Maier-Saupe Theory for LC Phase Formation

This is a **mean field** theory, in which the energy of a molecule does not depend on its particular environment.

Energy is a function of the orientation distribution of the molecules, described by the **order parameter S**.

It is assumed that this can be described simply by the first **P₂** term (Legendre polynomial) of an expansion, but in reality there will be higher order moments of the distribution which are ignored in this approach.

Energy of jth molecule

$$u_j = -CS\frac{1}{2}(3\cos^2\theta_j - 1)$$

where C is a constant, assumed independent of T.

Thus the interaction of a given rod depends on its particular orientation θ_j, and how it interacts with the average orientation expressed by S.

This is a purely geometric argument, and ignores, for instance, any particular dipolar interactions.

$$<u_j> = -CS(\frac{1}{2} < 3\cos^2 \theta_j > -1)$$

$$\Rightarrow <u_j> = -CS^2$$

or $\qquad$ **$U = -1/2\ N_A CS^2$ per mole**
(the factor of 1/2 arises to avoid double counting.)

The energy decreases as the alignment increases i.e. as S→1.

Thus alignment decreases the contribution of U to the internal energy.

However this is offset by the entropic term: entropy decreases as orientation improves.

Partition function Z_j for the jth molecule given by

$$Z_j = \int_0^1 \exp(-u_j/kT)\ d(\cos \theta_j)$$

substituting for u_j yields

$$Z_j = \exp -\left(\frac{C\,S}{2kT}\right) + \int_0^1 \exp\left(\frac{C\,S\ 3\cos^2\theta_j}{2kT}\right) d\cos\theta_j$$

But S = kln Z,

Thus the entropy per mole compared with the isotropic state is

$$S = N_A k \left[\left(\frac{CS}{2kT} \right) - \log \left\{ \int_0^1 \exp\left(\frac{CS3\cos^2\theta_j}{2kT} \right) d\cos\theta_j \right\} \right]$$

Combining the entropy and internal energy terms, (and assuming the volume is essentially independent of S) yields

$$\Delta G = - N_A kT \left[\frac{CS(S+1)}{2kT} - \log \left\{ \int_0^1 \exp\left(\frac{C S 3\cos^2\theta_j}{2kT} \right) d\cos\theta_j \right\} \right]$$

Plots of how $\Delta G/N_A kT$ vary with S show how the phase equilibrium shifts with temperature.

There is one temperature at which there are two minima with the same energy: one for $S = 0$ (i.e isotropic) and one for finite S.

This corresponds to the liquid crystal to isotropic phase transition temperature, $T_{LC \rightarrow I}$.

Occurs for $C/kT = 4.55$ and $S = 0.43$.

Thus theory says that as you warm an LC phase up there is a critical value of S at which system transforms (in a universal way) to an isotropic fluid.

As with all mean field theories, this only works up to a point.

Liable to be wrong in the vicinity of the phase transition, where critical exponents in particular will be incorrectly predicted; theory is ignoring fluctuations which will be very important here.

Also the theory takes no account of specific shape of the molecules involved, e.g. axial ratio.

This is particularly important for polymers.

Other approaches suit polymers better for this reason, when both length and stiffness can be properly accounted for.

One of the most successful models is the Flory Lattice Model, which builds on the more general Onsager theory.

This is specifically a steric theory and takes no account of specific intermolecular attractions, so has a different range of limitations.

The Onsager theory is essentially the rod-equivalent of a hard sphere fluid: **the rod-rod interaction energy is zero except when they overlap in space – when it is infinite.**

This leads to a reduction in translational entropy, as there is less space for the rods to explore.

This **excluded volume decreases** as the rods align, and this factor provides the driving force for the formation of the nematic phase.

Onsager Theory

When orientation is reduced there is a loss of orientational entropy S_{orient}.

In general, for a distribution of rods f(θ), the Boltzmann formula ($S = \sum p_i \ln p_i$) gives
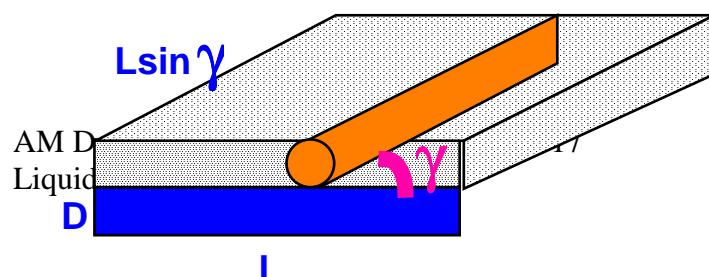
$$S_{orient} = -k_B \int f(\theta) \ln f(\theta) d\Omega$$

In the isotropic state $f(\theta) = 1/4\pi$
So the change in orientational entropy in going from the isotropic to nematic state is

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

But an additional term for the loss of translational entropy must also be included due to the excluded volume effect.

Excluded volume is $2L^2D\left|\sin\gamma\right|$ where γ is the angle the rods make with each other.

Let p[f(θ)] = <|sinγ|> then

$$p[f(\theta)] = <|\sin\gamma|> = \iint f(\theta)f(\theta')\sin\gamma\, d\Omega d\Omega'$$

and hence the contribution to the free energy due to the excluded volume effect on the entropy can be calculated.

Aside on the free energy of a hard sphere fluid:
For an ideal gas, N atoms in volume V

$$S_{ideal} = k_B \ln\left(\frac{aV}{N}\right) \qquad \text{where a is a}$$

constant.

