1 Liquid Crystals (Doi Chapter 5, Selinger, Soft-Matter)

A liquid crystal is a state of matter which has an intermediate order between liquid and crystal. While fluid in nature, liquid crystals possess order in molecular orientation. Due to this ordering, the molecular orientation of liquid crystals is easily controlled by relatively weak external forces such as electric fields. In usual liquids, a very large electric field (of the order of MV/mm) is needed to orient the molecules which are vigorously moving by thermal motion. Once the material is in the liquid crystalline state, the molecular orientation can be controlled by field strengths of a few tenths of a V/mm. This aspect of liquid crystals is extensively used in display devices. A liquid crystal is an example that shows that the collective nature of soft matter is created by phase transitions. The molecules constituting liquid crystals are not large (their size is ca. 1nm), but in the liquid crystalline state, these molecules arrange themselves in order, and move collectively. In this chapter, we shall discuss how the interaction of molecules creates spontaneous ordering in materials. This phenomenon is generally called an order-disorder transition. The transition from normal liquid to liquid crystal is an instructive example of order-disorder transition.

There are many types of liquid crystalline order, but here we shall focus on a specific type, i.e., the nematics. Nematics are the simplest type of liquid crystals, yet it is the most widely used type. The nematic phase is formed by rod-like molecules. At high temperature, the orientation of the molecules is completely random, and the system is an isotropic liquid. With decreasing temperature, the molecules start to orient in a common direction —and form the nematic phase. The nematic phase is an anisotropic liquid: its optical, electrical, and magnetic properties are anisotropic like a crystal, yet the system is still in a liquid state and can flow. Apart from a few exceptions, nematics are uniaxial, i.e., the system has a rotational symmetry around a certain axis. This axis is called the director, and is specified by a unit vector $\vec{n}$.

The most apparent characteristic of the nematic phase is birefringence, i.e., anisotropy in the transmission of light. Consider a nematic sample sandwiched between two polarizing films (polarizer and analyser), with their polarization axes set orthogonal to each other, and incident light directed normal to the film. If the sample is an isotropic liquid, the intensity of the transmitted light is zero since the polarization axes of the two films are orthogonal. If the sample is nematic, however, a certain amount of the incident light is transmitted. The intensity of the transmitted light is a function of the angle θ that the director $\vec{n}$ makes with the polarizing axis; the transmission is zero when θ is equal to 0 or $\pi/2$, and takes a maximum when $\theta = \pi/4$. Since the director $\vec{n}$ can be changed by an electric field, the transmission of light can be easily controlled. This is the principle of how nematics work in display devices.

1.1 Orientational distribution function

To distinguish the nematic phase from the isotropic phase, let us consider the distribution of the molecular orientation. Let $\vec{u}$ be a unit vector ($|u| = 1$) in the direction of the long axis of the molecule. In the isotropic phase, $\vec{u}$ will be uniformly distributed on a unit sphere. In the nematic phase, the distribution of $\vec{u}$ becomes non-uniform on the sphere. Let $\psi(\vec{u})$ be the distribution function of $\vec{u}$ on the unit sphere. It is normalized as

$$\int d\vec{u}\psi(\vec{u}) = 1$$

where $d\vec{u}$ stands for the surface element of the sphere $|u| = 1$, and the integral is done over the entire surface. In the isotropic phase, $\psi(\vec{u})$ is constant, independent of $\vec{u}$, and therefore

$$\psi(\vec{u}) = \frac{1}{4\pi}$$

On the other hand, in the nematic phase, $\psi(\vec{u})$ will be oriented toward the direction of the director $\vec{n}$ (also with unitary modulus) , and $\psi(u)$ becomes anisotropic.

1.2 Order parameter for nematics

Let us consider a parameter which characterizes the anisotropy of $\psi(\vec{u})$ in the nematic phase. An obvious candidate for such a parameter is the first moment, $< u_\alpha >$, ($\alpha = x, y, z$), where $< \cdots >$ stands for the average for the distribution function $\psi(\vec{u})$, i.e.,

$$< \cdots >= \int d\vec{u} \cdots \psi(\vec{u})$$

However, for the symmetric ellipsoidal molecules shown in Fig. 5.1(a), $< u_\alpha >$ is always equal to zero since the states specified by $\vec{u}$ and $-\vec{u}$ are identical, and therefore $\psi(\vec{u})$ has an inversion symmetry $\psi(\vec{u}) = \psi(-\vec{u})$.

One could then consider quantities like $\vec{u} \cdot \vec{u}$ or $\vec{u} \times \vec{u}$. Both of them would not work, giving a trivial one or zero value in all phases.

Let us therefore consider the second moment at tensorial level, $\mathbf{T} =< \vec{u} \otimes \vec{u} >$, or equivalently in term of components $< u_\alpha u_\beta >$.

In the isotropic state, $< u_\alpha u_\beta >\sim \delta_{\alpha\beta}$ since different directions are uncorrelated. Since, in addition $< u_{xx}^2 >=< u_{yy}^2 >=< u_{zz}^2 >$ and

$$\sum_\alpha < u_{\alpha\alpha}^2 >= 1$$

then

$$< u_\alpha u_\beta >= \frac{1}{3}\delta_{\alpha\beta}$$

In the isotropic phase, then **T** appears as

$$\mathbf{T} = \begin{pmatrix} \frac{1}{3} & 0 & 0 \\ 0 & \frac{1}{3} & 0 \\ 0 & 0 & \frac{1}{3} \end{pmatrix}$$

On the other hand, if $\vec{u}$ is completely aligned along $\vec{n}$ (maximum oriented state) and if we call $\hat{z}$ the direction of the nematic vector we have

$$\mathbf{T} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

proving that the tensor **T** is indeed able to discriminate between the isotropic and the nematic phases. To make **T** an even more convenient order parameter, one can subtract the value that **T** assumes in the isotropic phase. The new $\mathbf{T}' = \mathbf{T} - 1/3\mathbf{I}$ is such that its value in the isotropic phase is now zero. In the nematic phase

$$\mathbf{T}' = \begin{pmatrix} -\frac{1}{3} & 0 & 0 \\ 0 & -\frac{1}{3} & 0 \\ 0 & 0 & \frac{2}{3} \end{pmatrix}$$

Finally, just to make the order parameter to look better, we multiply it by 3/2 (not everybody does it). The final order parameter tensor, named **Q** is thus

$$\mathbf{Q} = \frac{3}{2}T' = < \frac{3}{2}\left(\vec{u} \otimes \vec{u} - \frac{1}{3}\mathbf{I}\right) >$$

or in terms of components

$$Q_{\alpha,\beta} = < \frac{3}{2}u_\alpha u_\beta - \frac{1}{2}\delta_{\alpha,\beta} > \tag{1}$$

$Q_{\alpha\beta}$ represents the orientational order of the molecules in the nematic phase and is called the *order parameter*. It is zero in the isotropic phase and

$$\mathbf{Q} = \begin{pmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

(non-zero) in the maximally oriented nematic phase. It is also evident that **Q** has two important properties: it is **symmetric** and it is **traceless**.

Let's now consider a case of partial ordering. Let' us also assume uniaxial symmetry around the axis of $\vec{n}$. This means that $\vec{u}$ has equal probability on the the plane perpendicular to $\vec{n}$. The three components of $\vec{u}$ can be written in spherical coordinates

$$\vec{u} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$$

and then

$$\mathbf{T} =< \begin{pmatrix} (\sin\theta\cos\phi)^2 & \sin\theta\cos\phi\sin\theta\sin\phi & \sin\theta\cos\phi\cos\theta \\ \sin\theta\sin\phi\sin\theta\cos\phi & (\sin\theta\sin\phi)^2 & \sin\theta\sin\phi\cos\theta \\ \sin\theta\cos\phi\cos\theta & \cos\theta\sin\theta\sin\phi & (\cos\theta)^2 \end{pmatrix} >$$

Due to the uniaxial property, the average of $\sin\phi$ and $\cos\phi$ is zero while the average of $\sin^2\phi$ and $\cos^2\phi$ is $1/2$. Then

$$\mathbf{T} =< \begin{pmatrix} \frac{1}{2}\sin^2\theta & 0 & 0 \\ 0 & \frac{1}{2}\sin^2\theta & 0 \\ 0 & 0 & \cos^2\theta \end{pmatrix} >$$

and

$$\mathbf{Q} = \frac{3}{2}\left(\mathbf{T} - \frac{1}{3}\mathbf{I}\right) =< \begin{pmatrix} \frac{3}{4}\sin^2\theta - \frac{1}{2} & 0 & 0 \\ 0 & \frac{3}{4}\sin^2\theta - \frac{1}{2} & 0 \\ 0 & 0 & \frac{3}{2}\cos^2\theta - \frac{1}{2} \end{pmatrix} >=$$

$$< \begin{pmatrix} \frac{3}{4}(1-\cos^2\theta) - \frac{1}{2} & 0 & 0 \\ 0 & \frac{3}{4}(1-\cos^2\theta) - \frac{1}{2} & 0 \\ 0 & 0 & \frac{1}{2}(3\cos^2\theta - 1) \end{pmatrix} >=< \begin{pmatrix} -\frac{S}{2} & 0 & 0 \\ 0 & -\frac{S}{2} & 0 \\ 0 & 0 & S \end{pmatrix} >$$

where

$$S =< \frac{1}{2}\left(3\cos^2\theta - 1\right) >= \frac{3}{2} < (\vec{u}\cdot\vec{n})^2 - \frac{1}{3} >$$

is the 2nd order Legendre polynomial. In case of ordering along x or along y we have correspondingly

$$\begin{pmatrix} S & 0 & 0 \\ 0 & -\frac{S}{2} & 0 \\ 0 & 0 & -\frac{S}{2} \end{pmatrix} \qquad \text{or} \qquad \begin{pmatrix} -\frac{S}{2} & 0 & 0 \\ 0 & S & 0 \\ 0 & 0 & -\frac{S}{2} \end{pmatrix}$$

If the distribution of $\vec{u}$ has a uniaxial symmetry around the axis of $\vec{n}$, $Q_{\alpha\beta}$ can be written as

$$Q_{\alpha\beta} = S\left(\frac{3}{2}n_\alpha n_\beta - \frac{1}{2}\delta_{\alpha\beta}\right) \tag{2}$$

This can be seen by explicitly writing $\mathbf{Q}$ for $\vec{n}$ along $\hat{z}$ as

$$\mathbf{Q} = S\left[\frac{3}{2}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} - \frac{1}{2}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\right] = S\left[\frac{3}{2}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & (\hat{z})_z(\hat{z})_z \end{pmatrix} - \frac{1}{2}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\right]$$

S is a parameter representing how perfectly the molecules are aligned along $\vec{n}$ or along -$\vec{n}$. If the alignment is perfect, S is equal to 1. If there is no alignment, S is equal to 0.

