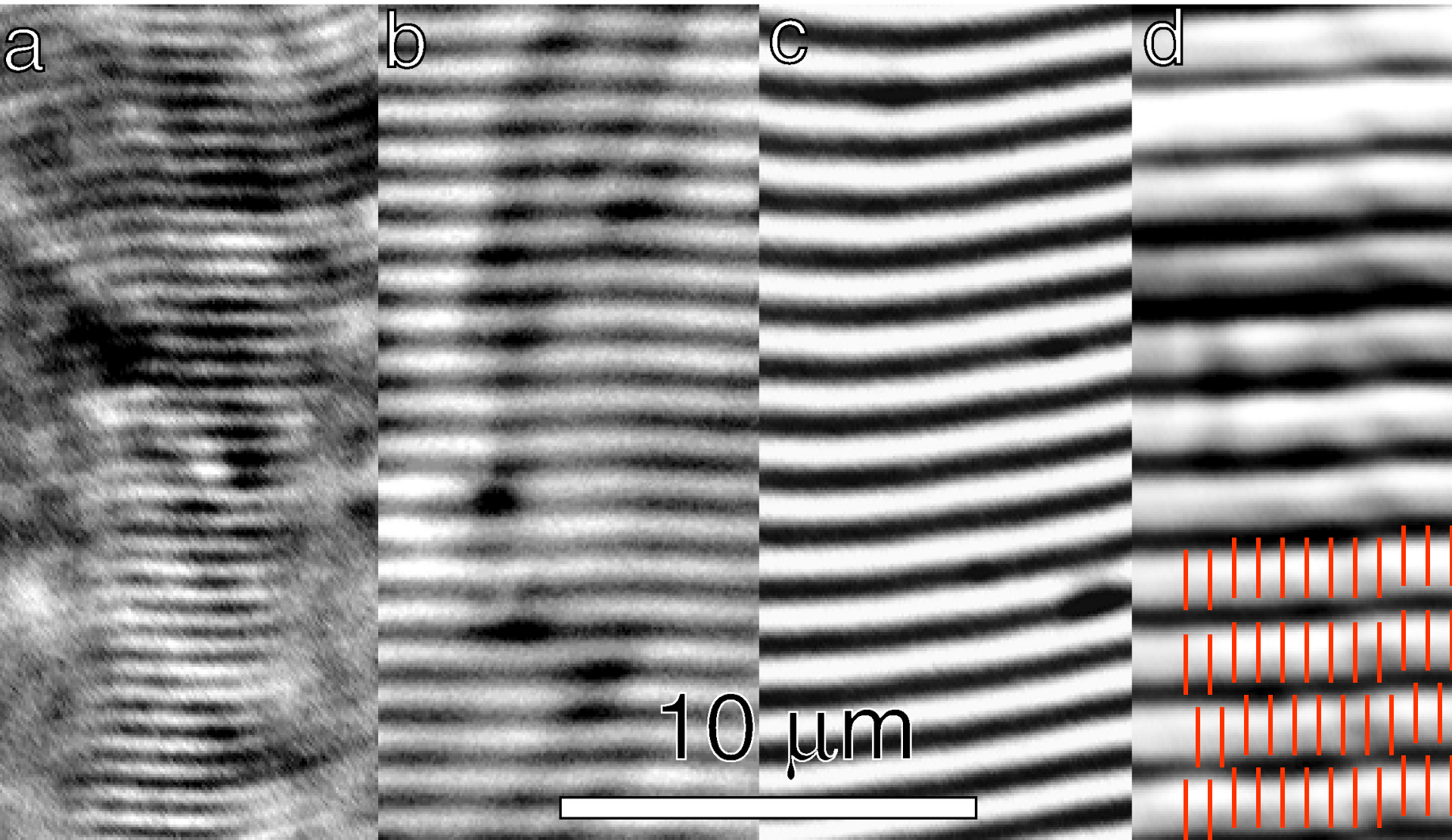


full spherocylinder



smectic layers

four mutants of m13, 0.4 μm to 1.2 μm

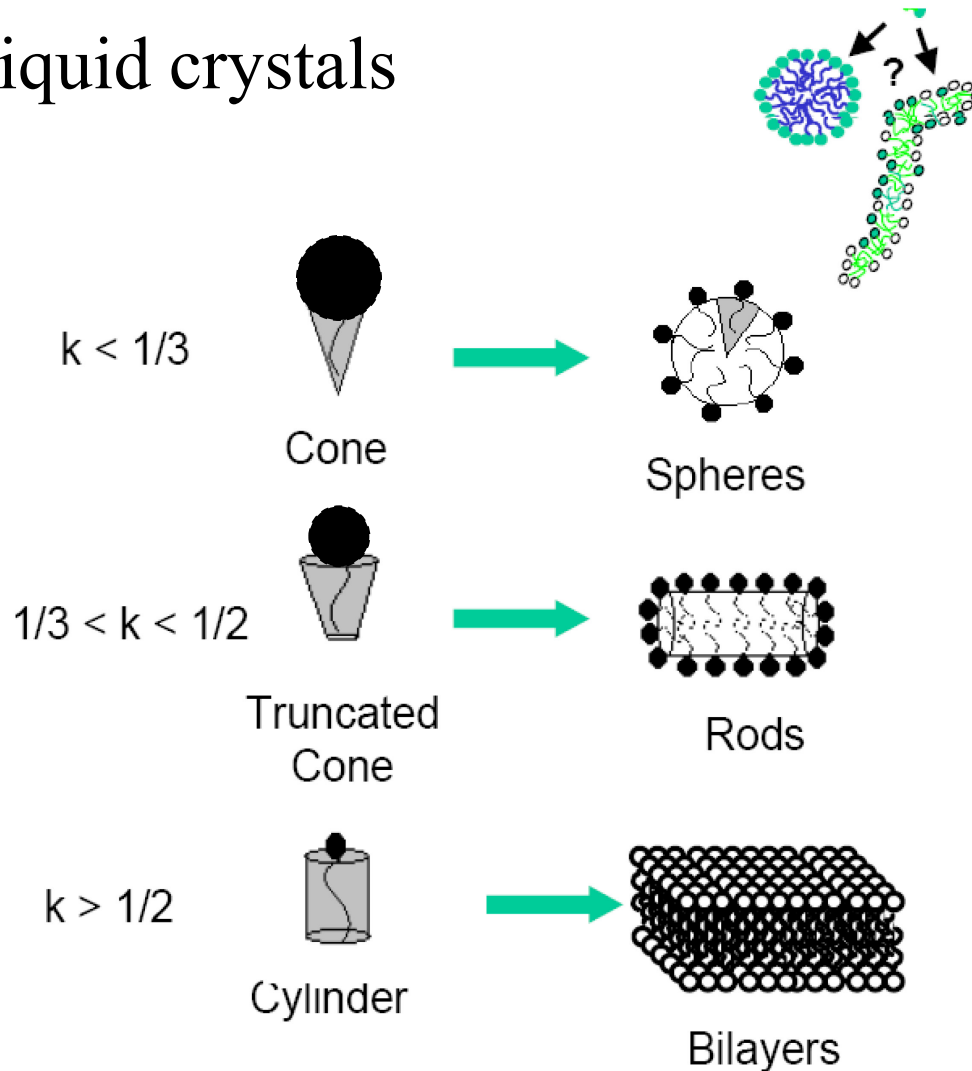
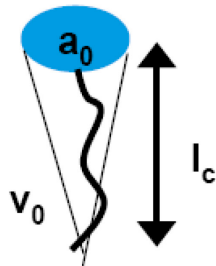


