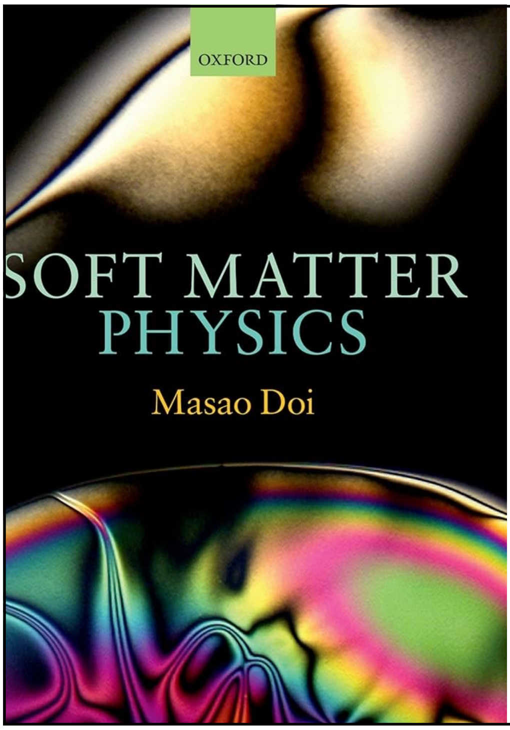
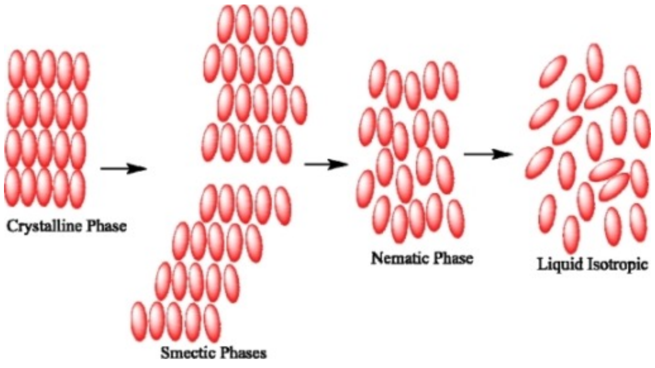


Liquid Crystals

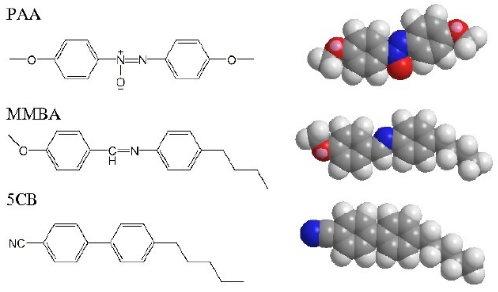
Liquid crystalline phases

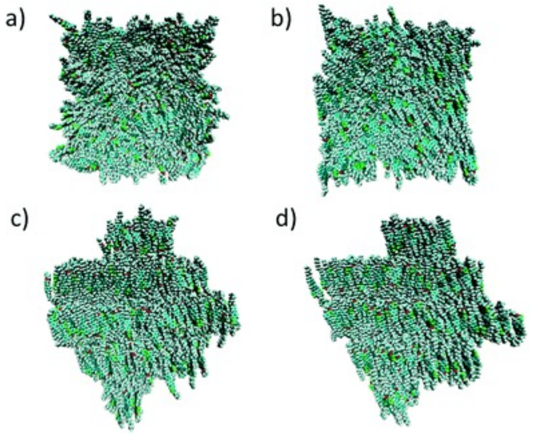
The nematic phase is formed by rod-like molecules. At high temperature, the orientation of the molecules is completely random, and the system is an isotropic liquid. With decreasing temperature, the molecules start to orient in a common direction and form the nematic phase.

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.



Common nematics





Orientational distribution function

Let us consider the distribution of the molecular orientation. Let u be a unit vector in the direction of the long axis of the molecule. In the isotropic phase, u will be uniformly distributed on a unit sphere |u| = 1.

In the nematic phase, the distribution of u becomes non-uniform on the sphere. Let ψ(u) be the distribution function of u on the unit sphere. It is normalized as

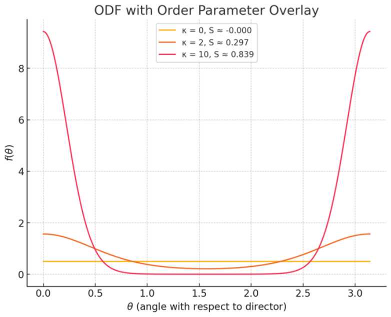
$$\int du\, \psi(u) = 1$$

where du= sinθdθdφ stands for the surface element of the sphere |u| = 1, and the integral is over the entire surface.

In the isotropic phase, ψ(u) is constant, independent of u, and therefore

$$\psi(u) = 1/4\pi$$

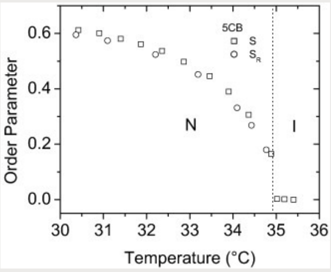
On the other hand, in the nematic phase, ψ(u) will be oriented toward the direction of the director **n**, and ψ(u) becomes anisotropic.