Thus S also represents the degree of the order in the nematic phase, and is called the scalar order parameter. To avoid confusion with S, Q is often called the tensor order parameter. The tensor order parameter $Q_{\alpha\beta}$ includes two pieces of information. One is how strongly the molecules are aligned; this is represented by the scalar order parameter S. The other is the direction in which the molecules are aligned; this is represented by the director $\vec{n}$. Note that the two other eigenvectors are degenerate, since there is no specific orientation on the plane perpendicular to $\vec{n}$ (uniaxial nematic). In principle, one could imagine also bi-axial nematics in which there is a preferential direction in the plane perpendicular to $\vec{n}$. Research on bi-axial nematic is underway.

From $\mathbf{Q}$ one can calculate S and $\vec{n}$ by diagonalizing the matrix and estimating the three eigenvalues and the three eigenvectors. S is the largest eigenvalue (the only one positive in the thermodynamic limit) and $\vec{n}$ is the corresponding eigenvector.

2 Landau-de Gennes theory

2.1 Expression for the free energy near the transition point

Phase transitions which involve changes in the ordering of molecules (or atoms) are generally called order-disorder transitions. The order-disorder transition is characterized by the order parameter which is equal to zero in the disordered state, and is non-zero in the ordered state. The isotropic-nematic transition is an example of an order-disorder transition. Another example of an order-disorder transition is the magnetic transition. The magnetic state of ferromagnets changes from an ordered state to a disordered state at a certain temperature T_c. Below T_c, the magnetic moments of atoms are ordered, and there is a spontaneous magnetic moment M. Above T_c, the magnetic moments of atoms become random, and M vanishes. Therefore the magnetic moment M can be regarded as the order parameter in the magnetic transition. Though the nematic transition looks similar to the magnetic transition, there is an essential difference. The difference exists in the behaviour of the order parameter near the phase transition. In the case of the magnetic transition, the magnetic moment M changes continuously as a function of temperature. The magnetic moment is zero above T_c, and is non-zero below T_c, but it changes continuously at T_c. On the other hand, in the case of the nematic transition, the order parameter S changes discontinuously at T_c.

As we have seen the (restricted) free-energy has the form

$$F(M,T) = F(0,T) + A(T - T_c)M^2 + BM^4$$

where the concavity at $M = 0$ changes at $T = T_c$.

An order-disorder transition in which the order parameter changes discontinuously at the transition point is called a discontinuous transition or first-order transition. On the other hand, a phase transition in which the order parameter changes continuously is called a continuous transition or second-order transition. Landau has shown that the distinction between these transitions has its root in the nature of the ordering that takes place at the transition. To see this, let us consider a simple case where the order-disorder transition is characterized by a single order parameter x. We assume that the system is in the disordered phase above T_c. Therefore the equilibrium value of x is zero above T_c, and becomes non-zero below T_c. Let $F(x, T)$ be the free energy (more precisely the restricted free energy) at temperature T for a given value of the order parameter x. For small x, $F(x, T)$ can be expressed as a power series in x:

$$F(x, T) = a_0(T) + a_1(T)x + a_2(T)x^2 + a_3(T)x^3 + a_4(T)x^4 + \cdots$$

Now since the disordered state becomes unstable at temperature T_c, the state of $x = 0$ changes from a local minimum of $F(x, T)$ to a local maximum. For this to happen, $a_1(T)$ must be identically zero, and $a_2(T)$ must have the form $a_2(T) = A(T - T_c)$, where A is a positive constant. Since the important point is that the sign of $a_2(T)$ changes at T_c, we may assume that a_3 and a_4 are constants independent of temperature. Therefore

$$F(x, T) = A(T - T_c)x^2 + a_3x^3 + a_4x^4$$

where the constant term a_0 has been ignored as it does not affect the behaviour of the transition. Now in the case of a magnetic transition, the free energy must be an even function of M since the state of $-M$ is obtained by rotating the system by 180 degrees, and (if there is no magnetic field) it must have the same free energy as the state of M. Therefore the coefficient a_3 must be zero. Above T_c, the minimum of $F(M, T)$ is at $M = 0$, and below T , the minima of the free energy are at $M = \pm\sqrt{A(T_c - T)/2a_4}$. The order parameter M changes continuously at T_c, and the transition is continuous. On the other hand, in the case of a nematic transition, the state of $-S$ is different from the state of S. In the state of $S > 0$, the molecules align in the z-direction, while in the state of $S < 0$, the molecules align normal to the z-axis. Hence a_3 is not equal to zero. Accordingly, the transition becomes discontinuous.

The above argument can be made clearer if we go back to the definition of the order parameter. The order parameter for the nematic phase is a tensor $\mathbf{Q}$, while the free energy is a scalar. If the free energy is expressed as a power series of the tensor $\mathbf{Q}$, the coefficients have to satisfy certain constraints. The free-energy does not have to change for rotations of the system. Hence it must be expressed in term of rotational-invariant quantities. In the case of a tensor of rank 2, like $\mathbf{Q}$, the rotational invariants are the trace, the determinant and $Tr(\mathbf{Q})^2 - Tr(\mathbf{Q}^2)$, respectively of order S, S^3 and S^2. Hence, one can immediately see that there is no linear term in $F(\mathbf{Q}, T)$ since the only scalar constructed from a symmetric tensor $\mathbf{Q}$ is $\mathrm{Tr}(\mathbf{Q})$, but $\mathrm{Tr}(\mathbf{Q})$ is zero by the definition of $\mathbf{Q}$. By similar reasoning, one can show that $F(\mathbf{Q}, T)$ must have the following form

$$F(\mathbf{Q}, T) = a_2(T)Tr(\mathbf{Q}^2) + a_3(T)Tr(\mathbf{Q}^3) + a_{4a}(T)Tr(\mathbf{Q}^4) + a_{4b}(T)[Tr(\mathbf{Q}^2)]^2$$

In this case, there is a third-order term in $\mathbf{Q}$.

Note that $Tr(\mathbf{Q}^2) = \sum_\alpha \sum_\beta Q^2_{\alpha,\beta}$. Indeed, if we evaluate the diagonal terms of $\mathbf{Q^2}$ we find

$$\begin{pmatrix} Q_{11} & Q_{12} & Q_{13} \\ Q_{21} & Q_{22} & Q_{23} \\ Q_{31} & Q_{32} & Q_{33} \end{pmatrix} \begin{pmatrix} Q_{11} & Q_{12} & Q_{13} \\ Q_{21} & Q_{22} & Q_{23} \\ Q_{31} & Q_{32} & Q_{33} \end{pmatrix} = \begin{pmatrix} Q^2_{11} + Q^2_{12} + Q^2_{13} & .... & .... \\ ... & Q^2_{12} + Q^2_{22} + Q^2_{23} & .... \\ .... & ... & Q^2_{13} + Q^2_{23} + Q^2_{33} \end{pmatrix}$$

Similarly $Tr(\mathbf{Q^3}) = \sum_\alpha \sum_\beta \sum_\gamma Q_{\alpha,\beta} Q_{\beta,\gamma} Q_{\gamma,\alpha}$. Since the trace is invariant for rotations, we can evaluate the value of it in the diagonal basis. Then

$$Tr(\mathbf{Q}^2) = Q^2_{11} + Q^2_{22} + Q^2_{33} = \frac{S^2}{4} + \frac{S^2}{4} + S^2 = \frac{3}{2} S^2$$

$$Tr(\mathbf{Q}^3) = Q^3_{11} + Q^3_{22} + Q^3_{33} = -\frac{S^3}{8} - \frac{S^3}{8} + S^3 = \frac{3}{4} S^3$$

$$Tr(\mathbf{Q}^4) = Q^4_{11} + Q^4_{22} + Q^4_{33} = \frac{S^4}{16} + \frac{S^4}{16} + S^4 = \frac{9}{8} S^4$$

Then,

$$F(\mathbf{Q}; T) = \frac{3}{2} a_2(T) S^2 + \frac{3}{4} a_3(T) S^3 + \left[\frac{9}{8} a_{4a}(T) + \frac{9}{4} a_{4b}(T) \right] S^4$$

$F(\mathbf{Q}, T)$ may thus be expressed as

$$F(S, T) = \frac{1}{2} A(T - T_c) S^2 - \frac{1}{3} B S^3 + \frac{1}{4} C S^4$$

where A, B, C are positive constants independent of temperature. Note that C has to be positive if we want a free energy that does not go to minus infinity for large values of S, consistent with the truncation of the series expansion. B is assumed to be positive for the time being. Such free energy for nematic forming materials is called the Landau-de Gennes free energy. The Landau-de Gennes free energy represents the essential feature of the isotropic-nematic transition, and is often used as a model free energy for the transition. The coefficients A, B, C can be calculated using mean field theory, and the result is $A \approx N k_B$, $B \approx N k_B T_c$, $C \approx N k_B T_c$.

Let's take a look at $F(S, T)$. This function has extrema as

$$\frac{\partial F}{\partial S} = A(T - T_c) S - B S^2 + C S^3 = 0 \tag{3}$$

and hence has as extrema always $S = 0$ and

$$S_{min} = \frac{B \pm \sqrt{B^2 - 4AC(T - T_c)}}{2C}$$

So, when

$$B^2 - 4AC(T - T_c) > 0 \qquad \text{or} \qquad T - T_c < \frac{B^2}{4AC}$$

two new solutions appear, beside $S = 0$. At this T, the free-energy of the new minimum is still higher than the free energy in $S = 0$.