If the gas atoms have finite volume b, then the volume accessible to other atoms is reduced to (V-Nb) so that

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

$$\sim S_{ideal} - k_B\left(\frac{N}{V}\right)b$$

and a corresponding free energy

$$F = F_{ideal} + k_B T\left(\frac{N}{V}\right)b = F_o + k_B T \log c + k_B Tcb$$

where c=N/V the concentration.

Equivalently for the hard rod fluid the free energy can be written

$$F = F_o + k_B T \left(\log c + \int f(\theta) \ln[4\pi f(\theta)]d\Omega + L^2 Dcp[f(\theta)] \right)$$

orientation   excluded volume

Put $\phi = c\pi LD^2/4$, the volume fraction of rods then

$$F = F_o' + k_B T \left(\log\left(\frac{L}{D}\phi\right) + \int f(\theta)\ln[4\pi f(\theta)]d\Omega + \frac{4}{\pi}\frac{L}{D}\phi p[f(\theta)] \right)$$

The free energy depends only on $\phi L/D$, the product of the volume fraction and the aspect ratio (L/D) of the rods.
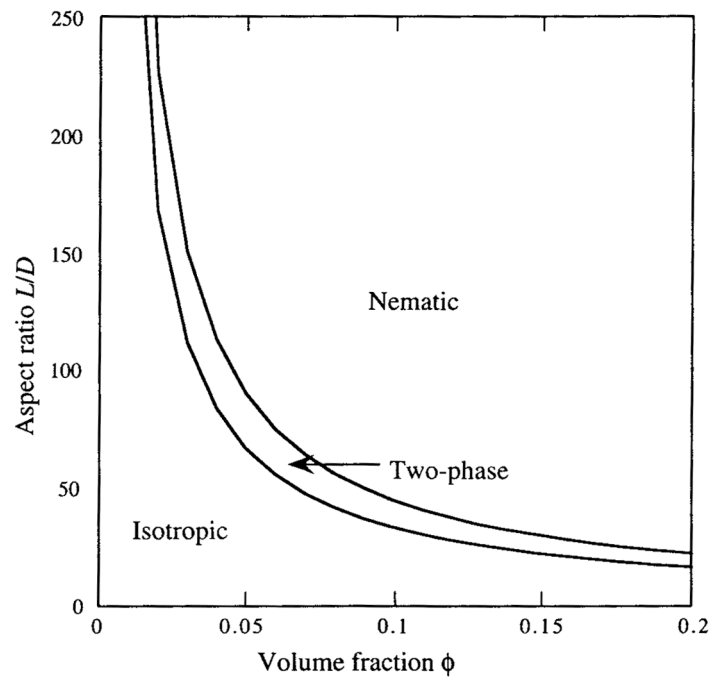
Because this involves a functional (a function of a function) it is messy to solve.

Schematically can see how the different terms contribute to the free energy, and consequences for the phase diagram.
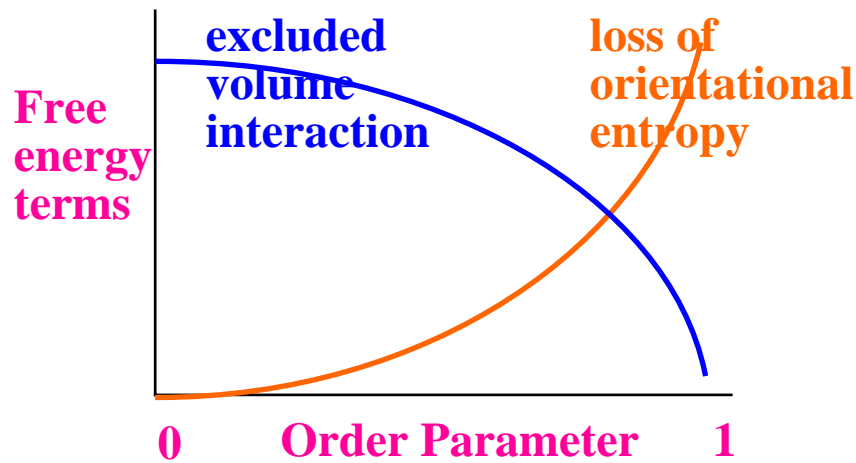
The relative importance of the two terms depends on φL/D: higher concentrations or higher aspect ratio rods leads to enhancement of this term.
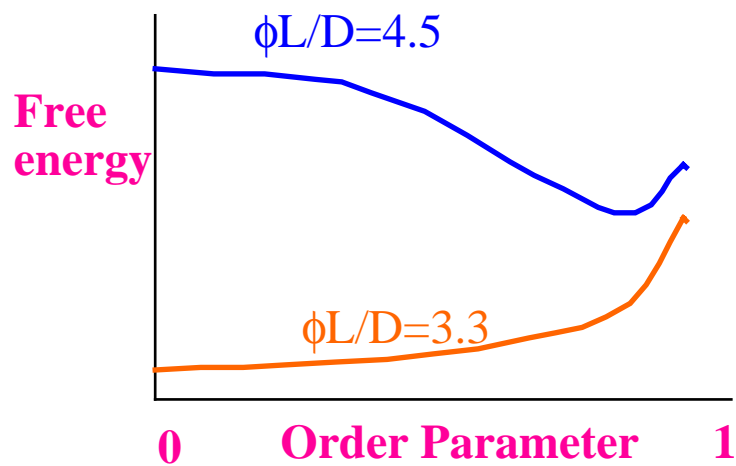
The free energy shows:

**an isotropic phase for $\phi L/D < 3.34$ (only minimum at S=0)
an anisotropic phase for $\phi L/D > 4.49$
and a biphasic region for intermediate values (S=0.84
in the anisotropic phase).**