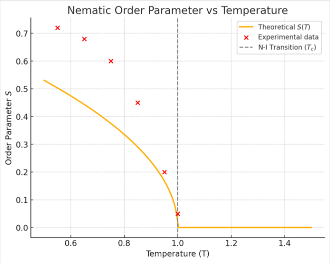


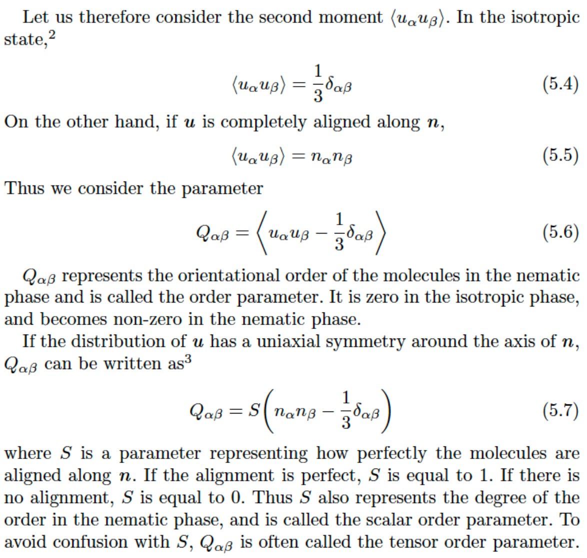
$$\psi(\boldsymbol{u}) = \psi(-\boldsymbol{u}).$$

$$\langle \cdots \rangle = \int d\boldsymbol{u} \cdots \psi(\boldsymbol{u})$$

Order parameter







Let us therefore consider the second moment $\langle u_\alpha u_\beta \rangle$. In the isotropic state,[2]

$$\langle u_\alpha u_\beta \rangle = \frac{1}{3}\delta_{\alpha\beta} \tag{5.4}$$

On the other hand, if $\boldsymbol{u}$ is completely aligned along $\boldsymbol{n}$,

$$\langle u_\alpha u_\beta \rangle = n_\alpha n_\beta \tag{5.5}$$

Thus we consider the parameter

$$Q_{\alpha\beta} = \left\langle u_\alpha u_\beta - \frac{1}{3}\delta_{\alpha\beta} \right\rangle \tag{5.6}$$

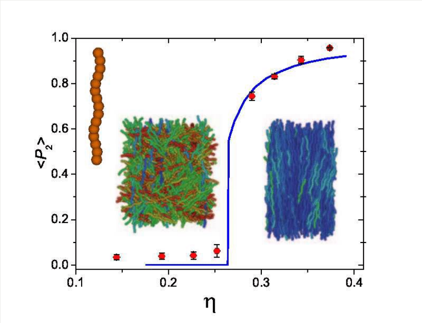
$Q_{\alpha\beta}$ represents the orientational order of the molecules in the nematic phase and is called the order parameter. It is zero in the isotropic phase, and becomes non-zero in the nematic phase.

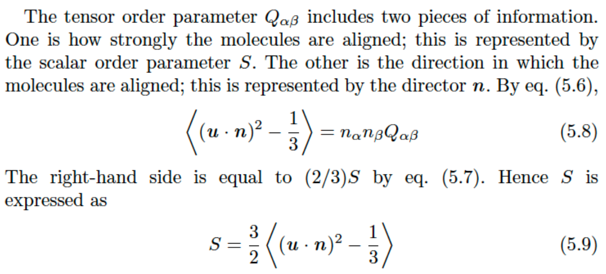
If the distribution of $\boldsymbol{u}$ has a uniaxial symmetry around the axis of $\boldsymbol{n}$, $Q_{\alpha\beta}$ can be written as[3]

$$Q_{\alpha\beta} = S\left(n_\alpha n_\beta - \frac{1}{3}\delta_{\alpha\beta}\right) \tag{5.7}$$

where S is a parameter representing how perfectly the molecules are aligned along $\boldsymbol{n}$. 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, $Q_{\alpha\beta}$ is often called the tensor order parameter.

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 $\boldsymbol{n}$. By eq. (5.6),

$$\left\langle (\boldsymbol{u}\cdot\boldsymbol{n})^2 - \frac{1}{3} \right\rangle = n_\alpha n_\beta Q_{\alpha\beta} \tag{5.8}$$

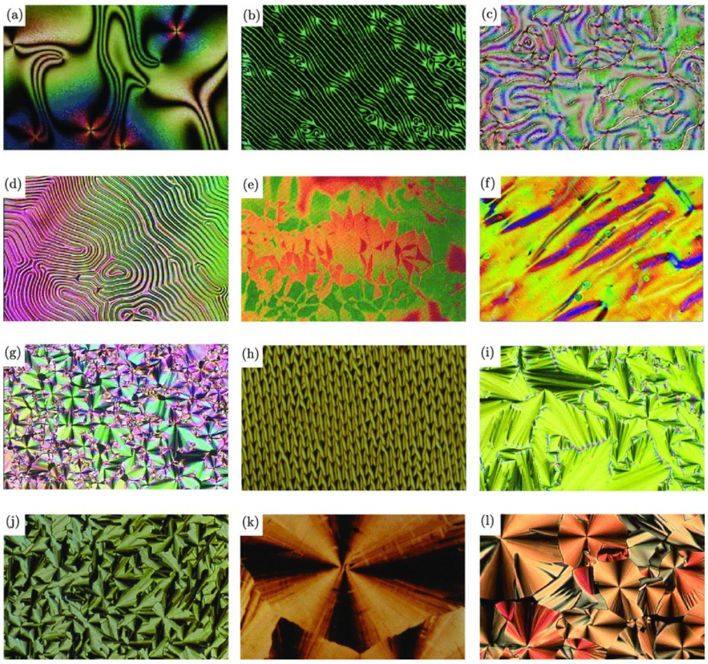
The right-hand side is equal to $(2/3)S$ by eq. (5.7). Hence S is expressed as

$$S = \frac{3}{2}\left\langle (\boldsymbol{u}\cdot\boldsymbol{n})^2 - \frac{1}{3} \right\rangle \tag{5.9}$$

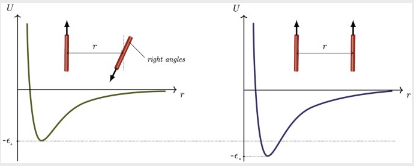
Textures

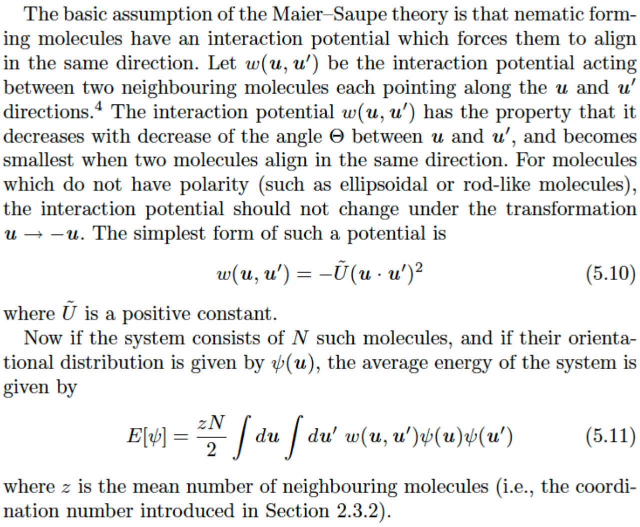
Birefringence: The colorful patterns arise due to the birefringent nature of liquid crystals, which split polarized light into two rays traveling at different speeds. When these rays recombine, they interfere, producing characteristic colors that depend on the molecular orientation and sample thickness.