Substituting Eq. 3 (dF/dS=0), re-written as

$$A(T - T_c) = BS_{min} - CS_{min}^2$$

in the free energy expression it becomes possible to calculate the value of the free energy in the minimum (for $S = S_{min}$) as

$$F(S_{min}) = \frac{1}{2}(BS_{min} - CS_{min}^2)S_{min}^2 - \frac{1}{3}BS_{min}^3 + \frac{1}{4}CS_{min}^4 = S_{min}^3\left[\left(\frac{1}{2} - \frac{1}{3}\right)B + S_{min}\left(-\frac{1}{2} + \frac{1}{4}\right)C\right]$$

$$= S_{min}^3\left(\frac{1}{6}B - S_{min}\frac{1}{4}C\right)$$

The free energy in the minimum is zero when

$$S_{min} = \frac{2B}{3C} \qquad \text{and} \quad A(T - T_c) = \frac{2B^2}{9C}$$

Before concluding, let's discuss briefly the case $B < 0$. The only difference is that the new minimum will appear at negative S. It is a theoretical possibility but it does not generally takes place in experiments. Hence we will not discuss it further.

2.2 Alignment of nematic molecules by a magnetic field

The Landau-de Gennes free energy is convenient to see the characteristic behaviour of the system near the transition temperature. As an example, let us consider the effect of a magnetic field on the molecular orientation. When a magnetic field H is applied to a nematic forming molecule, a magnetic moment is induced in the molecule. The induced magnetic moment m depends on the angle that the molecular axis $\vec{u}$ makes with the magnetic field H (see Fig. 5.6). Let $\alpha_{\|}$ (and $\alpha_{\perp}$) be the magnetic susceptibility of the molecule when the magnetic field $\vec{H}$ is applied parallel (and perpendicular) to the molecular axis u. A magnetic field H applied to a molecule pointing in the direction $\vec{u}$ can be split into a parallel and a perpendicular (to $\vec{u}$) components: $(\vec{H} \cdot \vec{u})\vec{u}$ and $\vec{H} - (\vec{H} \cdot \vec{u})\vec{u}$. Correspondingly, the molecule will have a magnetic moment $m = \alpha_{\|}(\vec{H} \cdot \vec{u})\vec{u}$ along $\vec{u}$, and a magnetic moment $m_{\perp} = \alpha_{\perp}[\vec{H} - (\vec{H} \cdot \vec{u})\vec{u}]$ in the direction normal to $\vec{u}$. Therefore the molecule feels a potential energy $-\vec{m} \cdot \vec{H}$

$$w_H(\vec{u}) = -\frac{1}{2}\alpha_{\|}(\vec{H} \cdot \vec{u})^2 - \frac{1}{2}\alpha_{\perp}[\vec{H} - (\vec{H} \cdot \vec{u})\vec{u}]^2 + \text{terms independent of } \vec{u}$$

and since $[\vec{H} - (\vec{H} \cdot \vec{u})\vec{u}]^2 = |H|^2 + (\vec{H} \cdot \vec{u})^2 - 2(\vec{H} \cdot \vec{u})(\vec{H} \cdot \vec{u}) = |H|^2 - (\vec{H} \cdot \vec{u})^2$

$$= -\frac{1}{2}\alpha_d(\vec{H} \cdot \vec{u})^2 + \text{terms independent of } \vec{u}$$

where $\alpha_d = \alpha_{\|} - \alpha_{\perp}$. If $\alpha_d > 0$, the magnetic field tends to align the molecule in the direction of $\vec{H}$, while if $\alpha_d < 0$, the magnetic field tends to rotate the molecule to the direction perpendicular to $\vec{H}$. In what follows, we assume $\alpha_d > 0$. If there are N molecules in the system, the total potential energy due to the magnetic field is given by

$$F_H = -\frac{N}{2}\alpha_d < (\vec{H} \cdot \vec{u})^2 >$$

Using the definition of $\mathbf{Q} =< u_\alpha u_\beta - 1/3\delta_{\alpha\beta} >$, this can be written as (ignored the terms which do not depend on $\mathbf{Q}$

$$F_H = -\frac{N}{2}\alpha_d \vec{H} \cdot \mathbf{Q} \cdot \vec{H}$$

Indeed, $(\vec{H} \cdot \vec{u})^2 = (u_x H_x + u_y H_y + u_z H_z)^2$ which is the sum of the same 9 terms you obtain by calculating $\vec{H} \cdot \mathbf{Q} \cdot \vec{H}$ (ignoring the terms of the type $\delta_{\alpha\beta}$).

Since $\mathbf{Q}$ can be expressed as $\mathbf{Q} = S < n_\alpha n_\beta - 1/3\delta_{\alpha\beta} >$ in an analogous way $(\vec{H} \cdot \vec{n})^2 = (n_x H_x + n_y H_y + n_z H_z)^2$

$$F_H = -N\alpha_d S(\vec{H} \cdot n)^2$$

Therefore the total free energy of the system is

$$F(\mathbf{Q}; T) = \frac{1}{2}A(T - T_c)S^2 - \frac{1}{3}BS^3 + \frac{1}{4}CS^4 - \frac{N\alpha_d S}{2}(\vec{H} \cdot n)^2$$

The order parameter $\mathbf{Q}$ in the presence of the magnetic field is given by S and $\vec{n}$ which minimize the previous expression. The response of $\mathbf{Q}$ to the magnetic field is quite different in the disordered phase and in the ordered phase.

2.2.1 Response to the magnetic field in the disordered phase

In the disordered phase, the order parameter S is zero when there is no magnetic field. When a magnetic field is applied, S becomes non-zero but is small, and the ordering process is completely induced by $\vec{H}$. Then $\vec{n} = \hat{H}$ Therefore we may approximate the free energy as

$$F(\mathbf{Q}; T) = \frac{1}{2}A(T - T_c)S^2 - \frac{N\alpha_d S}{2}H^2$$

where we have used the fact that $\vec{n}$ is parallel to $\vec{H}$. Minimization of this with respect to S gives

$$S = \frac{N\alpha_d H^2}{2A(T - T_c)}$$

This equation indicates that as we approach T_c, the order parameter S increases, and diverges at $T = T_c$. The divergence of S at T_c is due to the appearance of some locally ordered region in the disordered phase. In the disordered phase, there is no macroscopic order, but the tendency that neighbouring molecules align in the same direction increases as T approaches T_c. Accordingly, near T_c, the system is divided into regions within which the molecules align in the same direction. The size of such ordered regions increases as T approaches T_c, and therefore S diverges at T_c. The phenomenon that the response to external fields in the disordered phase diverges at T_c is seen quite generally in order-disorder transitions and is called a critical phenomenon. In a continuous transition, the divergence is always seen since the system remains in the disordered phase as long as T is larger than T_c. In a discontinuous transition, the divergence may not be seen since the transition to the ordered phase can take place before the factor $1/(T - T_c)$ becomes dominant. In the isotropic-nematic transition, the temperatures T_{c1}, T_e, and T_{c2} are close to each other, and the divergence has been observed.

2.2.2 Response in the ordered phase

In the ordered phase, S has a non-zero value S_{eq} in the absence of a magnetic field. If a magnetic field is applied, S changes slightly from S_{eq}, but the deviation $S - S_{eq}$ is very small (being of the order of $\alpha_d H^2/k_B T_c$) Therefore the magnetic field has little effect on the scalar order parameter S. On the other hand, the magnetic field has a crucial effect on the tensor order parameter $\mathbf{Q}$ since the director $\vec{n}$ is strongly affected by the magnetic field. In the disordered phase, the rotation of molecules is essentially independent of each other. Therefore if one wants to align the molecules, one needs to apply a very large magnetic field which satisfies $\alpha_d H^2 > k_B T$. On the other hand, in the ordered phase, N molecules move together as a single entity. Therefore if one applies a magnetic field which satisfies $S_{eq} N \alpha_d H^2 > k_B T$, one can rotate all molecules in the system. Since N is a macroscopic number ($N \approx 10^{20}$), the necessary magnetic field is very small. This is another example of the principle that molecular collectivity produces a very large response to external fields.

3 Mean field theory for the isotropic-nematic transition

Free energy functional for the orientational distribution function Let us now study the phase transition from the isotropic state to the nematic state. Theories for phase transitions usually become approximate, involving some kind of mean field approximation. In the case of the isotropic-nematic transition of rod-like molecules, Onsager showed that rigorous theory can be developed in the limit of large aspect ratio. This beautiful theory is for the phase transition in lyotropic liquid crystals (liquid crystals formed in solutions by a change of concentration). It is discussed at the end of this chapter. Here, we present another classical theory due to Maier and Saupe. It is a mean field theory for thermotropic liquid crystals (liquid crystals formed by a change of temperature). The basic assumption of the

Maier-Saupe theory is that nematic forming molecules have an interaction potential which forces them to align in the same direction. Let $w(\vec{u}, \vec{u}')$ be the interaction potential acting between two neighbouring molecules each pointing along the $\vec{u}$ and $\vec{u}'$ directions. The interaction potential $w(\vec{u}, \vec{u}')$ has the property that it decreases with decrease of the angle θ between $\vec{u}$ and $\vec{u}'$, and becomes smallest when two molecules align in the same direction. For molecules which do not have polarity (such as ellipsoidal or rod-like molecules), the interaction potential should not change under the transformation $\vec{u} \to -\vec{u}$ The simplest form of such a potential is

$$w(\vec{u}, \vec{u}') = -U(\vec{u} \cdot \vec{u}')^2$$

where U is a positive constant. Note that the interaction potential generally depends not only on the orientation vectors $\vec{u}$ and $\vec{u}'$, but also on the vector $\mathbf{r}$ which joins the centres of the two molecules. Here $w(\vec{u}, \vec{u}')$ represents the effective potential in which the average for $\mathbf{r}$ has already been taken.

