Self-Assembly

Lecture 5-6

Self-Assembly of Colloids.

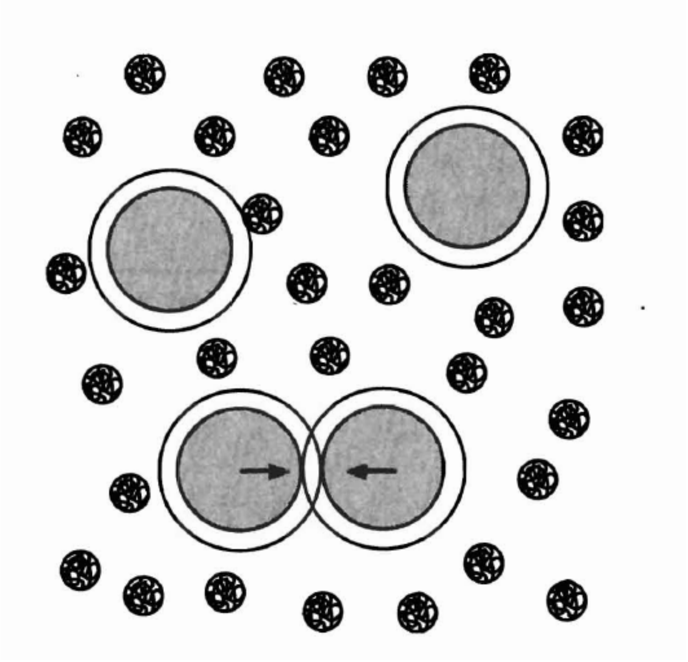
Liquid crystallinity

Colloidal Stability and Phases

- The range of forces attractive and repelling forces exists between the colloidal particles
  - van der Waals (attraction)
  - electrostatic double layer interaction (repulsive)
  - steric interaction of grafted polymer layers (repulsive)
  - depletion interaction (attractive)
- Those interaction can lead to phase behaviour similar to the phase behaviour of matter where colloidal particles play role of molecules

Depletion interactions

- Arise when solution contains in addition to the suspended particles other particles intermediate in size between the colloids and solvent molecules

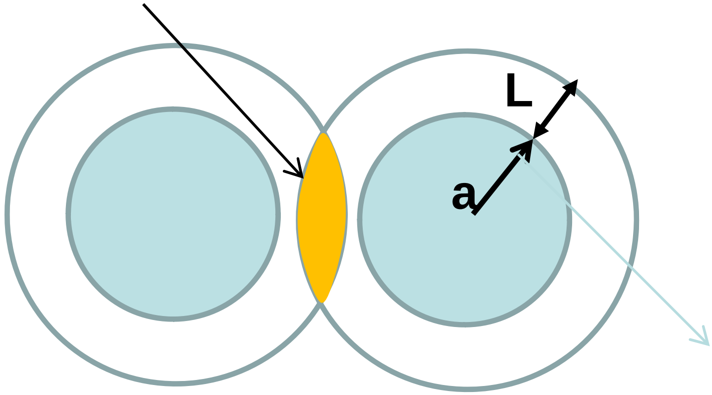


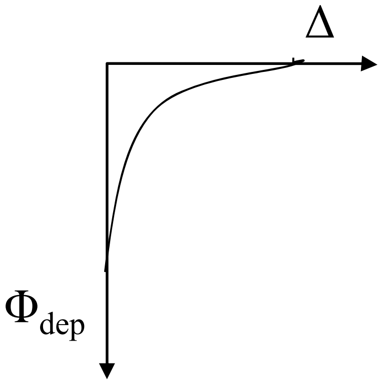
- For a diluted solution of non-interacting particles:

$$\Pi = [B]RT = \frac{N}{V}kT$$

$$\Phi_{dep}(r,a,L) = -V_{ov}(r,a,L)\cdot\Pi$$

interaction potential



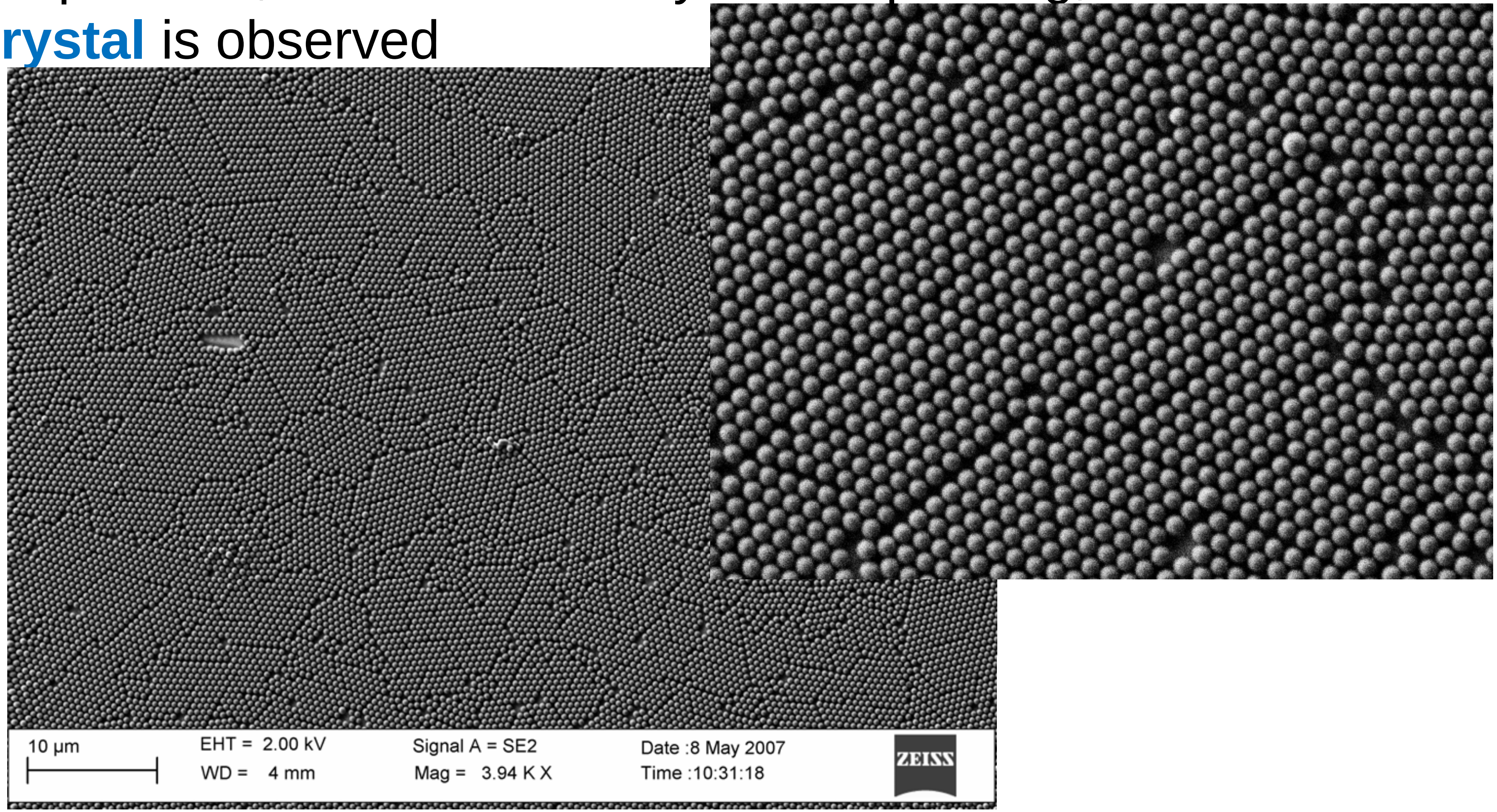


Colloidal Stability and Phases

- Ways to tune the interaction:
  - changing ionic strength or pH for electrostatically stabilized colloids
  - adding poor (bad) solvent to polymerically stabilized colloids – increased attraction
  - physical or chemical removal of grafted polymer – increased attraction
  - adding non-adsorbing polymer – increased depletion interaction (attraction)