Concentration AND temperature are both important in phase behavior of amphiphiles
Energy and Entropy contribute equally

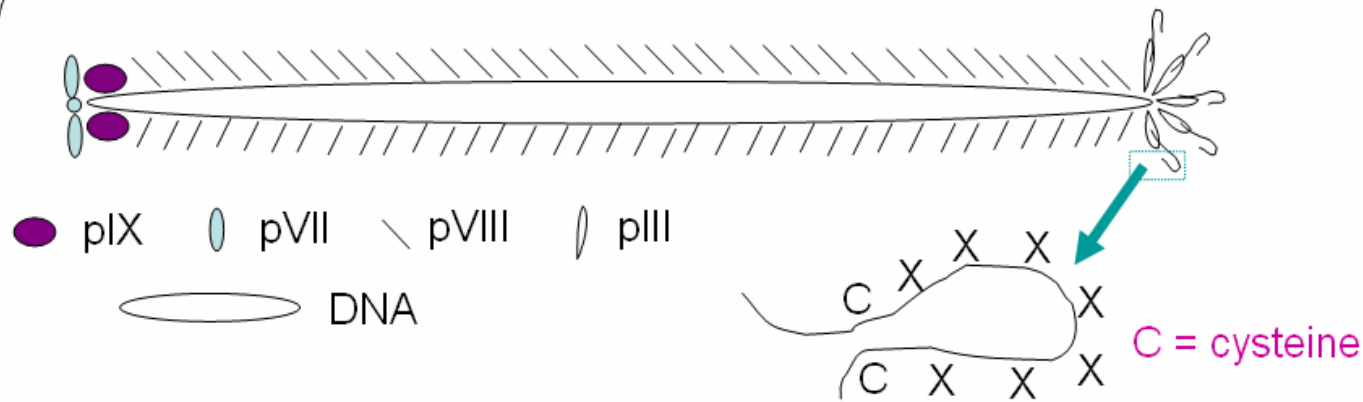
Mesophase occurrence often caused by same reason: molecular frustration