Defects and Director Fields: The observed textures provide insights into the director field configurations and the presence of defects. For instance, the number and arrangement of brushes in schlieren textures can help determine the type and strength of disclinations.



Maier-Saupe





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 $w(\boldsymbol{u}, \boldsymbol{u}')$ be the interaction potential acting between two neighbouring molecules each pointing along the $\boldsymbol{u}$ and $\boldsymbol{u}'$ directions.[4] The interaction potential $w(\boldsymbol{u}, \boldsymbol{u}')$ has the property that it decreases with decrease of the angle Θ between $\boldsymbol{u}$ and $\boldsymbol{u}'$, 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 $\boldsymbol{u} \to -\boldsymbol{u}$. The simplest form of such a potential is

$$w(\boldsymbol{u}, \boldsymbol{u}') = -\tilde{U}(\boldsymbol{u} \cdot \boldsymbol{u}')^2 \tag{5.10}$$

where $\tilde{U}$ is a positive constant.

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

$$E[\psi] = \frac{zN}{2} \int d\boldsymbol{u} \int d\boldsymbol{u}' \; w(\boldsymbol{u}, \boldsymbol{u}')\psi(\boldsymbol{u})\psi(\boldsymbol{u}') \tag{5.11}$$

where z is the mean number of neighbouring molecules (i.e., the coordination number introduced in Section 2.3.2).

MS Free energy

F = E -TS

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 $\psi(\boldsymbol{u})$, the orientational entropy is given by[5]

$$S[\psi] = -Nk_B \int d\boldsymbol{u}\ \psi(\boldsymbol{u}) \ln \psi(\boldsymbol{u}) \tag{5.13}$$

and therefore the free energy of the system is given by

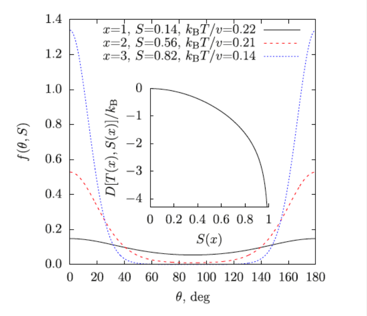
$$\begin{aligned} F[\psi] &= E[\psi] - TS[\psi] \\ &= N\left[k_BT \int d\boldsymbol{u}\ \psi(\boldsymbol{u}) \ln \psi(\boldsymbol{u}) - \frac{U}{2} \int d\boldsymbol{u} \int d\boldsymbol{u}'\ (\boldsymbol{u}\cdot\boldsymbol{u}')^2 \psi(\boldsymbol{u})\psi(\boldsymbol{u}')\right] \end{aligned} \tag{5.14}$$

where $U = z\tilde{U}$.

The orientational distribution at equilibrium is determined by the condition that eq. (5.14) be a minimum with respect to $\psi(\boldsymbol{u})$, i.e., by the condition

$$\frac{\delta}{\delta\psi}\left[F[\psi] - \lambda \int d\boldsymbol{u}\psi(\boldsymbol{u})\right] = 0 \tag{5.15}$$

Boltzmann distribution for *ψ*



For $F[\psi]$ given by eq. (5.14), eq. (5.15) gives

$$k_BT\left[\ln \psi(\boldsymbol{u}) + 1\right] - U \int d\boldsymbol{u}'\ (\boldsymbol{u}\cdot\boldsymbol{u}')^2 \psi(\boldsymbol{u}') - \lambda = 0 \tag{5.16}$$

This gives

$$\psi(\boldsymbol{u}) = C \exp[-\beta w_{mf}(\boldsymbol{u})] \tag{5.17}$$

where $\beta = 1/k_BT$, C is a normalization constant, and $w_{mf}(\boldsymbol{u})$ is given by

$$w_{mf}(\boldsymbol{u}) = -U \int d\boldsymbol{u}'\ (\boldsymbol{u}\cdot\boldsymbol{u}')^2 \psi(\boldsymbol{u}') \tag{5.18}$$

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

Details of the SC solution

$W_{mf}(u) = - U\, S\, u_z^2 + C$

The mean field potential in eq. (5.18) is written as

$$w_{mf}(\boldsymbol{u}) = -U u_\alpha u_\beta \langle u'_\alpha u'_\beta \rangle = -U u_\alpha u_\beta \langle u_\alpha u_\beta \rangle \tag{5.19}$$

where we have used the fact that the distribution of $\boldsymbol{u}'$ is the same as that of $\boldsymbol{u}$. The average in eq. (5.19) can be expressed by the scalar order parameter S. Let us take the z-axis in the direction of $\boldsymbol{n}$. Then eq. (5.9) is written as

$$S = \frac{3}{2}\left\langle u_z^2 - \frac{1}{3}\right\rangle \tag{5.20}$$

Since the distribution of $\boldsymbol{u}$ has uniaxial symmetry around the z-axis, $\langle u_\alpha u_\beta \rangle$ is zero for $\alpha \neq \beta$, and the other components are calculated from eq. (5.20) as

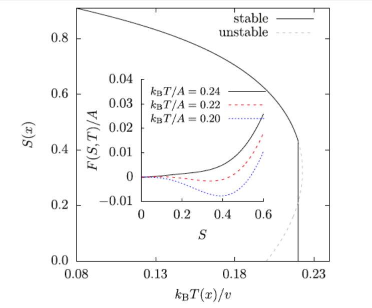
$$\langle u_z^2 \rangle = \frac{1}{3}(2S+1) \tag{5.21}$$

$$\langle u_x^2 \rangle = \langle u_y^2 \rangle = \frac{1}{2}\left(1 - \langle u_z^2 \rangle\right) = \frac{1}{3}(-S+1) \tag{5.22}$$