Now if the system consists of N such molecules, and if their orientational distribution is given by $\psi(\vec{u})$, the average energy of the system is given by

$$E[\psi] = \frac{zN}{2} \int d\vec{u} \int d\vec{u}' w(\vec{u}, \vec{u}')\psi(\vec{u})\psi(\vec{u}')$$

where z is the mean number of neighbouring molecules (i.e., the coordination number). The interaction potential tends to align the molecules in the same direction, but this is opposed by thermal motion which tends to randomize the molecular orientation. For a given orientational distribution $\psi(\vec{u})$, the orientational entropy can be estimated as

$$S[\psi] = -Nk_B \int d\vec{u}\psi(\vec{u}) \ln \psi(\vec{u})$$

To grasp this expression consider that the surface of the unit sphere $|u| = 1$ is divided into M small cells of area $du = 4\pi/M$, each pointing to the direction $\vec{u}_i$ $(i = 1, 2, ..., M)$. If their orientational distribution function is $\psi(\vec{u})$, the number of molecules in region i is $N_i = N\psi(\vec{u}_i)du$ (N being the total number of molecules in the system). The number of ways of putting the molecules in such a state is $W = N!/(N_1!N_2!...N_M!)$. Therefore the entropy is given by

$$S = k_B \ln W = k_B(\ln N! - \sum_{i=1}^{M} \ln N_i!) = k_B \left[N(\ln N - 1) - \sum_{i=1}^{M} N_i(\ln N_i - 1) \right] =$$

$$k_B \left[N \ln N - \sum_{i=1}^{M} N_i \ln N_i \right] = k_B \left[\sum_{i=1}^{M} N_i(\ln N - \ln N_i) \right] = -k_B \left[\sum_{i=1}^{M} N_i \ln \frac{N_i}{N} \right]$$

and therefore the free energy of the system is given by

$$F[\psi] = E[\psi] - TS[\psi] = N \left[-\frac{zU}{2} \int d\vec{u} \int d\vec{u}' (\vec{u} \cdot \vec{u}')^2 \psi(\vec{u})\psi(\vec{u}') + k_B T \int d\vec{u}\psi(\vec{u}) \ln \psi(\vec{u}) \right] \tag{4}$$

The orientational distribution at equilibrium is determined by the condition that Eq.4 be a minimum with respect to $\psi(\vec{u})$, i.e., by the condition

$$\frac{\delta}{\delta\psi}\left[F[\psi] - \lambda\int d\vec{u}\psi(\vec{u})\right] = 0$$

where $\frac{\delta}{\delta\psi}$ stands for the functional derivative with respect to ψ. The second term on the left-hand side is introduced to account for the normalization condition for ψ.

3.0.1 Functional derivative

To evaluate the functional derivative of a generic functional $G = \int dx f(\psi(x))$ one need to calculate the change in the functional when the function changes of a small quantity in all points $\delta\psi(x)$

$$\delta G[\psi] \equiv G[\psi + \delta\psi] - G[\psi] = \int dx f(\psi(x) + \delta\psi(x)) - \int dx f(\psi(x))$$

This is formally written, considering only terms linear in $\psi(x)$ as

$$\int dx \frac{\delta G}{\delta\psi(x)}\delta\psi(x)$$

where $\frac{\delta G}{\delta\psi(x)}$ is named functional derivative.

For the term $\int d\vec{u}\psi(\vec{u})\ln\psi(\vec{u})$

$$\delta\int d\vec{u}\psi(\vec{u})\ln\psi(\vec{u}) = \int d\vec{u}(\psi(\vec{u}) + \delta\psi)\ln(\psi(\vec{u}) + \delta\psi)) - \int d\vec{u}\psi(\vec{u})\ln\psi(\vec{u})$$

$$\int d\vec{u}(\psi(\vec{u}) + \delta\psi)\ln[\psi(\vec{u})(1 + \delta\psi/\psi(\vec{u}))] - \int d\vec{u}\psi(\vec{u})\ln\psi(\vec{u})$$

$$\int d\vec{u}(\psi(\vec{u}) + \delta\psi)[\ln\psi(\vec{u}) + \delta\psi/\psi(\vec{u}))] - \int d\vec{u}\psi(\vec{u})\ln\psi(\vec{u}) =$$

$$\int d\vec{u}(\delta\psi + \delta\psi\ln\psi(\vec{u}) + \delta\psi^2/\psi(\vec{u}))] = \int d\vec{u}[1 + \ln\psi(\vec{u})]\delta\psi$$

such that the functional derivative is

$$\frac{\delta\int d\vec{u}\psi(\vec{u})\ln\psi(\vec{u})}{\delta\psi(x)} = [1 + \ln\psi(\vec{u})]$$

For the term $\int d\vec{u}\int d\vec{u}'(\vec{u}\cdot\vec{u}')^2\psi(\vec{u})\psi(\vec{u}')$

$$\delta\int d\vec{u}\int d\vec{u}'(\vec{u}\cdot\vec{u}')^2\psi(\vec{u})\psi(\vec{u}') = \int d\vec{u}\int d\vec{u}'(\vec{u}\cdot\vec{u}')^2[(\psi(\vec{u})+\delta\psi(\vec{u})][\psi(\vec{u}')+\delta\psi(\vec{u}')] - \int d\vec{u}\int d\vec{u}'(\vec{u}\cdot\vec{u}')^2\psi(\vec{u})\psi(\vec{u}')$$

$$\int d\vec{u} \int d\vec{u}'(\vec{u}\cdot\vec{u}')^2[(\psi(\vec{u})\delta\psi(\vec{u}') + \psi(\vec{u}')\delta\psi(\vec{u}) + \delta\psi(\vec{u}')\delta\psi(\vec{u})]$$

and neglecting the term quadratic in $\delta\psi$

$$2\int d\vec{u} \int d\vec{u}'(\vec{u}\cdot\vec{u}')^2\psi(\vec{u})\delta\psi(\vec{u}') = 2\int d\vec{u} \int d\vec{u}'(\vec{u}\cdot\vec{u}')^2\psi(\vec{u}')\delta\psi(\vec{u})$$

where the last equality arises from the symmetry of the integrand.

Finally, the term $\int d\vec{u}\psi(\vec{u})$ gives

$$\delta\int d\vec{u}\psi(\vec{u}) = \int d\vec{u}(\psi(\vec{u}) + \delta\psi) - \int d\vec{u}\psi(\vec{u}) = \int d\vec{u}\delta\psi$$

such that

$$\frac{\delta\int d\vec{u}\psi(\vec{u})}{\delta\psi} = 1$$

As a result,

$$\frac{\delta}{\delta\psi}\left[F[\psi] - \lambda\int d\vec{u}\psi(\vec{u})\right] = 0$$

becomes

$$\left\{k_BT[1 + \ln\psi(\vec{u})] - U\int d\vec{u}'(\vec{u}\cdot\vec{u}')^2\psi(\vec{u}') - \lambda\right\} = 0$$

This gives

$$\psi(\vec{u}) = Ce^{-\beta w_{mf}(\vec{u})}$$

where C is a normalization constant, and $w_{mf}(\vec{u})$ is given by

$$w_{mf}(\vec{u}) = -U\int d\vec{u}'(\vec{u}\cdot\vec{u}')^2\psi(\vec{u}')$$

This equation indicates that at equilibrium, the distribution of $\vec{u}$ is given by the Boltzmann distribution in the mean field potential $w_{mf}(\vec{u})$. Equations (5.17) and (5.18) form an integral equation for $\psi(\vec{u})$. This integral equation can be solved rigorously as we shall see in the next section.

3.1 Self-consistent equation

The mean field potential can be written as

$$w_{mf}(\vec{u}) = -U\int d\vec{u}'(\sum_\alpha u_\alpha u'_\alpha)^2\psi(\vec{u}') = -U\int d\vec{u}'(\sum_\alpha\sum_\beta u_\alpha u'_\alpha u_\beta u'_\beta)\psi(\vec{u}')$$

$$w_{mf}(\vec{u}) = -U \sum_{\alpha} \sum_{\beta} u_\alpha u_\beta < u'_\alpha u'_\beta >$$

where we have used the fact that the distribution of $\vec{u}'$ is the same as that of $\vec{u}$. The average can be expressed by the scalar order parameter S. Let us take the z-axis in the direction of $\vec{n}$. Then

$$S = \frac{3}{2} < u_z^2 - \frac{1}{3} >$$

Since the distribution of $\vec{u}$ has uniaxial symmetry around the z-axis, $< u_\alpha u_\beta >= 0$ for $\alpha \neq \beta$ and the other components are calculated as

$$< u_z^2 >= \frac{1}{3}(2S+1)$$

$$< u_x^2 >=< u_y^2 >= \frac{1}{2}(1- < u_z^2 >) = \frac{1}{3}(-S+1)$$

Hence the mean field potential

$$w_{mf}(\vec{u}) = -U \sum_{\alpha} \sum_{\beta} u_\alpha u_\beta < u'_\alpha u'_\beta >= -U(u_x^2 < u_x^2 > + u_y^2 < u_y^2 > + u_z^2 < u_z^2 >=$$

$$-U(u_x^2 + u_y^2)\frac{1}{3}(-S+1) + u_z^2 \frac{1}{3}(2S+1) = -U(1-u_z^2)\frac{1}{3}(-S+1) + u_z^2\frac{1}{3}(2S+1) =$$

$$= -USu_z^2 + \text{ constant}$$

Therefore the equilibrium distribution function is given by

$$\psi(\vec{u}) = Ce^{\beta U S u_z^2}$$

Now that we know $\psi(\vec{u})$, we can evaluate S, using the definition $S = 3/2 < u_z^2 - 1/3 >$. One then obtain the following self-consistent equation for S

$$S = \frac{\int d\vec{u}\psi(\vec{u})\frac{3}{2}\left(u_z^2 - \frac{1}{3}\right)}{\int d\vec{u}\psi(\vec{u})} = \frac{\int d\vec{u}e^{\beta U S u_z^2}\frac{3}{2}\left(u_z^2 - \frac{1}{3}\right)}{\int d\vec{u}e^{\beta U S u_z^2}} = \frac{\int du_z e^{\beta U S u_z^2}\frac{3}{2}\left(u_z^2 - \frac{1}{3}\right)}{\int du_z e^{\beta U S u_z^2}}$$

We introduce the parameter $x = \beta U S$ and define $t \equiv u_z$. The previous equation is then written as

$$\frac{k_B T}{U} x = I(x)$$

where (being the integrand even in u_x)

$$I(x) = \frac{3}{2} \frac{\int_0^1 dt \left(t^2 - \frac{1}{3}\right) e^{xt^2}}{\int_0^1 dt e^{xt^2}}$$

Note that $I(0) = 0$, and hence $x = 0$ is always a solution.