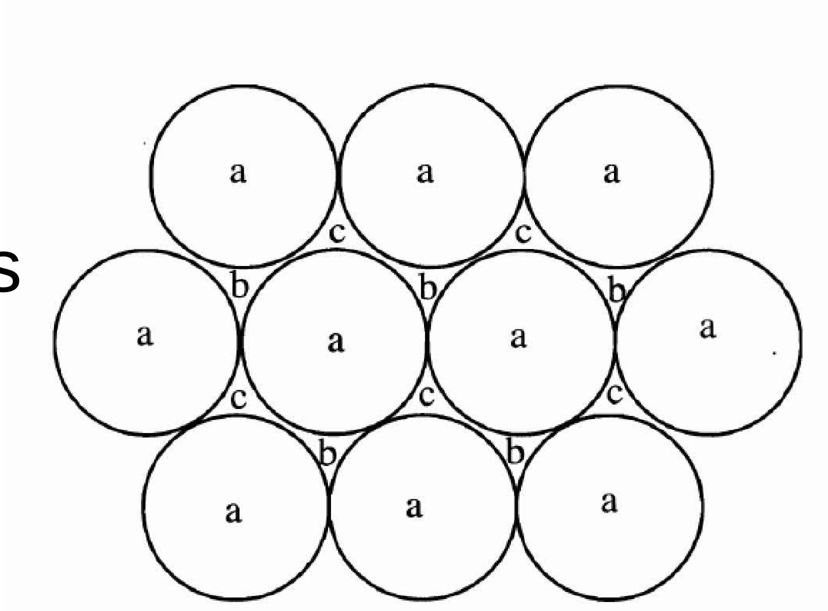
Crystallization of Hard-Sphere Colloids

- In a stable colloidal suspension, the interparticle forces are repulsive at all separation
- If the concentration of particles increased, e.g. by droplet evaporation, a transition to crystalline packing, a **colloidal crystal** is observed



Crystallization of Hard-Sphere Colloids

- Theoretically:
  - regular closest packing has a volume fraction of spheres (packing parameter) ~0.74
  - closest random packing ~0.63



- Experimentally:
  - at a volume fraction of 0.494 a spontaneous transition to a crystal with packing 0.545 is observed

HCP (hexagonal closed packed): **abababab...**
FCC (face centered cubic): **abcabcabc...**

What is the driving force of this transition?

Crystallization of Hard-Sphere Colloids

- **The driving force is entropy!**
  - – the entropy is lost due to ordered state of a crystal
  - – the entropy is gained due to larger available volume per particle

Ideal gas:

$$S_{ideal} = k_B \ln\left(a \frac{V}{N} \right)$$

excluded volume

Gas of particles of finite size b:

$$S = k_B \ln\left(a \frac{V - Nb}{N} \right) = S_{ideal} + k_B \ln\left(1 - \frac{Nb}{V} \right)$$

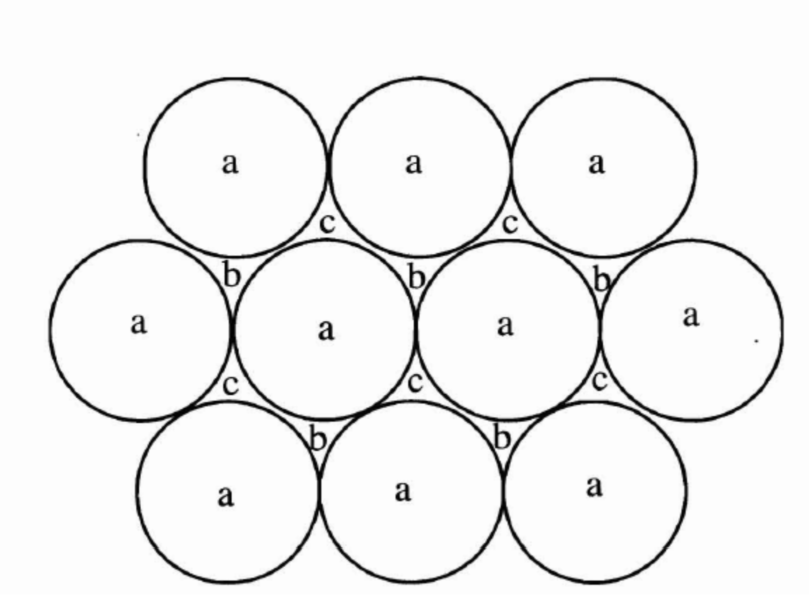
$$S = S_{ideal} - k_B \left(\frac{Nb}{V} \right)$$

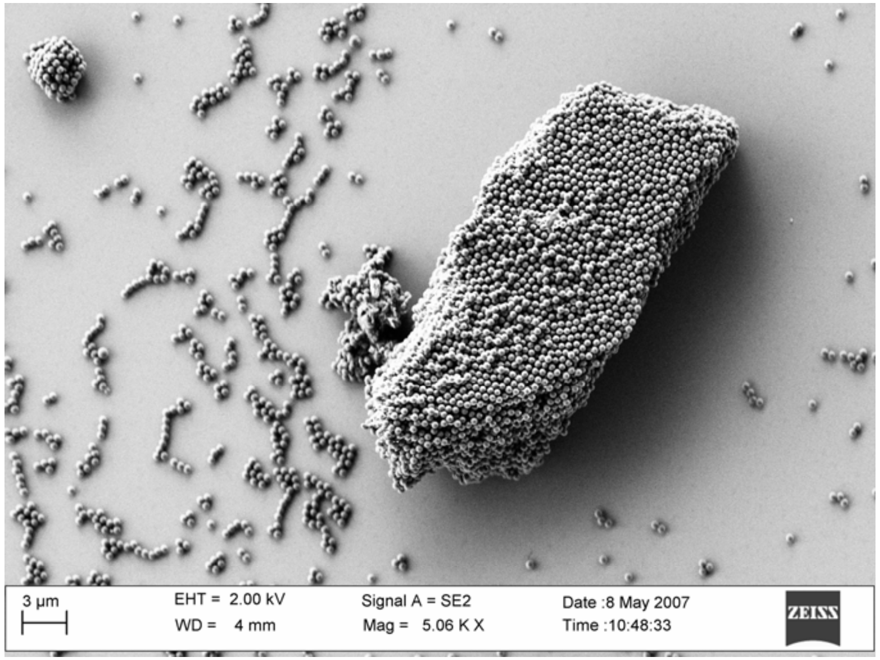
$$F = F_{ideal} + k_B T \left(\frac{Nb}{V} \right)$$

Of course the approximation of low particle volume is not valid close to crystallization transition, but with some refinements this approach forms a basis of modern theories