Hence the mean field potential (5.19) is calculated as

$$\begin{aligned} w_{mf}(\boldsymbol{u}) &= -U\left[u_x^2 \langle u_x^2 \rangle + u_y^2 \langle u_y^2 \rangle + u_z^2 \langle u_z^2 \rangle\right] \\ &= -U\left[\frac{1}{3}(-S+1)\left(u_x^2 + u_y^2\right) + \frac{1}{3}(2S+1)u_z^2\right] \\ &= -U\left[\frac{1}{3}(-S+1)\left(1 - u_z^2\right) + \frac{1}{3}(2S+1)u_z^2\right] \\ &= -USu_z^2 + \text{constant} \end{aligned} \tag{5.23}$$

MS order parameter



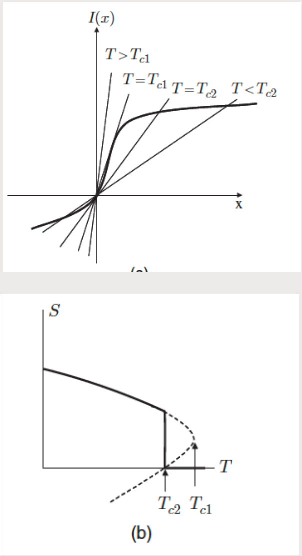
Therefore the equilibrium distribution function is given by

$$\psi(\boldsymbol{u}) = Ce^{\beta U S u_z^2} \tag{5.24}$$

Equations (5.20) and (5.24) give the following self-consistent equation for S

$$S = \frac{\int d\boldsymbol{u}\,\frac{3}{2}\left(u_z^2 - \frac{1}{3}\right)e^{\beta U S u_z^2}}{\int d\boldsymbol{u}\, e^{\beta U S u_z^2}} \tag{5.25}$$

Graphical solution



We introduce the parameter $x = \beta US$. Equation (5.25) is then written as

$$\frac{k_B T}{U} x = I(x) \tag{5.26}$$

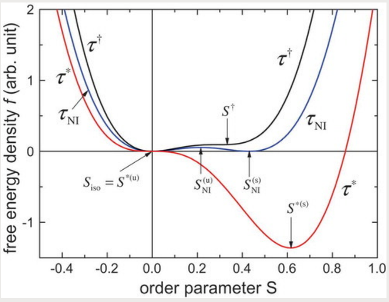
where

$$I(x) = \frac{\int_0^1 dt \, \frac{3}{2}(t^2 - \frac{1}{3}) e^{xt^2}}{\int_0^1 dt \, e^{xt^2}} \tag{5.27}$$

Equation (5.26) can be solved by a graphical method: the solution is given by the intersection between the line $y = (k_B T/U)x$ and the curve $y = I(x)$. This is done in Fig. 5.3(a). 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 Fig. 5.3(a).

With decreasing the temperature further, one solution increases, while the other solution decreases, crossing zero at the temperature T_{c2}. Figure 5.3(b) summarizes this behaviour of the solution S plotted against the temperature T.

Free energy



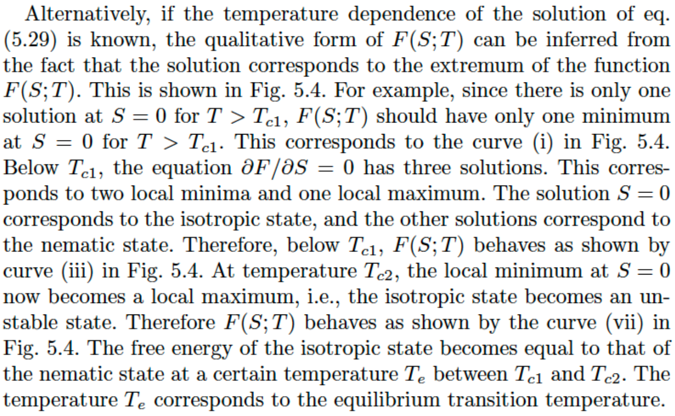
In order to identify the transition temperature, we consider the free energy $F(S;T)$ of the system for a given value of the order parameter S. $F(S;T)$ represents the free energy of a system in which the order parameter is hypothetically constrained at S. If the system consists of N molecules each pointing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

$$\frac{1}{N} \sum_i \frac{3}{2} \left(u_{iz}^2 - \frac{1}{3} \right) = S \tag{5.28}$$

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. A general discussion on the restricted free energy is given in Appendix B.

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.,

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



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 $\partial F/\partial S = 0$ 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., 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.

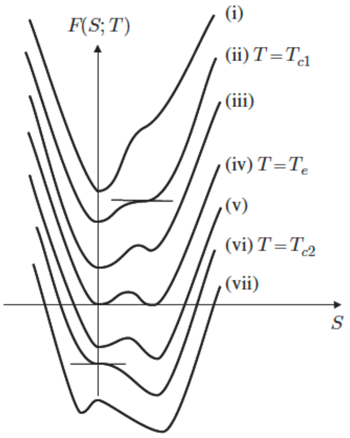
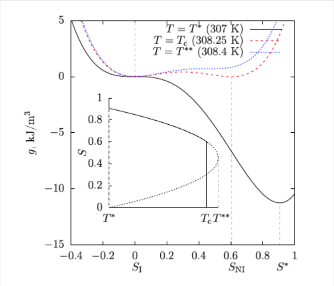
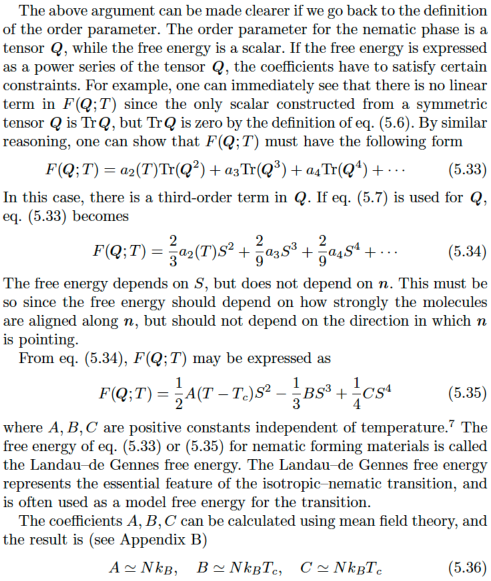


Fig. 5.4 Temperature dependence of the free energy curve $F(S;T)$ which gives the curve $S(T)$ shown in Fig. 5.3(b).