The equation $\frac{k_BT}{U}x = I(x)$ can be solved by a graphical method: the solution is given by the intersection between the line $y = (k_BT/U)x$ and the curve $y = I(x)$. This shown in the figure. At high temperature, there is only one solution at $x = 0$ which corresponds to the isotropic phase ($S = 0$). With decreasing temperature, two non-zero solutions appear below the temperature T_{c1} defined in the figure. With decreasing the temperature further, one solution increases, while the other solution decreases, crossing zero at the temperature T_{c2}. Part (b) of the figure summarizes this behaviour of the solution S plotted against the temperature T.

3.2 Free energy function for the order parameter

In order to identify the transition temperature, we consider the free energy $F(S, T)$ of the system for a given value of the order parameter S. $F(S, T)$ represents the free energy of a system in which the order parameter is hypothetically constrained at S. If the system consists of N molecules each pointing the direction u_i ($i = 1, 2, ..., N$), $F(S, T)$ is defined as the free energy of the system under the constraint

$$\frac{1}{N}\sum_i \frac{3}{2}\left(u_{iz}^2 - \frac{1}{3}\right) = S$$

In general, the free energy under certain constraints is called the restricted free energy. $F(S, T)$ is an example of the restricted free energy. If the free energy $F(S, T)$ is known, the equilibrium value of S is determined by the condition that $F(S, T)$ becomes a minimum at equilibrium, i.e.,

$$\frac{\partial F}{\partial S} = 0$$

In the mean field approximation, $F(S, T)$ can be calculated by minimizing the free energy functional with respect to ψ under the constraint

$$\int \vec{u}\psi(\vec{u})\frac{3}{2}\left(u_z^2 - \frac{1}{3}\right) = S$$

Alternatively, if the temperature dependence of the solution of eq. (5.29) is known, the qualitative form of $F(S, T)$ can be inferred from the fact that the solution corresponds to the extremum of the function $F(S, T)$. This is shown in Fig. 5.4. For example, since there is only one solution at $S = 0$ for $T > T_{c1}$, $F(S, T)$ should have only one minimum at $S = 0$ for $T > T_{c1}$. This corresponds to the curve (i) in Fig. 5.4. Below T_{c1}, the equation $\frac{\partial F}{\partial S} = 0$ has three solutions. This corresponds to two local minima and one local maximum. The solution $S = 0$ corresponds to the isotropic state, and the other solutions correspond to the nematic state. Therefore, below T_{c1}, $F(S, T)$ behaves as shown by curve (iii) in Fig. 5.4. At temperature T_{c2}, the local minimum at $S = 0$ now becomes a local maximum, i.e.,

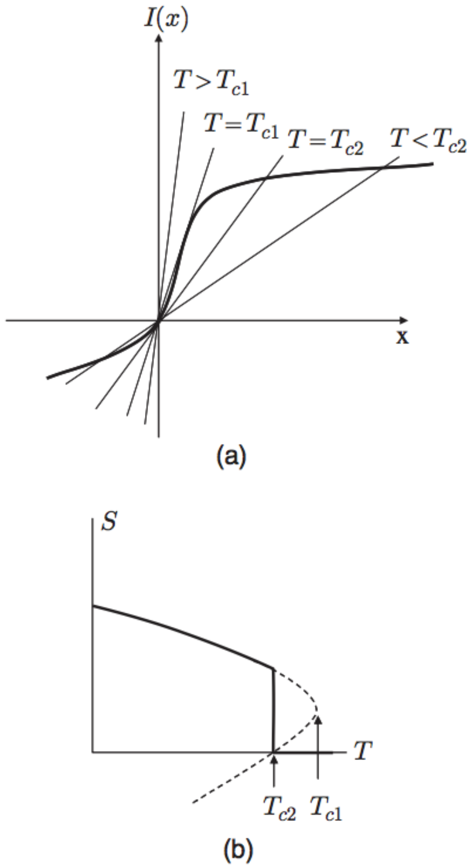


Fig. 5.3 (a) Graphical solution of eq. (5.26). T_{c1} corresponds to the temperature at which the line $y = (k_B T/U)x$ touches the curve $y = I(x)$ at certain positive x. T_{c2} corresponds to the temperature at which the line $y = (k_B T/U)x$ touches the curve $y = I(x)$ at $x = 0$. (b) The scalar order parameter S is plotted against temperature. The solid line indicates the trajectory that the system follows when the temperature is decreased continuously.

the isotropic state becomes an unstable state. Therefore $F(S,T)$ behaves as shown by the curve (vii) in Fig. 5.4. The free energy of the isotropic state becomes equal to that of the nematic state at a certain temperature T_e between T_{c1} and T_{c2}. The temperature T_e corresponds to the equilibrium transition temperature.

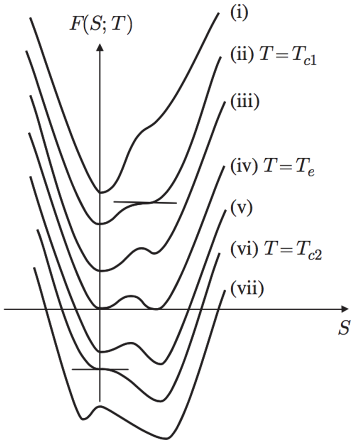


Fig. 5.4 Temperature dependence of the free energy curve $F(S;T)$ which gives the curve $S(T)$ shown in Fig. 5.3(b).

4 Effect of a spatial gradient on the nematic order

4.1 Free energy functional for a non-uniformly ordered state

So far, we have been assuming that the order parameter does not depend on position, i.e., the system is spatially uniform. Let us now consider the situation that the order parameter $\mathbf{Q}$ varies with position. This situation has practical importance since the order parameter of nematics contained in a cell is strongly influenced by the constraints imposed by the cell walls. To discuss the equilibrium of a non-uniformly ordered state, we consider the free energy functional $F_{tot}[\mathbf{Q}(\vec{r})]$ that is representative of the system in which the order parameter at position $\vec{r}$ is $\mathbf{Q}(\vec{r})$. If there are no external fields, and no boundaries, the equilibrium state should be the uniform state in which the order parameter $\mathbf{Q}(\vec{r})$ is independent of position $\vec{r}$. If the order parameter varies with position, the free energy of the system must be larger than that of the uniform state. Therefore $F_{tot}[\mathbf{Q}(\vec{r})]$ should be written as follows

$$F_{tot} = \int d\vec{r}[f(\mathbf{Q}(\vec{r})) + f_{el}(\mathbf{Q}(\vec{r}), \nabla\mathbf{Q}(\vec{r}))]$$

The first term $f(\mathbf{Q}(\vec{r}))$ is the free energy density for a uniform system, and is essentially the same studied previously. (A small letter f is used to emphasize that it is a free energy per unit volume.) The second term $f_{el}(\mathbf{Q}(\vec{r}), \nabla\mathbf{Q}(\vec{r}))]$ is the excess free energy due to the spatial gradient of $\mathbf{Q}$. If $\nabla\mathbf{Q}(\vec{r}))$ is small, f_{el} can be expanded as a power series of $\nabla\mathbf{Q}(\vec{r}))$. Since the free energy is a minimum in the uniform state (the state of $\nabla\mathbf{Q}(\vec{r})) = 0)$, the lowest term must be written as

$$f_{el}(\mathbf{Q}(\vec{r}), \nabla\mathbf{Q}(\vec{r})) = \frac{1}{2}K_{\alpha\beta\gamma,\alpha'\beta'\gamma'}\nabla_\alpha Q_{\beta\gamma}\nabla_{\alpha'}Q_{\beta'\gamma'}$$

Since this is an expansion with respect to $\nabla\mathbf{Q}(\vec{r}))$, the coefficient $K_{\alpha\beta\gamma,\alpha'\beta'\gamma'}$ does not depend on $\nabla\mathbf{Q}(\vec{r}))$, but can depend on $\mathbf{Q}$. It represents the component of a positive definite symmetric tensor. We shall now discuss the explicit form of $f_{el}(\mathbf{Q}(\vec{r}), \nabla\mathbf{Q}(\vec{r}))$ for the isotropic and nematic states.

4.1.1 Effect of the gradient terms in the disordered phase

In the isotropic state, we may assume that $K_{\alpha\beta\gamma,\alpha'\beta'\gamma'}$ is independent of $\mathbf{Q}$ since $\mathbf{Q}$ is small in the isotropic state. Hence f_{el} is a scalar constructed by a quadratic form of $\nabla\mathbf{Q}(\vec{r}))$. Using the properties $Q_{\alpha\beta} = Q_{\beta\alpha}$ and $\sum_\alpha Q_{\alpha\alpha} = 0$, we can show that f_{el} is written in the following form:

$$f_{el}(\mathbf{Q}(\vec{r}), \nabla\mathbf{Q}(\vec{r})) = \frac{1}{2}K_1\nabla_\alpha Q_{\beta\gamma}\nabla_\alpha Q_{\beta\gamma} + \frac{1}{2}K_2\nabla_\alpha Q_{\alpha\gamma}\nabla_\beta Q_{\beta\gamma}$$

where K_1 and K_2 are positive constants. Thus the free energy functional in the isotropic state is written as

$$F_{tot} = \int d\vec{r}\left[\frac{1}{2}A(T-T_c)S^2 + \frac{1}{2}K_1\nabla_\alpha Q_{\beta\gamma}\nabla_\alpha Q_{\beta\gamma} + \frac{1}{2}K_2\nabla_\alpha Q_{\alpha\gamma}\nabla_\beta Q_{\beta\gamma}\right]$$

where we have ignored higher order terms in $\mathbf{Q}$.

Note that the scalar $\nabla_\alpha Q_{\beta\gamma}\nabla_\beta Q_{\alpha\gamma}$ is not included since it is transformed to the second term on the right-hand side f_{el} by integration by parts.