Crystallization of Hard-Sphere Colloids

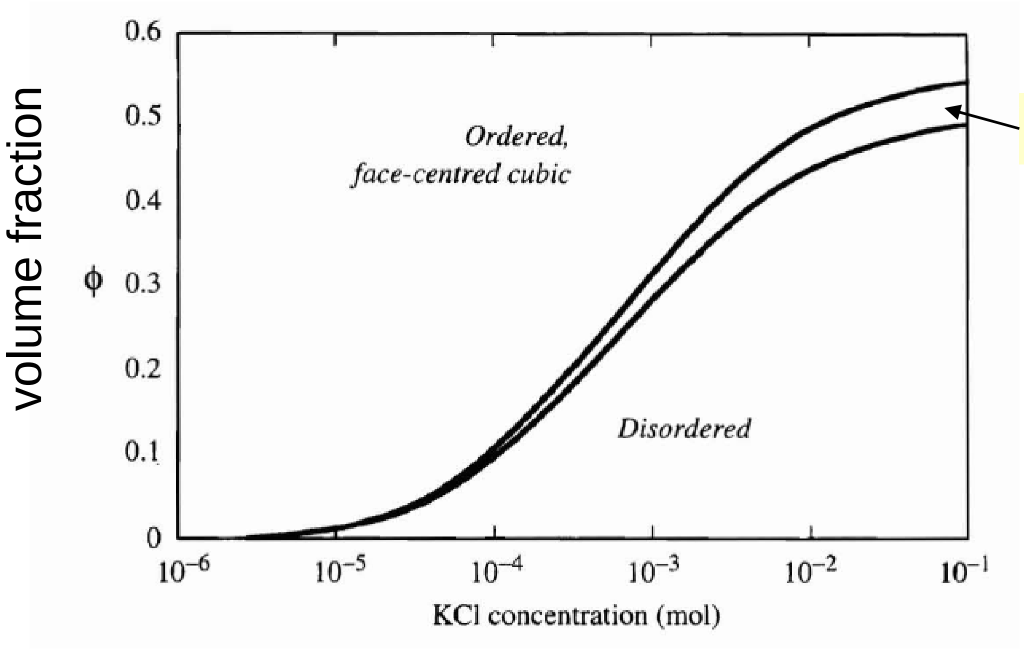
- 3D colloidal crystals are promising materials for photonic band gap structures
- However, experimentally they form HCP with random plane sequence (stacking faults). Theory predicts that FCC structure corresponds to slightly low energy and might be prepared defect-free.





Colloids with longer range repulsion

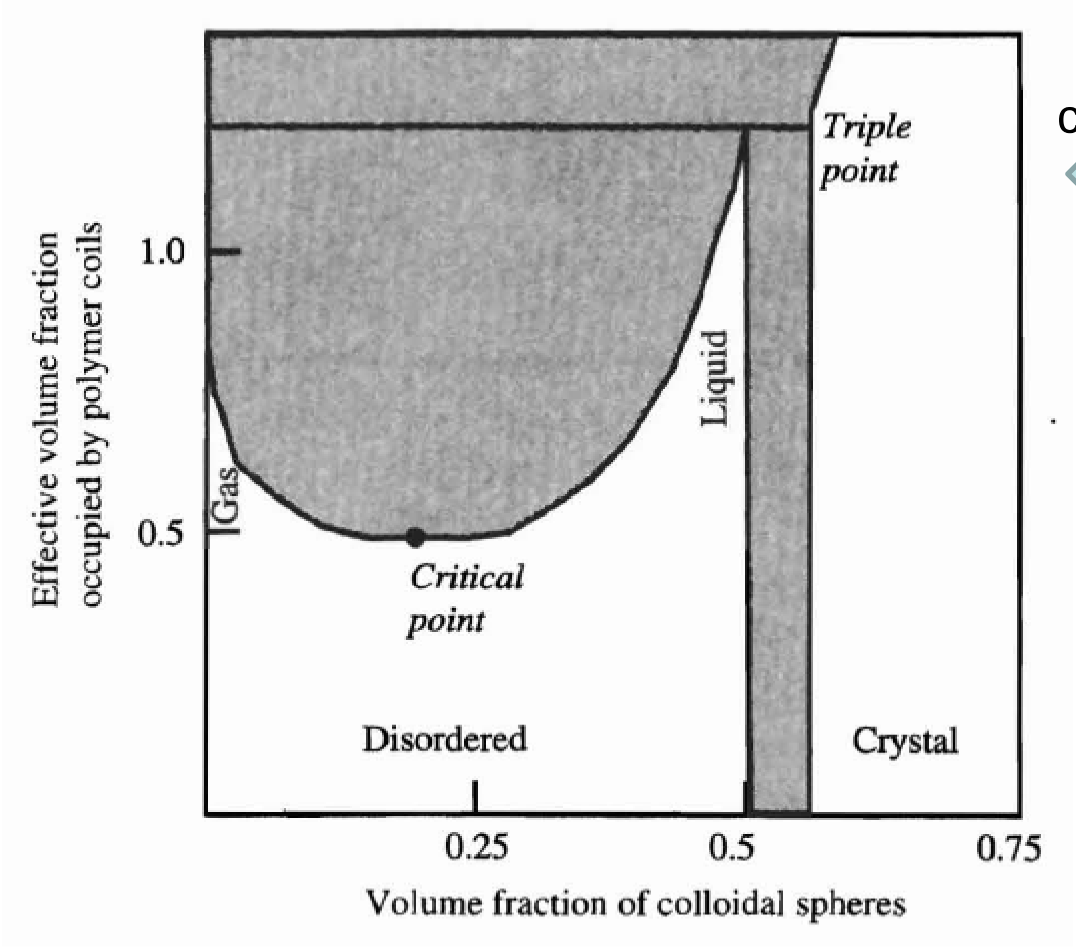
- can be produced by
  - electrostatic interaction in an electrolyte with low ionic strength or by
  - grafting long polymer chains to the surface
- if the (repulsion range) << (particle size), it can be considered as a pertrubation to the hard-sphere interaction case (with larger effective sphere diameter)



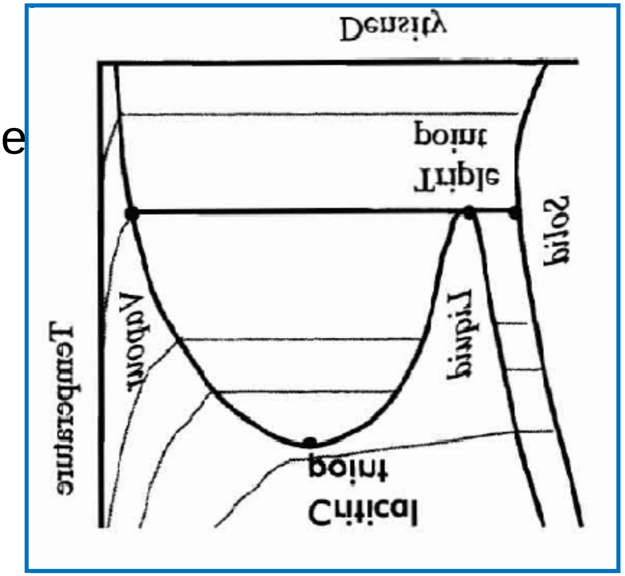
two phase region

Colloids with weakly attractive interaction

- similar to “usual matter” we expect “gas-liquid” transition here
- the situation can be created by addition of polymer to the solution (depletion interaction)



compare



“usual” one component phase diagram

Colloids with strongly attractive interactions

- the diagrams considered before are **equilibrium phase diagrams**, the interaction strength is comparable with kT and equilibrium is reached
- in case of stronger interaction, particles stick together and cannot re-arrange forming **fractal structures**