Landau-de Gennes





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 $\boldsymbol{Q}$, while the free energy is a scalar. If the free energy is expressed as a power series of the tensor $\boldsymbol{Q}$, the coefficients have to satisfy certain constraints. For example, one can immediately see that there is no linear term in $F(\boldsymbol{Q};T)$ since the only scalar constructed from a symmetric tensor $\boldsymbol{Q}$ is $\mathrm{Tr}\,\boldsymbol{Q}$, but $\mathrm{Tr}\,\boldsymbol{Q}$ is zero by the definition of eq. (5.6). By similar reasoning, one can show that $F(\boldsymbol{Q};T)$ must have the following form

$$F(\boldsymbol{Q};T) = a_2(T)\mathrm{Tr}(\boldsymbol{Q}^2) + a_3\mathrm{Tr}(\boldsymbol{Q}^3) + a_4\mathrm{Tr}(\boldsymbol{Q}^4) + \cdots \tag{5.33}$$

In this case, there is a third-order term in $\boldsymbol{Q}$. If eq. (5.7) is used for $\boldsymbol{Q}$, eq. (5.33) becomes

$$F(\boldsymbol{Q};T) = \frac{2}{3}a_2(T)S^2 + \frac{2}{9}a_3S^3 + \frac{2}{9}a_4S^4 + \cdots \tag{5.34}$$

The free energy depends on S, but does not depend on $\boldsymbol{n}$. This must be so since the free energy should depend on how strongly the molecules are aligned along $\boldsymbol{n}$, but should not depend on the direction in which $\boldsymbol{n}$ is pointing.

From eq. (5.34), $F(\boldsymbol{Q};T)$ may be expressed as

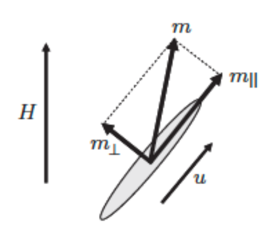
$$F(\boldsymbol{Q};T) = \frac{1}{2}A(T - T_c)S^2 - \frac{1}{3}BS^3 + \frac{1}{4}CS^4 \tag{5.35}$$

where A, B, C are positive constants independent of temperature.[7] The free energy of eq. (5.33) or (5.35) 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 (see Appendix B)

$$A \simeq Nk_B, \quad B \simeq Nk_BT_c, \quad C \simeq Nk_BT_c \tag{5.36}$$

External magnetic field



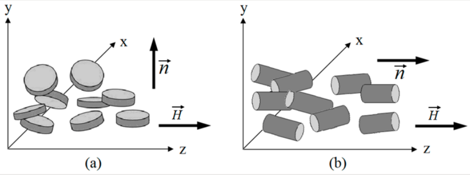
When a magnetic field $\boldsymbol{H}$ is applied to a nematic forming molecule, a magnetic moment is induced in the molecule. The induced magnetic moment $\boldsymbol{m}$ depends on the angle that the molecular axis $\boldsymbol{u}$ makes with the magnetic field $\boldsymbol{H}$ (see Fig. 5.6). Let $\alpha_\parallel$ (and $\alpha_\perp$) be the magnetic susceptibility of the molecule when the magnetic field $\boldsymbol{H}$ is applied parallel (and perpendicular) to the molecular axis $\boldsymbol{u}$. If a magnetic field $\boldsymbol{H}$ is applied to a molecule pointing in the direction $\boldsymbol{u}$, the molecule will have a magnetic moment $\boldsymbol{m}_\parallel = \alpha_\parallel(\boldsymbol{H}\cdot\boldsymbol{u})\boldsymbol{u}$ along $\boldsymbol{u}$, and a magnetic moment $\boldsymbol{m}_\perp = \alpha_\perp[\boldsymbol{H} - (\boldsymbol{H}\cdot\boldsymbol{u})\boldsymbol{u}]$ in the direction normal to $\boldsymbol{u}$ (see Fig. 5.6). Therefore the molecule feels a potential energy

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

$$\begin{aligned} w_H(\boldsymbol{u}) &= -\frac{1}{2}\alpha_\parallel(\boldsymbol{H}\cdot\boldsymbol{u})^2 - \frac{1}{2}\alpha_\perp[\boldsymbol{H} - (\boldsymbol{H}\cdot\boldsymbol{u})\boldsymbol{u}]^2 \\ &= -\frac{1}{2}\alpha_\parallel(\boldsymbol{H}\cdot\boldsymbol{u})^2 + \frac{1}{2}\alpha_\perp(\boldsymbol{H}\cdot\boldsymbol{u})^2 + \text{terms independent of } \boldsymbol{u} \\ &= -\frac{1}{2}\alpha_d(\boldsymbol{H}\cdot\boldsymbol{u})^2 + \text{terms independent of } \boldsymbol{u} \end{aligned} \tag{5.37}$$

where $\alpha_d = \alpha_\parallel - \alpha_\perp$. If $\alpha_d > 0$, the magnetic field tends to align the molecule in the direction of $\boldsymbol{H}$, while if $\alpha_d < 0$, the magnetic field tends to rotate the molecule to the direction perpendicular to $\boldsymbol{H}$. In what follows, we assume $\alpha_d > 0$.