As an application, let us consider the local ordering induced by a wall of solid substrate. The molecules near the wall feel the potential of the wall, and their orientational distribution is not isotropic even in the isotropic state. Consider the situation shown in Fig. 5.7(a), where the molecules tend to align in the direction normal to the wall. If we take the x, y, z coordinates as in Fig. 5.7(a), the order parameter $Q_{\alpha\beta}(x)$ can be written as follows

$$Q_{xx} = S, \quad Q_{yy} = Q_{zz} = -\frac{1}{2}S, \quad Q_{xy} = Q_{yz} = Q_{zx} = 0$$

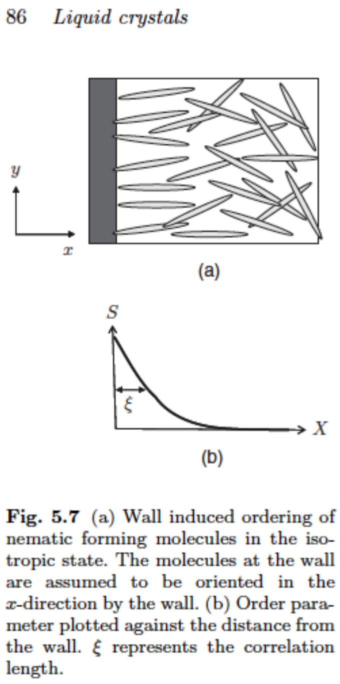

86 *Liquid crystals*

Fig. 5.7 (a) Wall induced ordering of nematic forming molecules in the isotropic state. The molecules at the wall are assumed to be oriented in the x-direction by the wall. (b) Order parameter plotted against the distance from the wall. ξ represents the correlation length.

Substituting this for $Q_{\alpha\beta}(x)$, we have that the only non zero contributions are the one arising from the d/dx terms. Then

$$\nabla_\alpha Q_{\beta\gamma}\nabla_\alpha Q_{\beta\gamma} = \sum_\alpha\sum_\beta\sum_\gamma \nabla_\alpha Q_{\beta\gamma}\nabla_\alpha Q_{\beta\gamma} = \sum_\beta\sum_\gamma (\nabla_x Q_{\beta\gamma})^2 = (\nabla_x Q_{xx})^2 + (\nabla_x Q_{yy})^2 + (\nabla_x Q_{zz})^2 =$$

$$= \left(\frac{dS}{dx}\right)^2 \left(1 + \frac{1}{4} + \frac{1}{4}\right) = \frac{3}{2}\left(\frac{dS}{dx}\right)^2$$

and

$$\nabla_\alpha Q_{\alpha\gamma}\nabla_\beta Q_{\beta\gamma} = \sum_\alpha\sum_\beta\sum_\gamma \nabla_\alpha Q_{\alpha\gamma}\nabla_\beta Q_{\beta\gamma} = \sum_\gamma \nabla_x Q_{x\gamma}\nabla_x Q_{x\gamma} = (\nabla_x Q_{xx})^2$$

where we have imposed that both α β and γ have to be x to obtain a non-zero result. Then

$$\nabla_\alpha Q_{\alpha\gamma}\nabla_\beta Q_{\beta\gamma} = \left(\frac{dS}{dx}\right)^2$$

resulting in

$$F_{tot} = \int dx \left[\frac{1}{2}A(T - T_c)S^2 + \frac{3}{4}K_1\left(\frac{dS}{dx}\right)^2 + \frac{1}{2}K_2\left(\frac{dS}{dx}\right)^2\right] =$$

$$\frac{1}{2}A(T-T_c)\int dx\left[S^2+\xi^2\left(\frac{dS}{dx}\right)^2\right]$$

where ξ is defined by

$$\xi=\sqrt{\frac{(3K_1+2K_2)}{2A(T-T_c)}} \tag{5}$$

To calculate δF_{tot} we write

$$(S+\delta S)^2+\xi^2\left(\frac{d(S+\delta S)}{dx}\right)^2-\left[S^2+\xi^2\left(\frac{dS}{dx}\right)^2\right]=$$

$$S^2+\delta S^2+2S\delta S+\xi^2\left(\frac{dS}{dx}\right)^2+\left(\frac{d\delta S}{dx}\right)^2+2\frac{d\delta S}{dx}\frac{dS}{dx}-\left[S^2+\xi^2\left(\frac{dS}{dx}\right)^2\right]=$$

and neglecting higher orders in δS,

$$=2S\delta S+2\xi^2\frac{d\delta S}{dx}\frac{dS}{dx}$$

So that

$$\delta F_{tot}=A(T-T_c)\int dx\left(S\delta S+\xi^2\frac{d\delta S}{dx}\frac{dS}{dx}\right)$$

and integrating by part and neglecting the boudary value (assuming $\delta S=0$ at $x=0$ ($S(0)$ is fixed by the boundary) and $dS/dx=0$ at $x=\infty$)

$$\delta F_{tot}=A(T-T_c)\int dx\left(S-\xi^2\frac{d^2S}{dx^2}\right)\delta S$$

Thus the condition that minimize the free energy is

$$\xi^2\frac{d^2S}{dx^2}=S$$

Therefore

$$S=S_0e^{-x/\xi}$$

where S_0 is the value of S at the wall.

The previous equation indicates that the wall affects the molecular orientation up to the distance ξ from the wall. Notice that the wall effect is intrinsically short ranged: only the molecules close to the wall feel the wall potential. However, the effect of the wall propagates into the bulk due to the tendency of the local ordering of the molecules. The length ξ represents how far this effect persists, and is called the correlation length.

The correlation length ξ can be regarded as the size of the locally ordered region in the disordered phase. As indicated by eq. 5, ξ diverges as T approaches T_c. Therefore, near the transition temperature, a large number of molecules move collectively. This is the reason why the response of the order parameter diverges at the transition temperature T_c.

4.1.2 Effect of the gradient terms in the ordered phase

As previously discussed when an external field is applied to the ordered phase, the scalar order parameter S changes little, while the director $\vec{n}$ changes drastically. Therefore we may assume that in the ordered phase the tensor order parameter $\mathbf{Q}$ can be written as

$$\mathbf{Q}(\vec{r}) = S_{eq}\left[n(\vec{r})n(\vec{r}) - \frac{1}{3}\mathbf{I}\right]$$

where S_{eq} is the equilibrium value of S in the absence of an external field. If this expression for $\mathbf{Q}$ is used, $f(\mathbf{Q})$ becomes constant, and may be dropped in the subsequent calculation. On the other hand, f_{el} can be written as a quadratic form of $\nabla\vec{n}$. The coefficient $K_{\alpha\beta\gamma,\alpha'\beta'\gamma'}$ may depend on $\vec{n}$. Repeating the same argument as in the previous section, it is possible to show that f_{el} can be written in the following form

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

where K_1, K_2, K_3 are constants having dimension of [J/m], and are called the Frank elastic constants. Note that in this way all contributions are quadratic in the gradient of $\vec{n}$ and are thus equal for positive or negative changes in $\vec{n}$. Each constant represents the resistance of the nematics to the spatial variation of $\vec{n}$ (see figure). The constants K_1, K_2, and K_3 are called the splay, twist, and bend constants, respectively.

Note that in the Figure 10.11 the gradient is always in the same direction (z direction). The three cases differ for having

- Splay

$$dn \parallel \hat{z} \qquad n \perp \hat{z}$$

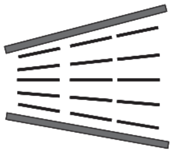
- Twish

$$dn \perp \hat{z} \qquad n \perp \hat{z}$$

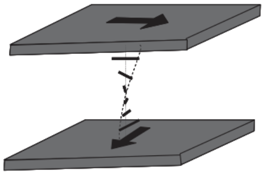
- Bend

$$dn \perp \hat{z} \qquad n \parallel \hat{z}$$

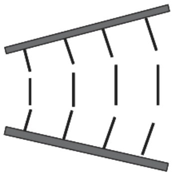
To be precise, there is also one additional mode, called saddle-splay, describing a surface elastic term, which is irrelevant when $\vec{n}$ is pinned at the interface.



(a) splay



(b) twist



(c) bend

Fig. 5.8 Examples of spatial variation of director $\boldsymbol{n}$ which gives the Frank elastic energy represented by eq. (5.53): (a) splay (for which $\boldsymbol{\nabla} \cdot \boldsymbol{n} \neq 0$); (b) twist ($\boldsymbol{\nabla} \times \boldsymbol{n} \neq 0$); (c) bend ($\boldsymbol{n} \times (\boldsymbol{\nabla} \times \boldsymbol{n}) \neq 0$).

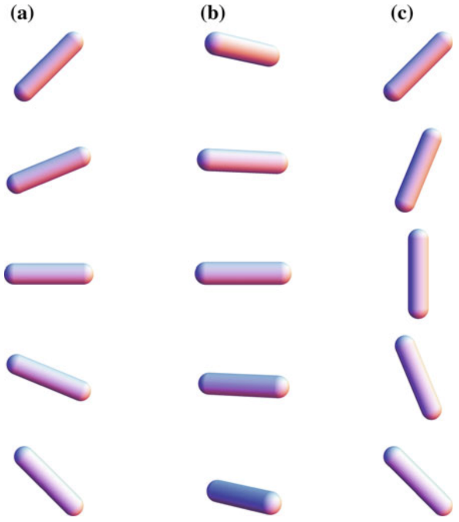


Fig. 10.11 Visualization of the three nematic modes of distortion: **a** Splay. **b** Twist. **c** Bend (Interactive version at http://www.springer.com/cda/content/document/cda_downloaddocument/Selinger+Interactive+Figures.zip?SGWID=0-0-45-1509169-p177545420.)

ditions at $x = 0$ and $x = L$. What will be the equilibrium configuration in this situation?