$$R \propto M^{1/d_f}$$

$$1 < d_f < 3$$

fractal dimension

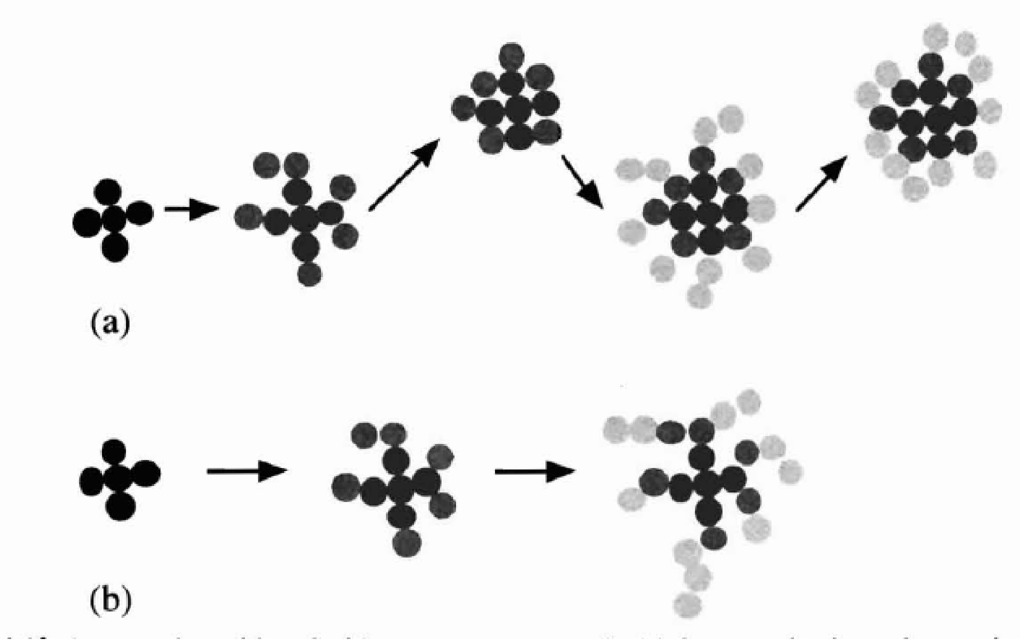
compare

$$R \propto M^{1/3}$$

usually

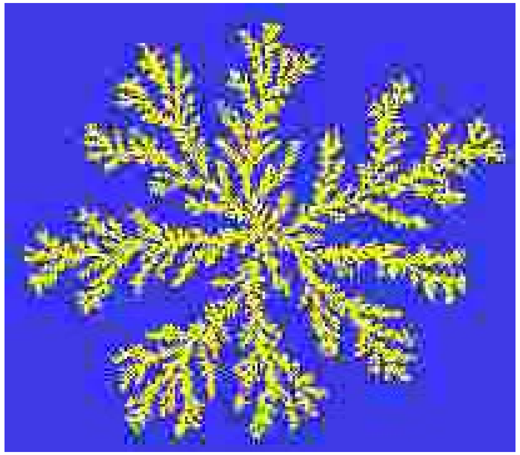
weak interaction, rearrangement into compact aggregates

strong interaction, open fractal structures are formed



Diffusion limited aggregation

- Common models:
  - **diffusion limited aggregation**: particle randomly diffuse until they touch a cluster **$d_f≈1.71$**
  - diffusion-limited cluster-cluster aggregation: clusters are allowed to aggregate **$d_f≈1.71$**
  - experimentally **$d_f≈1.75$**.
- See for example: *http://apricot.polyu.edu.hk/~lam/dla/dla.html*



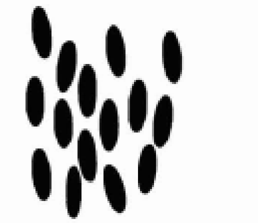
Liquid Crystallinity

- Intermediate order in soft matter:
  - **Liquid crystallinity** – equilibrium phases with intermediate degree of 3D cristallinity between liquid and solid crystals. Found in:
    - organic compounds with anisortopic shape
    - polymers composed of rigid units
    - polymers of aggregates composed of rigid rod-like structures
  - **Partial crystallinity** – non-equilibrium state in which system is prevented from reaching equilibrium state with long-range crystal order and where ordered and disordered region co-exist.

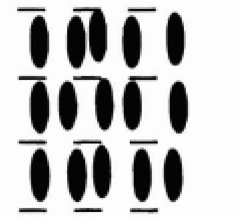
Liquid crystal phases

- **Crystal**: long-ranged, 3D positional and orientational order
- **Liquid**: only short range positional and orientational order
- Liquid crystalline **nematic** phase: no positional order, molecules on average are oriented along a **director**.
- **Cholesterics**: nematic phase formed by chiral molecules (chiral nematics), molecules have tendency to align at a slight angle to each other.
- **Smectics**: molecules are arranged in sheets, molecules are aligned within each layer, no positional order:
  - smectic A: director along the layer normal
  - smectic C: director makes an angle to normal
- **Discotics** (columnar phase): no positional order within a column, columns form regular 2D hexagonal lattice.

Isotropic liquid



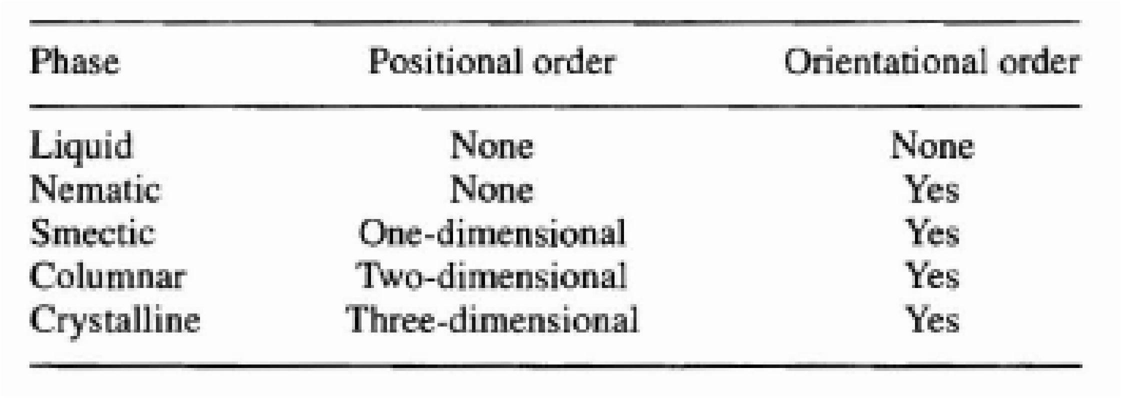
Nematic liquid crystal



Smectic A liquid crystal

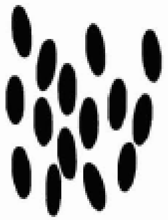
Liquid crystal phases

- Summary of order levels in various phases

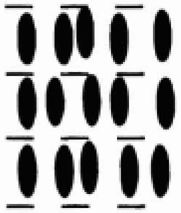


Phase	Positional order	Orientational order
Liquid	None	None
Nematic	None	Yes
Smectic	One-dimensional	Yes
Columnar	Two-dimensional	Yes
Crystalline	Three-dimensional	Yes

Isotropic
liquid



Nematic liquid
crystal



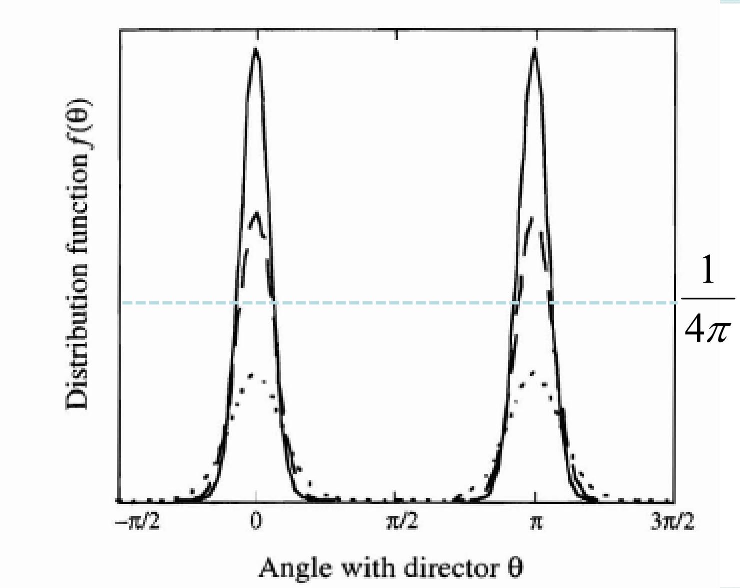
Smectic A liquid
crystal

increasingly ordered

Nematic-Isotropic transition

- In order to favour the ordering transition, a terms that favours orientation of molecules is required
- Let’s consider a distribution function for orientation of director: **orientation function**.