Discotic and rod like particles



(a) (b)

If there are N molecules in the system, the total potential energy due to the magnetic field is given by

$$F_H = -\frac{N}{2}\alpha_d\langle(\boldsymbol{H}\cdot\boldsymbol{u})^2\rangle \tag{5.38}$$

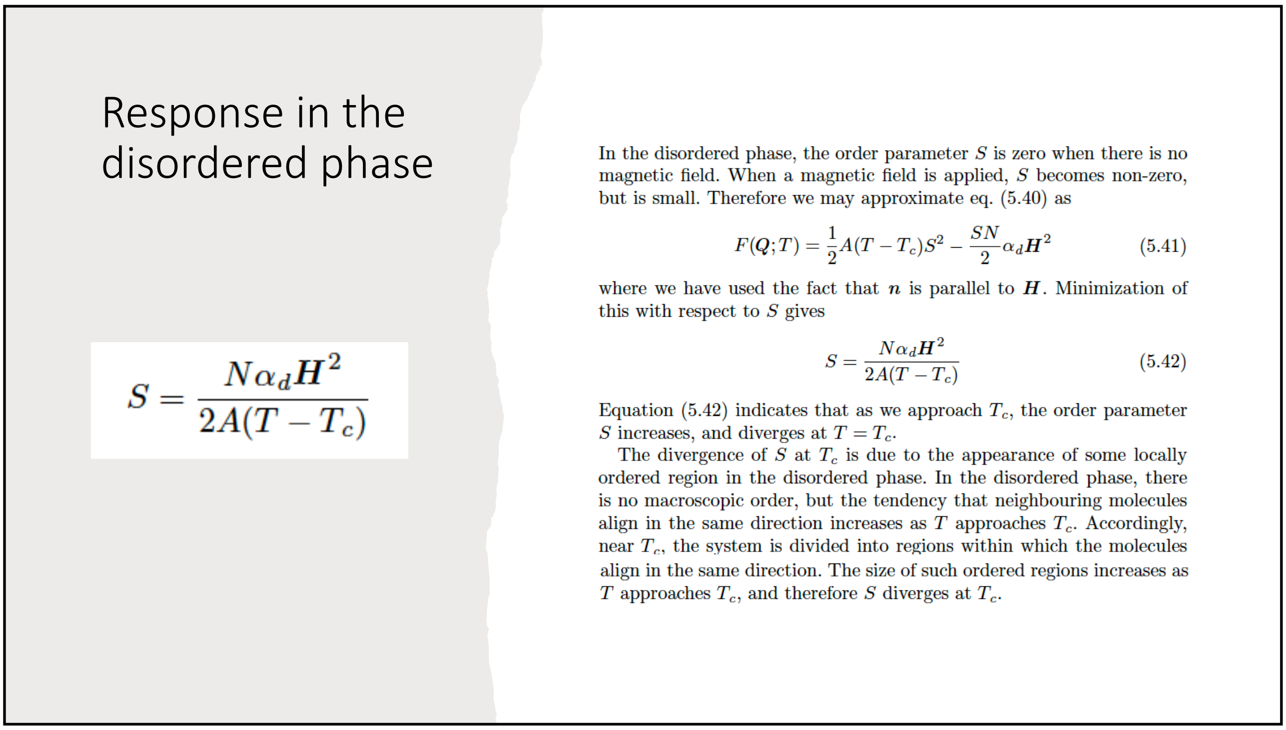
Using the definition of $\boldsymbol{Q}$ (eq. (5.6)), this can be written as

$$F_H = -\frac{N}{2}\alpha_d\boldsymbol{H}\cdot\boldsymbol{Q}\cdot\boldsymbol{H} = -\frac{N}{2}\alpha_d S(\boldsymbol{H}\cdot\boldsymbol{n})^2 \tag{5.39}$$

where we have used eq. (5.7) and ignored the terms which do not depend on $\boldsymbol{Q}$. Therefore the total free energy of the system is

$$F(\boldsymbol{Q};T) = \frac{1}{2}A(T-T_c)S^2 - \frac{1}{3}BS^3 + \frac{1}{4}CS^4 - \frac{SN}{2}\alpha_d(\boldsymbol{H}\cdot\boldsymbol{n})^2 \tag{5.40}$$

The order parameter $\boldsymbol{Q}$ in the presence of the magnetic field is given by S and $\boldsymbol{n}$ which minimize eq. (5.40). The response of $\boldsymbol{Q}$ to the magnetic field is quite different in the disordered phase and in the ordered phase.



Response in the disordered phase

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

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. Therefore we may approximate eq. (5.40) as

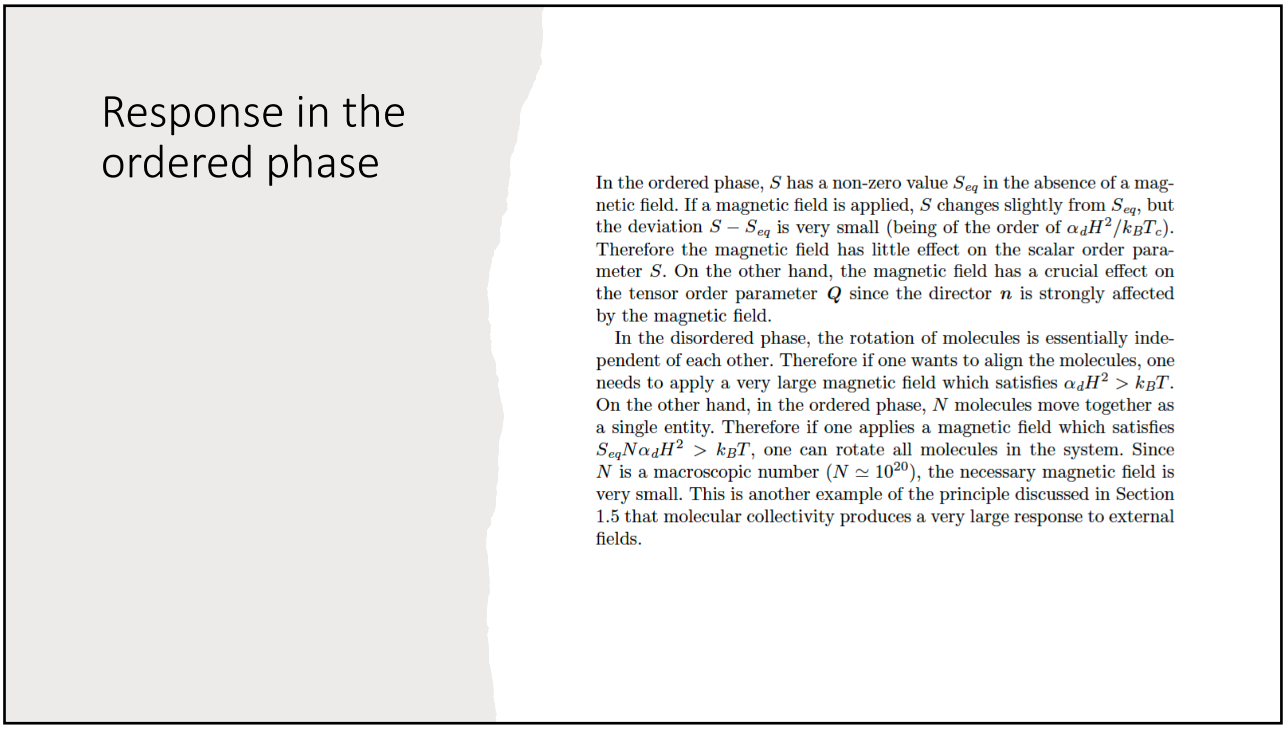
$$F(\boldsymbol{Q}; T) = \frac{1}{2}A(T - T_c)S^2 - \frac{SN}{2}\alpha_d \boldsymbol{H}^2 \tag{5.41}$$