Lyotropic liquid crystals

$$k = \frac{v_0}{a_0 l_c}$$



Filamentous phage architecture



Length = 880nm

Diameter = 6.6nm

Persistence length = 2200nm

Surface charge = 10e/nm

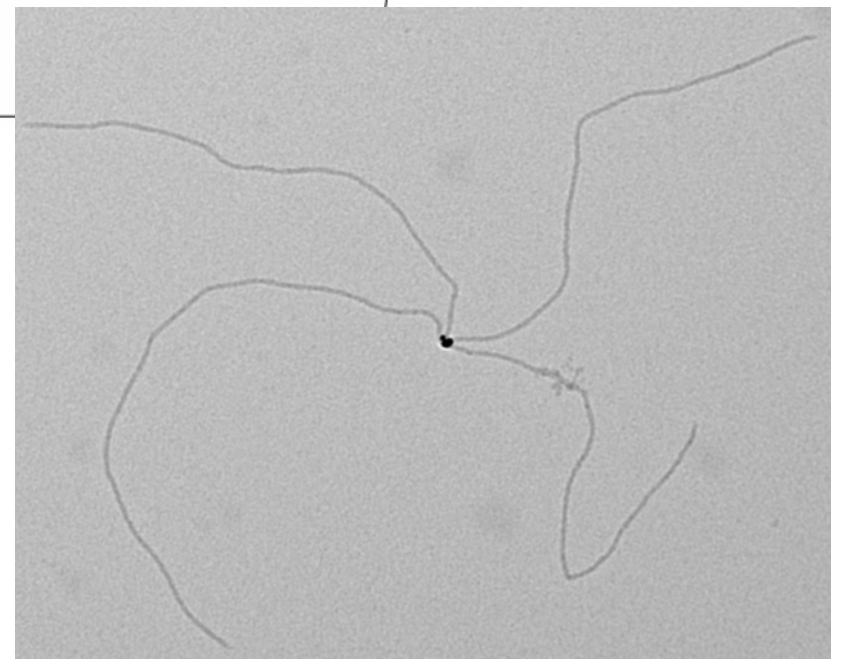
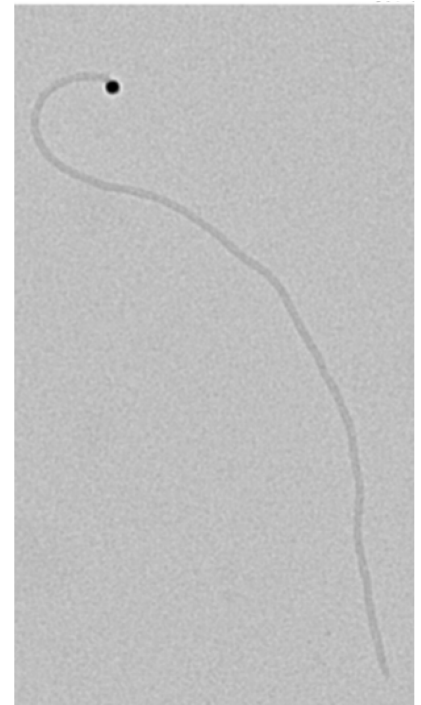
Phil Huang