$f(\theta)d\Omega$ fraction of molecules within angle dΩ; $f(\theta) = f(\pi - \theta)$



isotropic phase
(randomly oriented molecules)

order parameter $S = \frac{1}{2}\left\langle 3\cos^2\theta - 1 \right\rangle = \int \left(3\cos^2\theta - 1\right) f(\theta)d\Omega$

Nematic-Isotropic transition

- Possible aligning interaction:
  - van der Waals interaction ⇦ mainly for small molecules
  - excluded volume ⇦ mainly for very long rigid molecules

- Entropy loss due to orientation:

$$S_{orient} = -k_B \int f(\theta) \ln f(\theta) d\theta$$

$$\Delta S = -k_B \int f(\theta) \ln \left[4\pi f(\theta) \right] d\theta$$

- Total free energy according to Maier-Saupe theory:

$$\Delta F = -u \mathbb{S}^2 / 2 + k_B T \int f(\theta) \ln \left[4\pi f(\theta) \right] d\theta$$

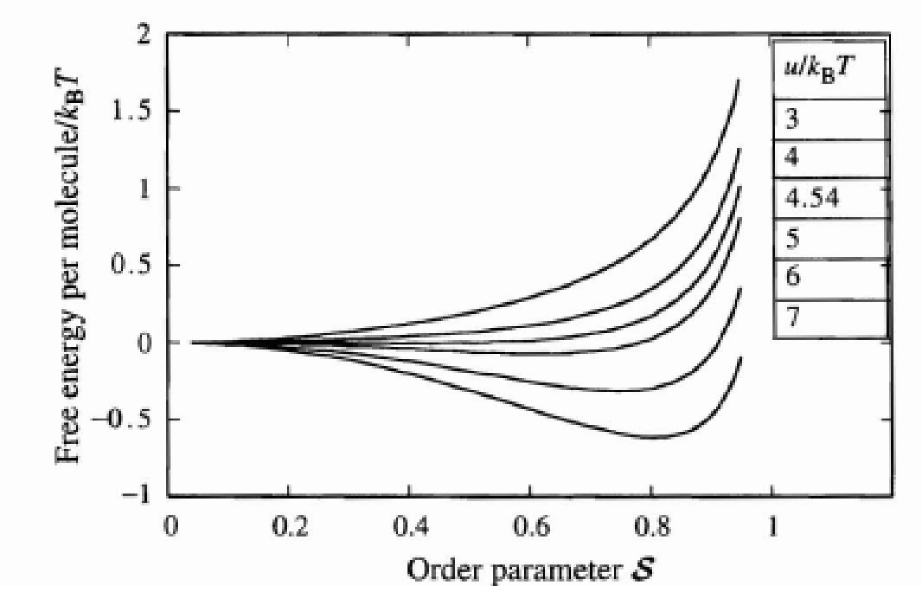
for a given value of order parameter S, a most probable distribution function f can be found that maximized the entropy

Nematic-Isotropic transition

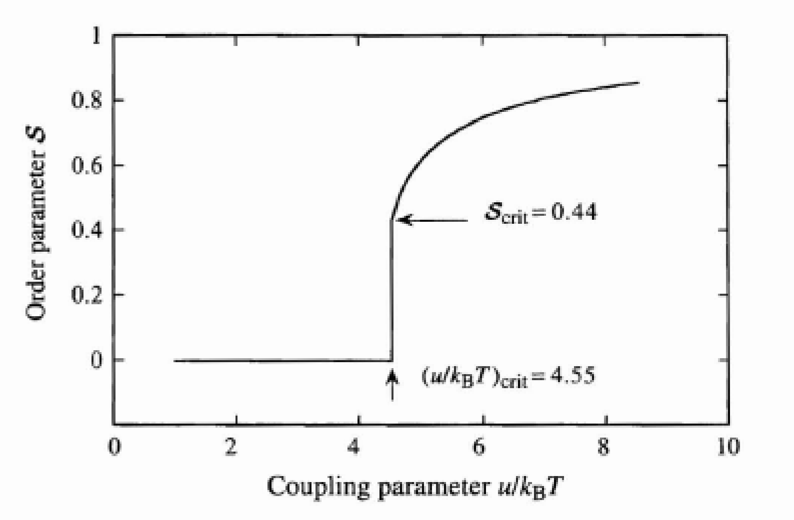
- The orientation function that solves the equation is:

$$f(\theta) = \exp(3\lambda \cos^2 \theta)$$

- The total energy behaviour:



- at u/kT<4.55 the only solution is S=0
- at u/kT=4.55 there is a discontinuous change of order parameter to S=0.44



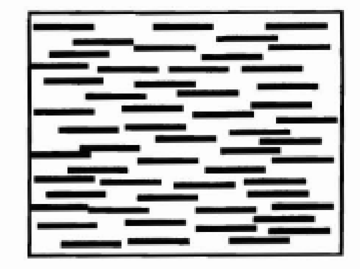
Problems with theory:

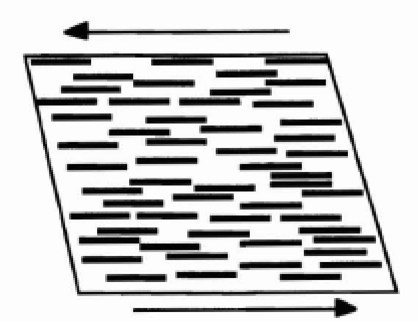
- fluctuations are neglected
- temperature dependence of ***u*** is neglected

Distortions and topological defects in liquid crystals

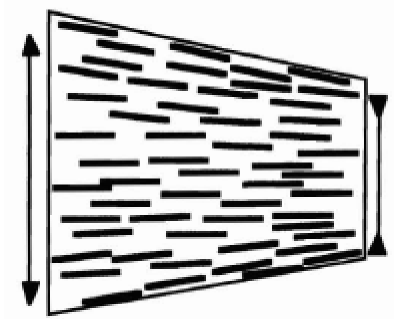
How deformation is transferred in a liquid crystal?

- if the deformation perturbs any long ranged order in the system, the deformation is opposed by the increase in elastic energy
- otherwise, the material will respond by flow.





no energy change, flow



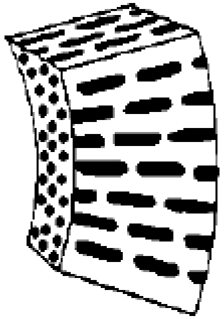
opposed by increase in elastic energy

Distortions and topological defects in liquid crystals

- If the vector field of director is **n**(**r**), the elastic energy per unit volume of nematic crystal:

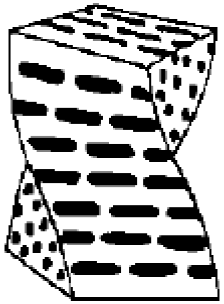
$$F_d = \frac{1}{2}K_1(\nabla\cdot\vec{n})^2 + \frac{1}{2}K_2(\vec{n}\cdot\nabla\times\vec{n})^2 + \frac{1}{2}K_3(\vec{n}\cdot\nabla\cdot\vec{n})^2$$

splay



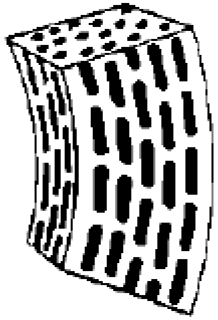
$\nabla\cdot\vec{n}\neq 0$

twist



$(\nabla\times\vec{n})\parallel\vec{n}$

bend



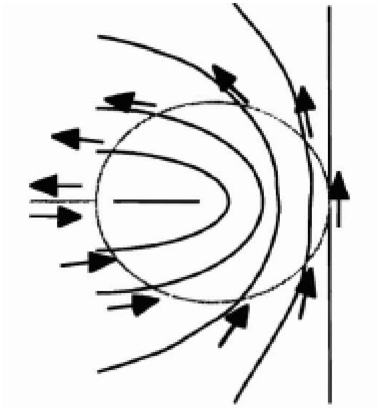
$(\nabla\times\vec{n})\perp\vec{n}$

Distortions and topological defects in liquid crystals

- Many surfaces impose some ordering on the liquid crystal director
  - homeotropic: perpendicular to the interface, e.g. by coating the surface with a surfactant
  - homogeneous: parallel to the surface, more common, achieved by e.g. rubbing the surface with a cloth
- That’s a consequence of broken symmetry, as the energy of nematic monodomain depend on the director orientation on the surface