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

$$S = \frac{N\alpha_d \boldsymbol{H}^2}{2A(T - T_c)} \tag{5.42}$$

Equation (5.42) 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.



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 $\boldsymbol{Q}$ since the director $\boldsymbol{n}$ 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 ($N \simeq 10^{20}$), the necessary magnetic field is very small. This is another example of the principle discussed in Section 1.5 that molecular collectivity produces a very large response to external fields.

Elastic energy

If there are no external fields, and no boundaries, the equilibrium state should be the uniform state in which the order parameter $\boldsymbol{Q}(\boldsymbol{r})$ is independent of position $\boldsymbol{r}$. If the order parameter varies with position, the free energy of the system must be larger than that of the uniform state. Therefore $F_{tot}[\boldsymbol{Q}(\boldsymbol{r})]$ should be written as follows

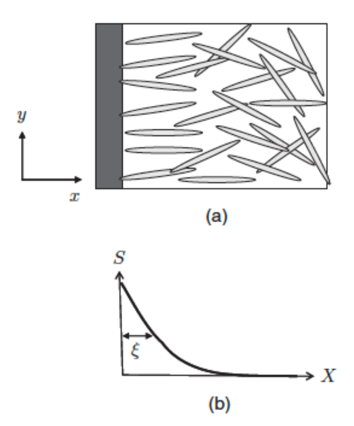
$$F_{tot} = \int d\boldsymbol{r}[f(\boldsymbol{Q}(\boldsymbol{r})) + f_{el}(\boldsymbol{Q}, \boldsymbol{\nabla Q})] \tag{5.43}$$

The first term $f(\boldsymbol{Q})$ is the free energy density for a uniform system, and is essentially the same as that given by (5.40). (A small letter f is used to emphasize that it is a free energy per unit volume.) The second term $f_{el}(\boldsymbol{Q}, \boldsymbol{\nabla Q})$ is the excess free energy due to the spatial gradient of $\boldsymbol{Q}$. If $\boldsymbol{\nabla Q}$ is small, f_{el} can be expanded as a power series of $\boldsymbol{\nabla Q}$. Since the free energy is a minimum in the uniform state (the state of $\boldsymbol{\nabla Q} = 0$), the lowest term must be written as

$$f_{el}(\boldsymbol{Q}, \boldsymbol{\nabla Q}) = \frac{1}{2} K_{\alpha\beta\gamma,\alpha'\beta'\gamma'} \nabla_\alpha Q_{\beta\gamma} \nabla_{\alpha'} Q_{\beta'\gamma'} \tag{5.44}$$

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

Isotropic state



(a)

(b)

In the isotropic state, we may assume that $K_{\alpha\beta\gamma,\alpha'\beta'\gamma'}$ is independent of $\boldsymbol{Q}$ since $\boldsymbol{Q}$ is small in the isotropic state. Hence f_{el} is a scalar constructed by a quadratic form of $\boldsymbol{\nabla Q}$. Using the properties $Q_{\alpha\beta} = Q_{\beta\alpha}$, and $Q_{\alpha\alpha} = 0$, we can show that f_{el} is written in the following form:[9]

$$f_{el} = \frac{1}{2} K_1 \nabla_\alpha Q_{\beta\gamma} \nabla_\alpha Q_{\beta\gamma} + \frac{1}{2} K_2 \nabla_\alpha Q_{\alpha\gamma} \nabla_\beta Q_{\beta\gamma} \tag{5.45}$$

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

$$F_{tot} = \int d\boldsymbol{r} \left[\frac{1}{2} A(T - T_c) S^2 + \frac{1}{2} K_1 \nabla_\alpha Q_{\beta\gamma} \nabla_\alpha Q_{\beta\gamma} + \frac{1}{2} K_2 \nabla_\alpha Q_{\alpha\gamma} \nabla_\beta Q_{\beta\gamma} \right] \tag{5.46}$$

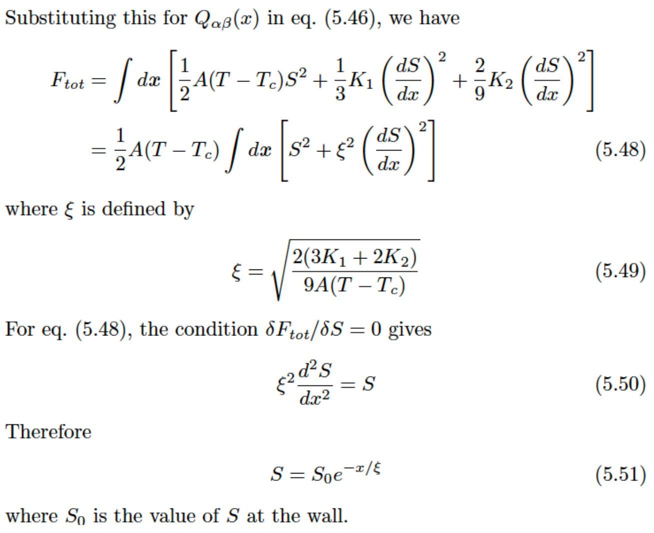
where we have ignored higher order terms in $\boldsymbol{Q}$.