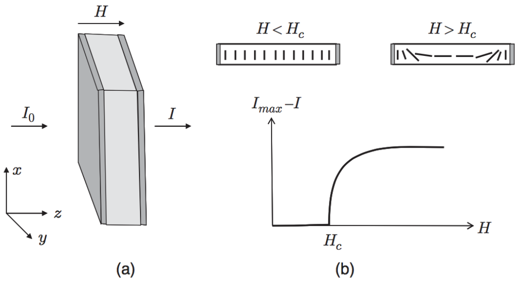


Fig. 5.9 (a) Model of an optical switch cell utilizing the Fredericks transition. Light is transmitted across the cell shown in Fig. 5.2, where the direction of the polarizer makes 45 degrees with the x-axis in the x–y plane. The cell consists of two polarizing plates and a nematic layer. The director $\boldsymbol{n}$ is fixed in the x-direction at the cell wall. Upon the inception of the magnetic field, the nematics tend to align in the z-direction. (b) If H is less than the critical field H_c, the nematic remains aligned in the x-direction, and the light is transmitted. If H is larger than H_c, the nematics start to align in the z-direction, and the light is not transmitted. The intensity of the transmitted light changes steeply at H_c.

4.1.3 Fredericks transition

As an application of the above theory, let us consider the problem illustrated in Fig. 5.9(a). A nematic liquid crystal is sandwiched between two plates. We take the z-axis normal to the plate. At the wall of the plate, we assume that the director is in the x-direction. Suppose that we apply a magnetic field H in the z-direction. Then the molecules tend to orient along the z direction, but this is not compatible with the boundary conditions at $x = 0$ and $x = L$. What will be the equilibrium configuration in this situation? We can call x the direction of $\vec{n}$ at $z = 0$ and assume that $\vec{n}$ is in $x - z$ plane, and only depends on the z-coordinate. Hence the x, y, z components of $\vec{n}$ are given by

$$\begin{aligned} n_x(z) &= \cos\theta(z) \\ n_y(z) &= 0 \\ n_z(z) &= \sin\theta(z). \end{aligned} \tag{6}$$

In this case, $\vec{n}\ \nabla \cdot \vec{n}$ and $\nabla \times \vec{n}$ are given by

$$\vec{n} = (\cos\theta, 0, \sin\theta)$$

$$\nabla \cdot \vec{n} = \frac{\partial n_z}{\partial z} = \cos\theta \frac{d\theta}{dz}$$

$$\nabla \times \vec{n} = \left(0, \frac{\partial n_x}{\partial z}, 0\right) = \left(0, -\sin\theta \frac{d\theta}{dz}, 0\right)$$

Since $\vec{n} \cdot (\nabla \times \vec{n}) = 0$, there is no twist ($K_2 = 0$) and the free energy is given by the sum of the elastic and of the magnetic terms

$$F_{tot} = \int dz(f_{el} + f_H) = \int dz \left[\frac{1}{2}K_1 \cos^2\theta \left(\frac{d\theta}{dz}\right)^2 + \frac{1}{2}K_3 \sin^2\theta \left(\frac{d\theta}{dz}\right)^2 - \frac{1}{2}\mathit{\Delta}\chi H^2 \sin^2\theta\right]$$

$\theta(z)$ has to satisfy the following boundary condition $\theta(0) = \theta(L) = 0$. The equilibrium solution is given by the $\theta(z)$ which minimizes the free-energy under the condition imposed by the boundary conditions at $x = 0$ and $x = L$ [$\theta(0) = \theta(L) = 0$]. If the magnetic field H is weak, the solution is given by $\theta(z) = 0$. As the magnetic field increases, the solution becomes unstable, and a new solution appears. Therefore the structure of the problem is the same as that in the order-disorder transition. To pursue this resemblance, we assume that the solution has the following functional form

$$\theta(z) = \theta_0 \sin\frac{\pi z}{L}$$

and express the free energy F_{tot} as a function of θ_0. If θ_0 is small, then $\cos^2\theta \approx 1$ and $\sin^2\theta \approx \theta_0^2 \sin^2\frac{\pi z}{L}$ so that F_{tot} can be calculated analytically to order θ_0^2, and it is given, piece by piece, by (remembering that $\int_0^\pi dxcos^2(x) = \frac{\pi}{2}$)

- $$\int dz \frac{1}{2} K_1 \cos^2\theta \left(\frac{d\theta}{dz}\right)^2 \approx \int dz \frac{1}{2} K_1 \left(\frac{d\theta}{dz}\right)^2 = \frac{1}{2} K_1 \int_0^L dz \left(\theta_0 \frac{\pi}{L} \cos \frac{\pi z}{L}\right)^2 =$$
  $$\frac{1}{2} K_1 \theta_0^2 \frac{\pi}{L} \int_0^L \frac{\pi}{L} dz \cos^2 \frac{\pi z}{L} = \frac{1}{2} K_1 \frac{\pi}{L} \theta_0^2 \frac{\pi}{2}$$
- $$\int dz \frac{1}{2} K_3 \sin^2\theta \left(\frac{d\theta}{dz}\right)^2 \approx \frac{1}{2} K_3 \int dz \theta_0^2 \sin^2 \frac{\pi z}{L} \left(\theta_0 \frac{\pi}{L} \cos \frac{\pi z}{L}\right)^2 \approx 0$$
  which can be neglected being order θ_0^4.
- $$\int dz \frac{1}{2} \Delta\chi H^2 \sin^2\theta \approx \frac{1}{2} \Delta\chi H^2 \frac{L}{\pi} \int_0^\pi sin^2 y dy = \frac{1}{2} \Delta\chi H^2 \frac{L}{2}$$

Thus to order θ_0^2,

$$F_{tot} = \frac{1}{4}\left[\frac{K_1 \pi^2}{L} - \Delta\chi H^2 L\right] \theta_0^2 = \frac{1}{4} \Delta\chi L (H_c^2 - H^2) \theta_0^2$$

where

$$H_c = \sqrt{\frac{K_1 \pi^2}{\Delta\chi L^2}}$$

Therefore if $H < H_c$, the solution $\theta_0 = 0$ is stable, and if $H > H_c$ the solution is unstable. Notice that the transition taking place at H_c is continuous, since the free energy is an even function of θ_0. Such a transition is called the Fredericks transition. The Fredericks transition is important in the application of nematics to displays since the light transmission across the nematic layer changes sharply at the critical field.

5 Onsager's theory

5.1 Nematic ordering in hard cylinders

While HS crystallisation, in two and three dimensions, shows the power of the entropy associated to particle center of mass position, the nematic transition provides evidence of the important entropic contributions arising from particle orientation. Interestingly, the possibility that entropy could act as an ordering force was already evident in Onsager's theory on the effect of shape in colloidal solutions, a contribution which had appeared in the Annales of the New York Academy of Science already in 1949, several years before the debate on hard-sphere crystallization.

Let's assume that particles can be considered distinct according to the orientation of their principal axis $\mathbf{a}$. The idea is to write the configurational part of the partition function $Z_{ig}(V)$ of an ideal gas of particles oriented according to some pre-defined distribution $\{N_i\}$, where N_i is the number of particles oriented in the solid angle $\varDelta\varOmega_i$. If the $\{N_i\}$ are chosen to be equally probable (isotropic distribution of orientations), then $\ln Z_{ig}(V)$ will provide the appropriate free energy (the entropy) of the isotropic phase. If the $\{N_i\}$ are chosen in such a way that one particular orientation is preferred, then the calculated $\ln Z_{ig}(V)$ will provide the entropy of the nematic phase described by $\{N_i\}$. This exercise can be repeated for several $\{N_i\}$ distributions to identify the most probable one (the one with the highest entropy). By comparing the entropy of the isotropic phase and the entropy of the most disordered nematic phase, Onsager predicted the existence of a first-order phase transition.

For a set of orientations $\{N_i\}$, with $N_i = Nf(\mathbf{a})\varDelta\varOmega$ (where $f(\mathbf{a})$ is the probability that the molecule is oriented along $\mathbf{a}$ in the solid angle $\varDelta\varOmega = d\mathbf{a}$) $Z_{ig}(V)$ can be written as (using the thermal wavelength as unit of length)

$$Z_{ig}(V) = \prod_i \frac{1}{N_i!}\left[\frac{\varDelta\varOmega}{4\pi}\int d\mathbf{r}\right]^{N_i} \tag{7}$$

corresponding, using Stirling's approximation, to an entropy $S(V) \equiv k_B \ln Z(V)$

$$\frac{S_{ig}(V)}{k_B} = \sum_i N_i \left[1 + \ln\left(\frac{V\varDelta\varOmega}{4\pi N_i}\right)\right]. \tag{8}$$

With a little bit of math,

$$\frac{S_{ig}(V)}{k_B} = \sum_i N_i \left[1 + \ln\left(\frac{V}{4\pi f(\mathbf{a})N}\right)\right] = N\left[1 + \ln\left(\frac{V}{N}\right)\right] + \int Nf(\mathbf{a})d\mathbf{a}\ln\left(4\pi f(\mathbf{a})\right)$$

where we recognize the translational entropy of the center of mass of each particle and the orientational entropy associated to the distribution $f(\mathbf{a})$. Naturally,

$$\int f(\mathbf{a})d\varOmega = 1. \tag{9}$$

If we add the virial contribution, therefore going beyond the ideal gas approximation, we obtain

$$\frac{S(V)}{k_B} = N\left[1 + \ln\left(\frac{V}{N}\right)\right] + \int Nf(\mathbf{a})d\mathbf{a}\ln\left(4\pi f(\mathbf{a})\right) + \frac{1}{2V}\sum_{i,j}\beta(\mathbf{a_i},\mathbf{a_j})N_iN_j, \tag{10}$$

where $\beta(\mathbf{a_i},\mathbf{a_j})$ is the virial coefficient (the excluded volume) between two particles oriented as $\mathbf{a_i}$ and $\mathbf{a_j}$. The virial contribution is strongly dependent on the relative orientation of the two particles, as shown in Fig. 1-(a-b). Parallel cylinders can be packed much more efficiently than perpendicular cylinders.