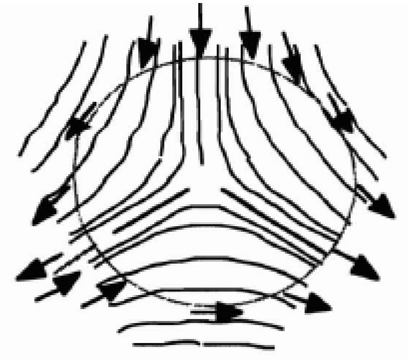
Distortions and topological defects in liquid crystals

- **Disclinations** – topological defects where orientation of the director changes discontineously
- Strength of a disclination – number of rotations undergone by a director around a closed loop centered at disclination
- Disclination character is the relative amount of splay, twist and bend distortion
- For elastically isotropic system ($K_1=K_2=K_3$), the disclination energy is independent on the character
- The disclination possess a line tension



rotation π

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



rotation -π

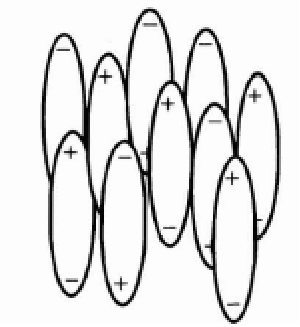
$$s=-\frac{1}{2}$$

$$\frac{E}{L}=\pi K s^2 l$$

a factor that varies only logarithmically with the core size, interdisclination spacing etc. size

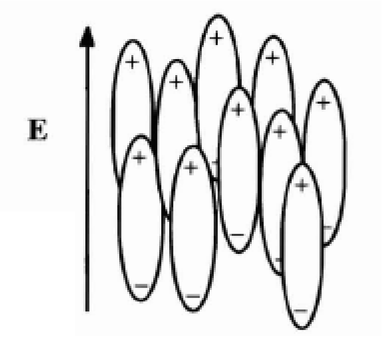
Electrical and magnetic properties of liquid crystals

- nematics are never ferroelectrics as there is no preferred axis in space (isotropic)
- most of the molecules have a permanent dipole along the molecular axis
- dielectric coefficient parallel to the director is larger



$$\vec{D} = \varepsilon_{\perp}\vec{E} + \left(\varepsilon_{\parallel} - \varepsilon_{\perp}\right)\left(\vec{n}\cdot\vec{E}\right)\vec{n}$$

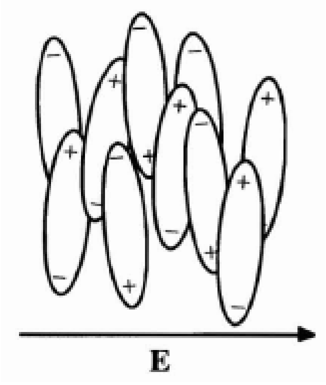
$$F_{el} = -\frac{1}{4}\pi\int \vec{D}d\vec{E} = -\frac{\varepsilon_{\perp}}{8\pi}E^{2} - \frac{\varepsilon_{a}}{8\pi}\left(\vec{n}\cdot\vec{E}\right)^{2}$$



the energy is reduced when crystal is aligned along the field

- in magnetic field similar anisotropy is observed, most molecules are diamagnetic

$$F_{mag} = -\int \vec{M}d\vec{H} = -\frac{\chi_{\perp}}{2}H^{2} - \frac{\chi_{a}}{2}\left(\vec{n}\cdot\vec{H}\right)^{2}$$



Frederiks transition and LCD

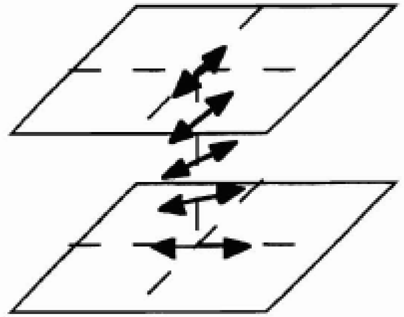
- **Frederics transitions**: transitions due to competing of several antagonistic aligning influences in liquid crystal

$$F_{tot} = F_{el} + F_{field} = \frac{1}{2} K_1 \left(\frac{\partial \delta \vec{n}(z)}{\partial z} \right)^2 - \frac{\varepsilon_a E^2}{8\pi} \delta \vec{n}(z)^2$$

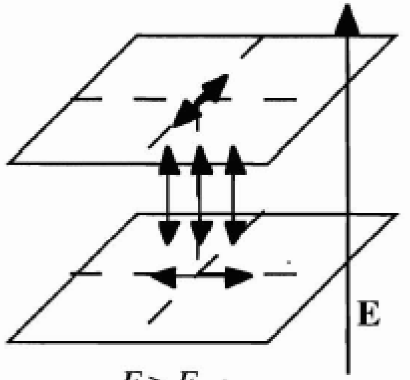
$$\delta \vec{n}(z) = \delta n \sin\left(\frac{\pi z}{d} \right)$$

$$\int_0^d F_{tot} dz = \delta n^2 \left[\left(\frac{K_1 \pi^2}{4d} \right) - \left(\frac{\varepsilon_a E^2 d}{16\pi} \right) \right]$$

$$E_{crit} = \frac{2\pi}{d} \sqrt{\frac{K_1 \pi}{\varepsilon_a}}$$



$E = 0$

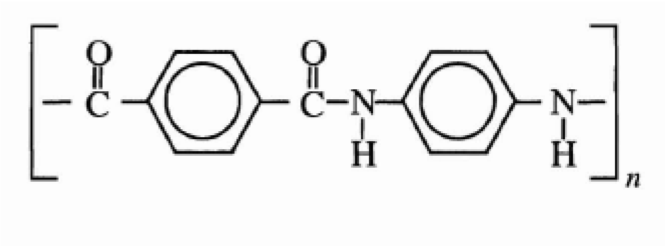


$E > E_{\mathrm{crit}}$

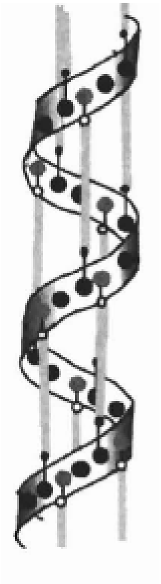
- Frederics transitions provide an experimental way to find the elastic constants in liquid crystal and form the basis of LCD

Polymer liquid crystals

- Liquid crystal polymers:
  - formed by monomer unit that allow only restricted rotation between unit resulting in tendency to a rigid or semi-rigid rod conformation
  - flexible backbone, but strong interaction between the neighboring monomers
- Divided into two classes:
  - **thermotropic** – transition is driven by changes in temperature
  - **lyotropic** – transition is driven by changes in concentration in solution