Gold bound to genetically modified m13 virus

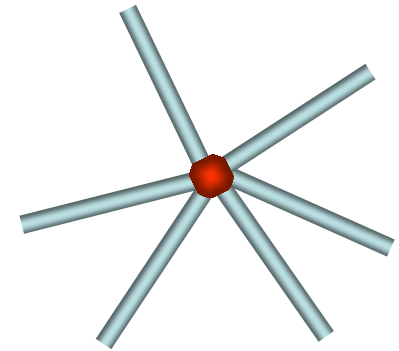
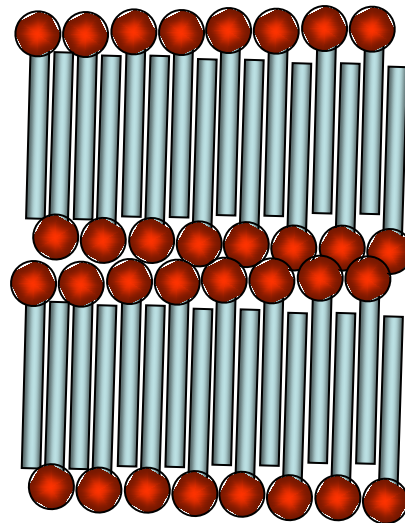
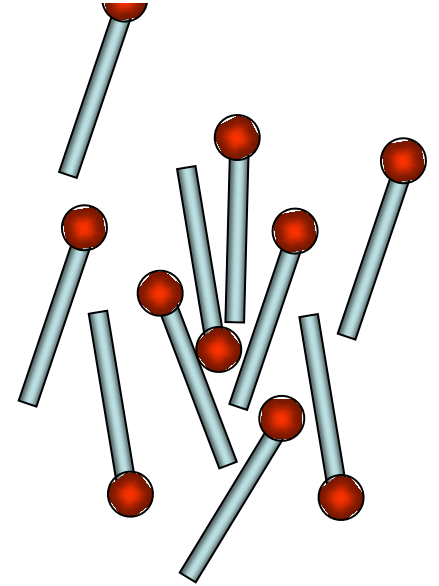
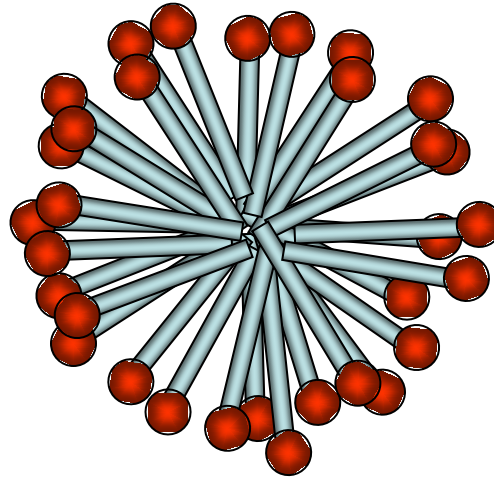
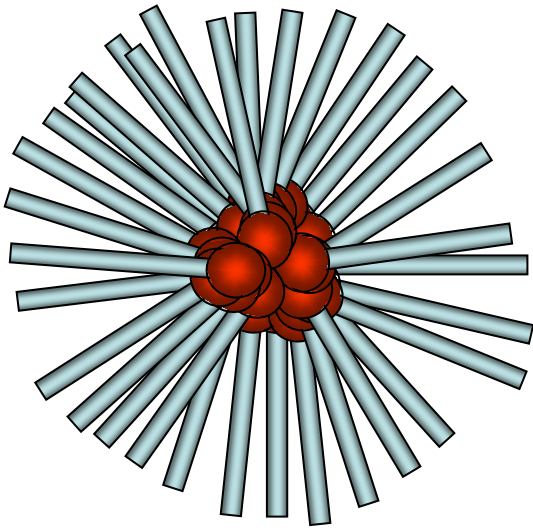
NEXT