For cylinders of length L and diameter D, indicating with γ the angle between $\mathbf{a_i}$ and $\mathbf{a_j}$

$$-\beta(\gamma) = \frac{\pi}{2}D^3 \sin\gamma + \frac{\pi}{2}LD^2 + \frac{\pi}{2}LD^2|\cos\gamma| + 2LD^2E(\sin\gamma) + 2L^2D|\sin\gamma|, \tag{11}$$

where

$$E(\sin\gamma) = \int_0^{\frac{\pi}{2}} (1-\sin^2\gamma\sin^2\phi)^{1/2}d\phi. \tag{12}$$

In the limit of elongated particles, $L \gg D$,

$$\beta(\gamma) = -2L^2D|\sin\gamma|. \tag{13}$$

Hence, in this limit, parallel cylinders do not exclude volume ($|\sin\gamma| = 0$), while perpendicular ones exclude the largest possible volume $2L^2D$.

In the isotropic phase all orientations are equally probable and $f(\mathbf{a}) = \frac{1}{4\pi}$.

In the nematic phase we do not know a priori $f(\mathbf{a})$. As commonly done by physicists, Onsager postulated a reasonable functional form for $f(\mathbf{a})$ based on a free parameter α, a form for which he was able to solve all integrals requested in the calculation of $S(V)$. The parameter α was then evaluated as the one that maximizes the resulting nematic entropy.

The functional form chosen by Onsager was based on the physical intuition that in the nematic phase all particles are essentially oriented around the nematic direction (as in matches or spaghetti in their boxes). $f(\mathbf{a})$ should then be peaked around $\theta = 0$ and $\theta = \pi$, indicating with θ the angle between $\mathbf{a}$ and the nematic direction. For mathematical convenience he chose the function

$$f(\theta) = \Big(\frac{\alpha}{4\pi\sinh\alpha}\Big)\cosh(\alpha\cos\theta), \tag{14}$$

whose angle dependence is reproduced in Fig. 1-(c). In the limit of $\alpha \gg 1$ this functional form is indeed peaked around $\theta = 0$ and $\theta = \pi$.

The entropy at the ideal gas level, for either the isotropic or the nematic phase is

$$-\frac{S_{ig}(V)}{k_B} = \sum_i N_i\left[1+\ln\left(\frac{V\mathit{\Delta\Omega}_i}{4\pi N_i}\right)\right] = \tag{15}$$

$$N\left[1+\ln\left(\frac{V}{N}\right)\right] - N\int f(\mathbf{a})\ln\left(4\pi f(\mathbf{a})\right)d\mathit{\Omega}$$

The first contribution is the entropy associated to the center of mass of the particles, the standard ideal gas contribution. The second contribution depends only on the distribution of orientations and defines the orientational entropy of the system.

In the isotropic case, the orientational contribution vanishes since $f(\mathbf{a}) = \frac{1}{4\pi}$ and

$$\int f(\mathbf{a}) \ln \left[4\pi f(\mathbf{a})\right] d\Omega. = 0 \tag{16}$$

In the nematic phase the ideal gas orientational entropy is not zero. For the functional form postulated by Onsager (Eq. 14) the orientational entropy can be calculated for large α resulting in

$$\int f(\mathbf{a}) \ln \left(4\pi f(\mathbf{a})\right) d\Omega = \log \alpha - 1 + \frac{2}{3\alpha}. \tag{17}$$

This contribution diverges to minus infinity on growing α, as expected by localization in classical physics.

The entropy associated to the excluded volume of course depends on the inter-particle orientation. Fig. 1-(a-b) shows the different excluded volume between pairs of cylinders perpendicularly or parallelely oriented. For the isotropic case, always in the limit $L \gg D$, (using $\int_0^\pi \sin^2 \gamma d\gamma = \pi/2$ and $\int_0^{2\pi} d\phi = 2\pi$) the virial contribution to entropy can be expressed as

$$\sum_{i,j} \beta(\mathbf{a_i}, \mathbf{a_j}) N_i N_j = 2L^2 D \int \int \beta(\gamma) \frac{N^2}{(4\pi)^2} d\Omega d\Omega' = \tag{18}$$

$$N^2 \frac{1}{4\pi} \int \beta(\gamma) sin\gamma d\gamma d\phi = -\frac{\pi}{2} L^2 D N^2.$$

The corresponding expression for the nematic case (see Onsager article)

$$\sum_{i,j} \beta(\mathbf{a_i}, \mathbf{a_j}) N_i N_j = N^2 \int \beta(\gamma) f(\Omega) f(\Omega') sin\gamma d\gamma d\phi \approx -2L^2 D N^2 \sqrt{\frac{\pi}{\alpha}}. \tag{19}$$

For each value of α, Onsager was than able to estimate the system entropy. By taking the derivative of the nematic entropy with respect to α and equating it to zero, he was also able to evaluate the value α_{max} for which the total entropy, sum of the ideal gas and of the virial term, is largest. Substitution of α_{max} in Eq. 19 and Eq. 17 provides the best approximation (based on the selected functional form Eq. 14) to the nematic free energy.

Fig. 1-(d) shows, for cylinders with $L = 5$ and $D = 1$, the orientational and virial contributions to the entropy. A significant volume dependence of the entropy is present in the virial component of the isotropic phase (due to the change in the available volume accessible to the center of mass) and in the orientational component of the nematic phase (due to progressive reduction of the particle orientation).

The resulting final expressions for the entropy in the isotropic and nematic phase as predicted by the Onsager theory for cylinders are (defining $\rho = N/V$)

$$S_{iso}^{Onsager} = N \left[-1 + \ln(\rho) + \rho \frac{\pi L^2 D}{4}\right] \tag{20}$$

and

$$S_{nematic}^{Onsager} = N\left[\ln\left(\rho^3 D^3 L^6 \frac{\pi^2}{16}\right)\right]. \tag{21}$$

Fig. 1-(e) shows $S_{iso}^{Onsager}$ and $S_{nematic}^{Onsager}$ (per particle) for $L/D = 5$ and again the ordered phase has a larger entropy at large densities. As in the previous HS case, the common tangent line to the expressions S vs V (equal P and μ) selects the densities of the two coexisting phases. For $L \gg D$ one finds for the two coexisting packing fractions

$$\phi_{isotropic} = \frac{3.3D}{L} \qquad \phi_{nematic} = \frac{4.5D}{L}.$$

Note that for very long cylinders, the nematic transition will be observed for very small packing fractions.

As a matter of terminology, if the isotropic-nematic transition is controlled by concentration, the system is called a lyotropic liquid crystal. By contrast, if the isotropic-nematic transition is controlled by temperature, the system is called a thermotropic liquid crystal. Hence, Onsager theory for hard rods in solution is an example of a lyotropic liquid crystal, and Maier-Saupe theory for interacting molecules is an example of a thermotropic liquid crystal.

The theory of Onsager, despite its approximations, has the strong merit of highlighting the important role of orientational entropy in the ordering process of colloidal anisotropic particles. Indeed, this theory has become the starting approach for understanding more and more complex mesophases (smectic, biaxial nematic, twist-bend nematic) progressively accompanying the synthesis of colloidal particles of more and more complex geometry, including ellipsoids, disks, helices and bent-shaped particles. It also provides a relevant framework for interpreting the self-assembly of colloidal particles aggregating in persistent one dimensional structures.

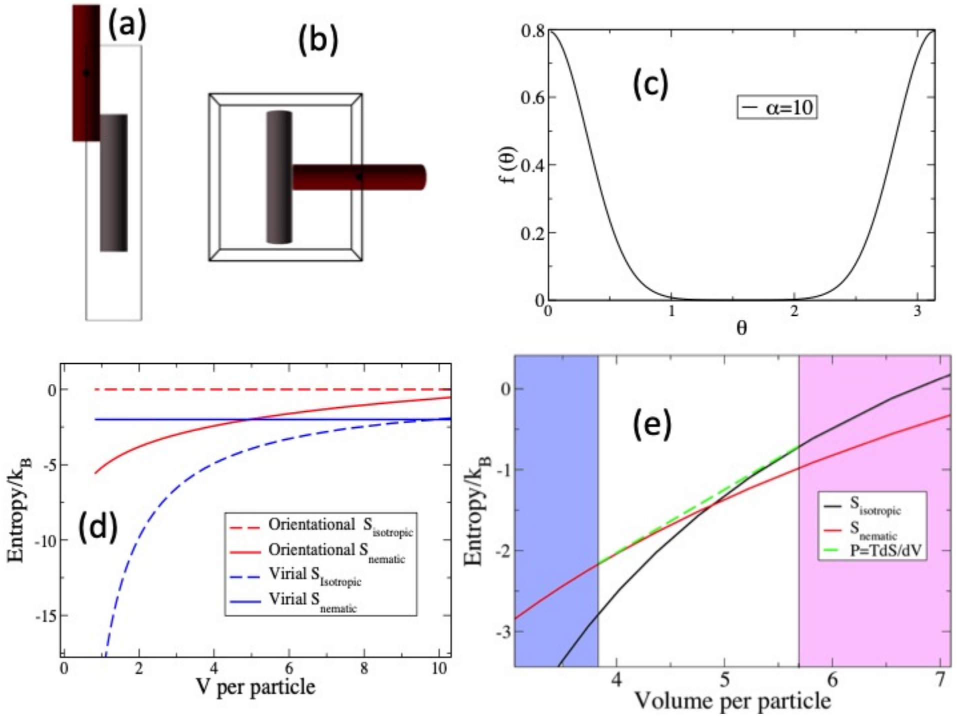


Figure 1: Isotropic-Nematic phase for hard cylinders. (a) Excluded volume between two coaxial cylinders. The center of mass of the red cylinder can not explore the volume $\pi D^2 L$, where D is the diameter and L the length. (b) Excluded volume between two perpendicular cylinders. The center of mass of the red cylinder can not explore the volume $\approx 2DL^2$. (c) The functional form for the probability of orientation θ with respect to the nematic vector selected by Onsager for the case $\alpha = 10$. (d) The volume V dependence of the different entropic contributions. (e) The entropy of the isotropic and of the nematic phase calculated according to the Onsager theory for cylinders of diameter $D = 1$ and $L = 5$. The dashed line is tangent to both the isotropic and the nematic entropy. Hence, since $P = TdS/dV$, the two tangent points indicate two volumes $V_{isotropic}$ and $V_{nematic}$ for which temperature, pressure, and chemical potential are identical.