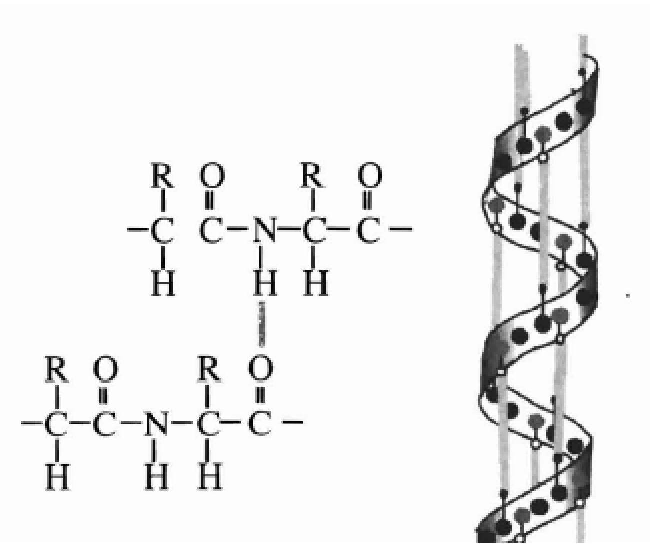


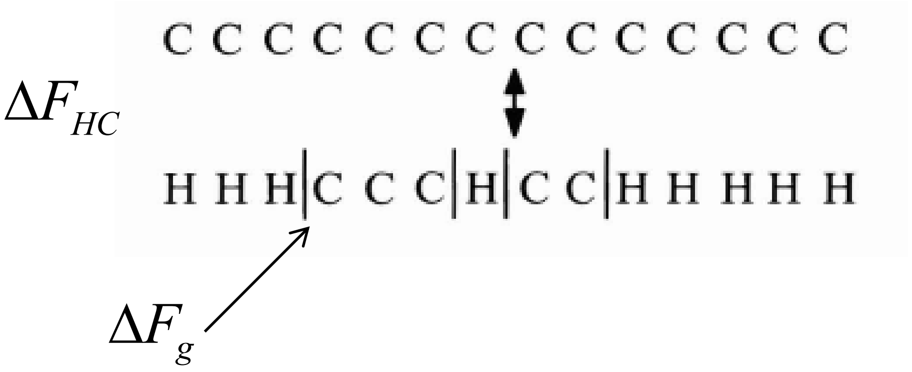
poly (p-phenyleneterephthalamide), or PPTA, Kevlar



Helix-coil transition

- In an α-helix structure of polypeptide a rigid rod is formed by hydrogen bonds between C=O group of i-th monomer and N-H group of i+4th monomer
- Helix-coil transition model:





helix-coil
transition energy

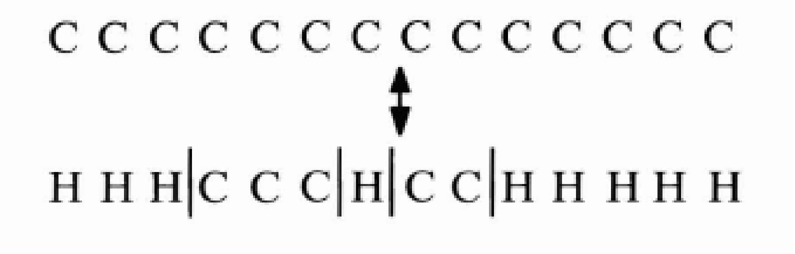
ΔF_{HC}

ΔF_{g}

boundary energy

Helix-coil transition

- Let’s find an energy of a chain of N untis required to go from all coil state to a state containing h helix segments and 2g boundaries



number of ways to arrange h objects in g boxes:

$$\Omega_h = \frac{h!}{g!(h-g)!};$$

same for the coil units

$$\Omega_c = \frac{(N-h)!}{g!(N-h-g)!}$$

$$\Delta S_c = k_B \ln\left(\Omega_c \Omega_h\right) = k_B h \ln h - (N-h)\ln(N-h) -$$
$$-2g \ln g - \left(h-g\right)\ln\left(h-g\right) - \left(N-h-g\right)\ln\left(N-h-g\right)$$

Helix-coil transition

- The total free energy is equal:

$$\Delta F(h,g) = h\Delta F_{HC} + 2g\Delta F_g - T\Delta S_c(h,g,N)$$

minimizing the energy:

$$\frac{\partial \Delta F(h,g)}{\partial h} = 0 \Rightarrow \frac{c(h-g)}{h(c-g)} = \exp\left(-\frac{\Delta F_{HC}}{k_B T}\right) = s$$

preference for coil state

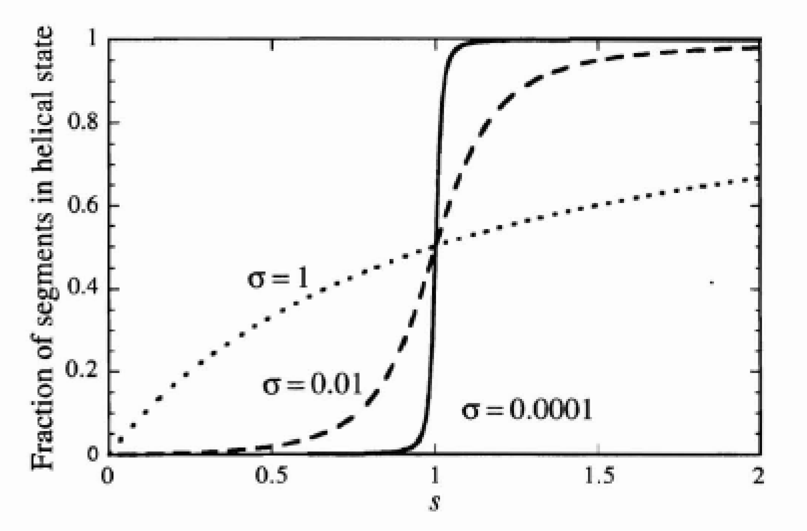
$$\frac{\partial \Delta F(h,g)}{\partial g} = 0 \Rightarrow \frac{g^2}{(c-g)(h-g)} = \exp\left(-\frac{2\Delta F_g}{k_B T}\right) = \sigma$$

$c = N - h$

measure of cooperativity

$$f_h = \frac{h}{N} = \frac{1}{2} + \frac{(s-1)}{2\sqrt{(s-1)^2 + 4s\sigma}}$$

- experimentally s is 10^{-3}-10^{-4}, so the transition is sharp
- not true phase transition as true phase transition are not possible in 1D systems



Isotropic/nematic transition for hard rod system

- Excluded volume as a function of orientation:
  - if a rod of length L and diameter D makes angle g with each other

$$2L^2 D\left|\sin\gamma\right|$$

$$\left\langle\left|\sin\gamma\right|\right\rangle = p\left[f(\theta)\right] = \iint f(\theta) f(\theta')\sin\gamma \, d\Omega d\Omega'$$

$$F = F^0 + kT\left(\ln c + \int f(\theta)\ln\left[4\pi f(\theta)\right]d\theta + L^2 Dcp\left[f(\theta)\right]\right)$$

volume fraction of rods

$$\varphi = c\pi LD^2/4$$

$$F = F^0 + kT\left(\ln\left(\frac{L}{D}\varphi\right) + \int f(\theta)\ln\left[4\pi f(\theta)\right]d\theta + \frac{4}{\pi}\frac{L}{D}\varphi p\left[f(\theta)\right]\right)$$

the only parameter

a trial orientational function that satisfy the equation,
uniform for α=0;
develops peaks at 0 and π as α increases.

$$f(\theta) = \frac{\alpha}{4\pi}\frac{\cosh\left(\alpha\cos(\theta)\right)}{\sinh\alpha}$$

Isotropic/nematic transition for hard rod system

- Model of a lyotropic liquid crystal – solution of hard rods
- No interaction between the rods (overlap is not allowed), the transition is driven by the excluded volume