DNA bound to genetically modified m13 virus

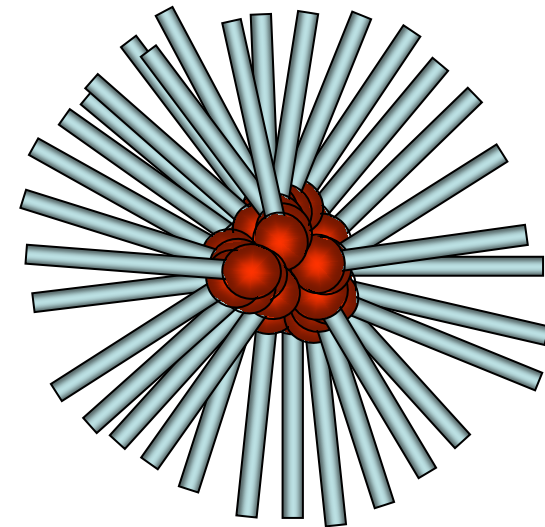
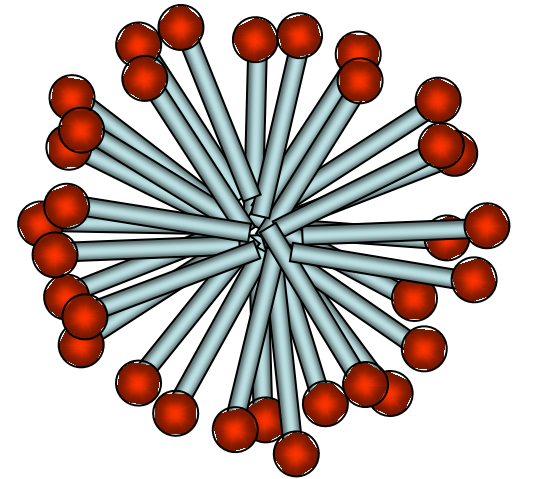
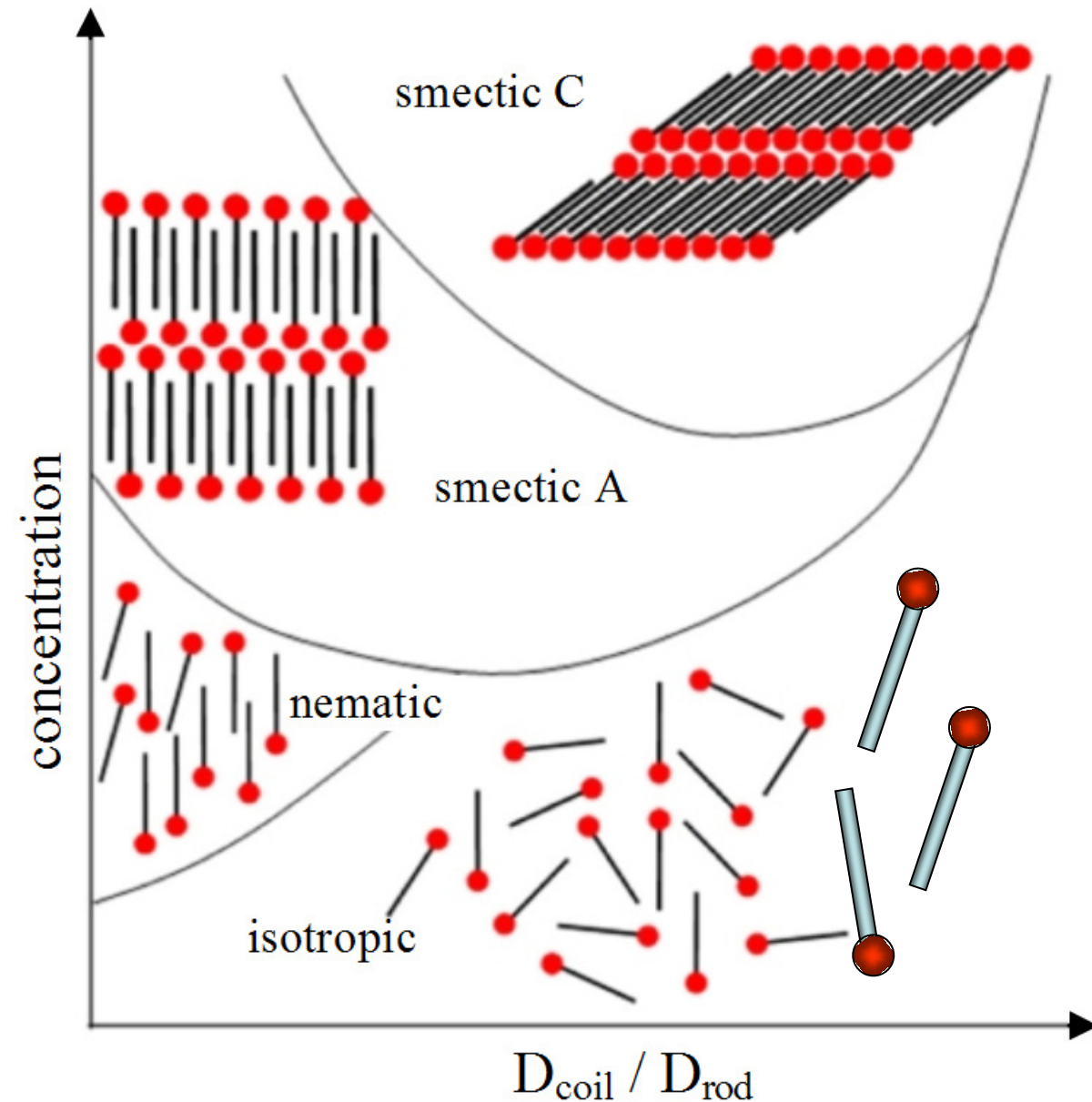
programmed self-assembly



Engineering entropy with shape surfactants



Engineering entropy with shape amphiphiles



with attraction