We have found for hard spheres:

$$S = S_{ideal} - k_B \left(\frac{Nb}{V} \right)$$

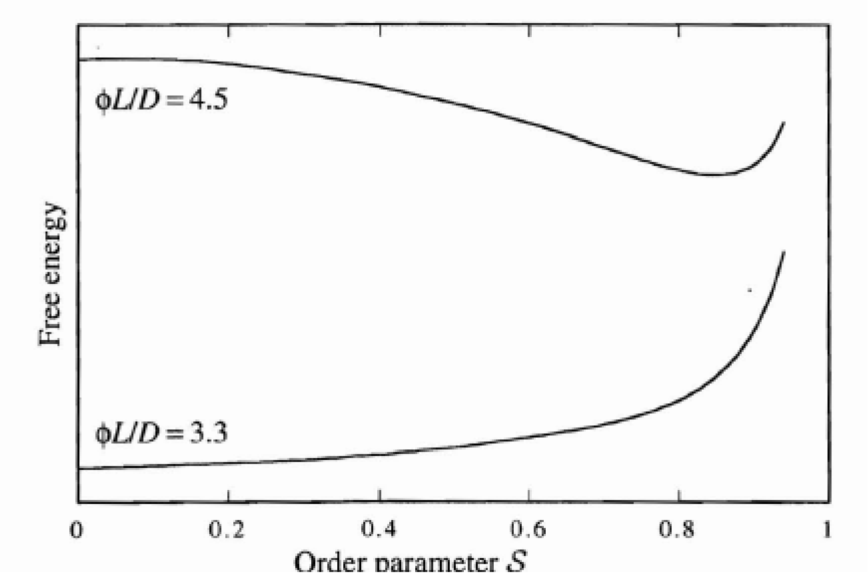
$$F = F_{ideal} + k_B T \left(\frac{Nb}{V} \right) = F^0 + kT \ln c + kTcb$$

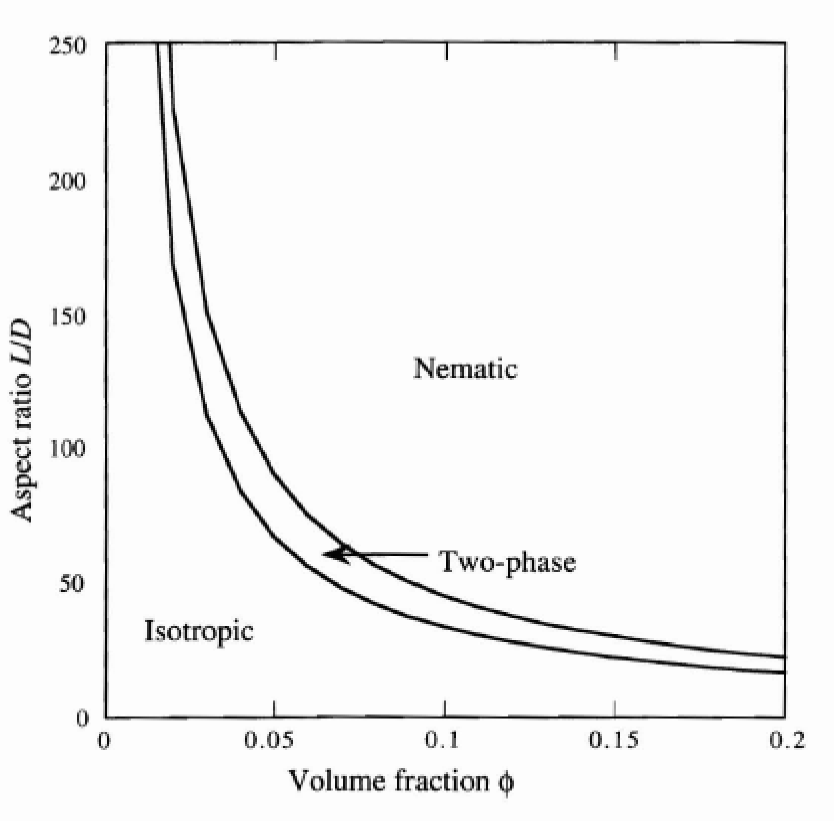
Additionally for the rods:

- loss of orientational entropy: $\Delta S = -k_B \int f(\theta) \ln \left[4\pi f(\theta) \right] d\theta$
- excluded volume is a function of orientation

Isotropic/nematic transition for hard rod system

- For values φL/D<3.34 a minimum only occur at S=0;
- For valuse φL/D<4.49 two phases coexist with order parameter for nematic phase S=0.84





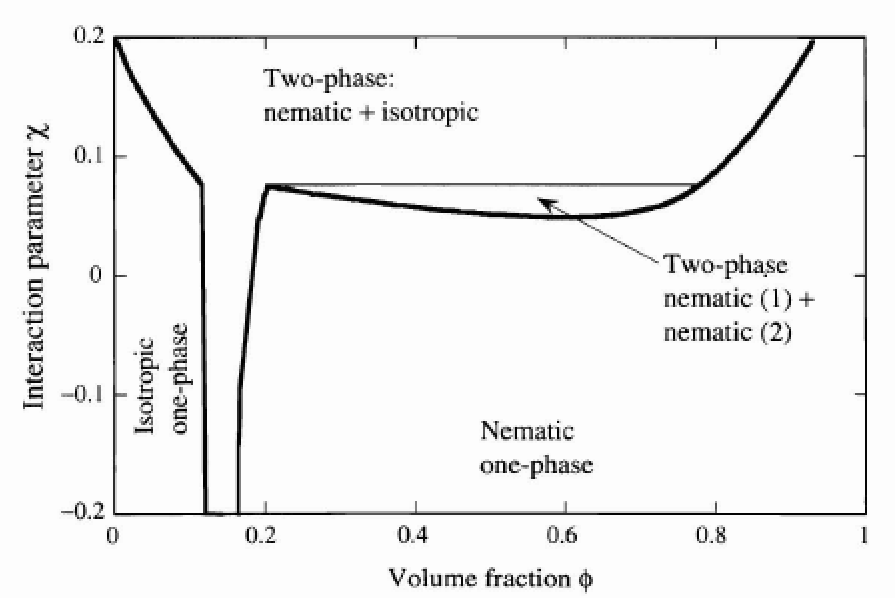
Transitions in real lyotropic systems

Difference with real systems:

- Additional interactions besides excluded volume
- The rods are not completely stiff

Leads to richer phase diagrams

- Additional interactions can be described by an interaction parameter χ, negative values correspond to repulsion, positive to attraction



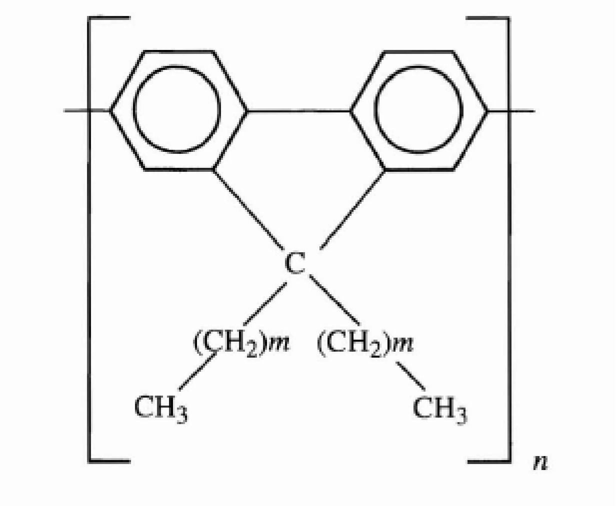
Phase diagram calculated for L/D=100

- Semi-flexibility required indroducing statistical length, volume fraction required for entering nematic phase will be larger

Thermotropic liquid crystals

How to reduce temperature of crystal->liquid crystal transition (thermotropic liquid cristalline polymer):

- inclusion of flexible units in the backbone
- using random copolymer (quenched disorder)
- attachment of large flexible side groups (hairy rod polymers)



m~7

Problems

- Consider a colloid of charged spheres of radius 100nm in aq. solution of NaCl.
  a) calculate the Debye screening length for 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2} M.
  b) for each salt concentration estimate the volume fraction for transition into ordered phase. Assume that the particles behave as hard spheres with the radius equal to the sum of the physical radius and Debye length.
- A biopolymer is observed to change from a helix to a coil state over a 5 K temperature interval centred on 343 K.
  a. Show that the width of the helix-coil transition in terms of the parameter *s* may be characterised by $\Delta s = 4\sigma^{1/2}$.
  b. Assuming that s is a linear function of temperature close to the midpoint of the transition, estimate the free energy, in units of $k_B T$, associated with ajunction between helical and coil sections, $\Delta F_g / k_B T$.
  c. How would you expect the width of the transition as the length of the biopolymer is increased? What is the significance of this result?