As an application of eq. (5.46), 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

$$Q_{xx} = \frac{2}{3} S, \quad Q_{yy} = Q_{zz} = -\frac{1}{3} S, \quad Q_{xy} = Q_{yz} = Q_{zx} = 0 \tag{5.47}$$

Correlation length

$$\xi = \sqrt{\frac{2(3K_1 + 2K_2)}{9A(T - T_c)}}$$



Substituting this for $Q_{\alpha\beta}(x)$ in eq. (5.46), we have

$$\begin{aligned} F_{tot} &= \int dx \left[\frac{1}{2}A(T-T_c)S^2 + \frac{1}{3}K_1\left(\frac{dS}{dx}\right)^2 + \frac{2}{9}K_2\left(\frac{dS}{dx}\right)^2\right] \\ &= \frac{1}{2}A(T-T_c)\int dx \left[S^2 + \xi^2\left(\frac{dS}{dx}\right)^2\right] \qquad (5.48) \end{aligned}$$

where ξ is defined by

$$\xi = \sqrt{\frac{2(3K_1 + 2K_2)}{9A(T-T_c)}} \qquad (5.49)$$

For eq. (5.48), the condition $\delta F_{tot}/\delta S = 0$ gives

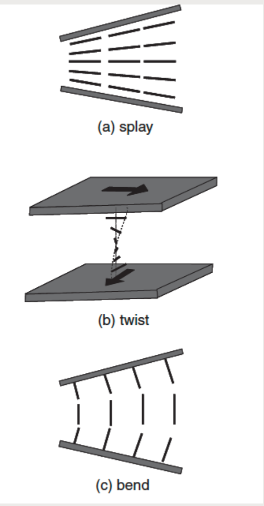
$$\xi^2 \frac{d^2 S}{dx^2} = S \qquad (5.50)$$

Therefore

$$S = S_0 e^{-x/\xi} \qquad (5.51)$$

where S_0 is the value of S at the wall.

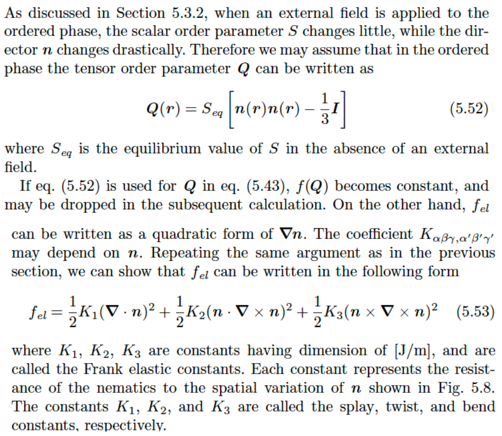
Frank elastic energy



(a) splay

(b) twist

(c) bend



As discussed in Section 5.3.2, when an external field is applied to the ordered phase, the scalar order parameter S changes little, while the director $\boldsymbol{n}$ changes drastically. Therefore we may assume that in the ordered phase the tensor order parameter $\boldsymbol{Q}$ can be written as

$$\boldsymbol{Q}(\boldsymbol{r}) = S_{eq}\left[\boldsymbol{n}(\boldsymbol{r})\boldsymbol{n}(\boldsymbol{r}) - \frac{1}{3}\boldsymbol{I}\right] \qquad (5.52)$$

where S_{eq} is the equilibrium value of S in the absence of an external field.

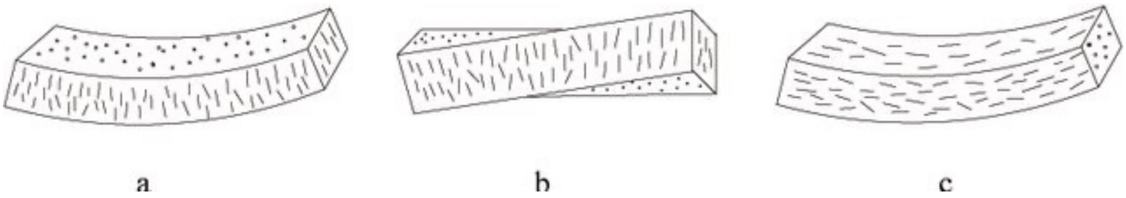
If eq. (5.52) is used for $\boldsymbol{Q}$ in eq. (5.43), $f(\boldsymbol{Q})$ becomes constant, and may be dropped in the subsequent calculation. On the other hand, f_{el}

can be written as a quadratic form of $\boldsymbol{\nabla n}$. The coefficient $K_{\alpha\beta\gamma,\alpha'\beta'\gamma'}$ may depend on $\boldsymbol{n}$. Repeating the same argument as in the previous section, we can show that f_{el} can be written in the following form

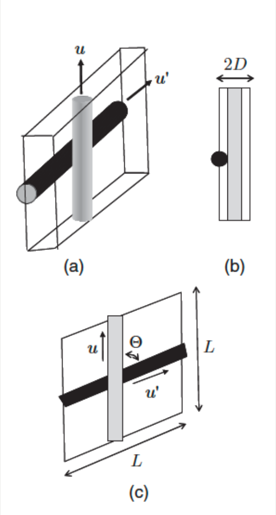
$$f_{el} = \frac{1}{2}K_1(\boldsymbol{\nabla}\cdot\boldsymbol{n})^2 + \frac{1}{2}K_2(\boldsymbol{n}\cdot\boldsymbol{\nabla}\times\boldsymbol{n})^2 + \frac{1}{2}K_3(\boldsymbol{n}\times\boldsymbol{\nabla}\times\boldsymbol{n})^2 \qquad (5.53)$$

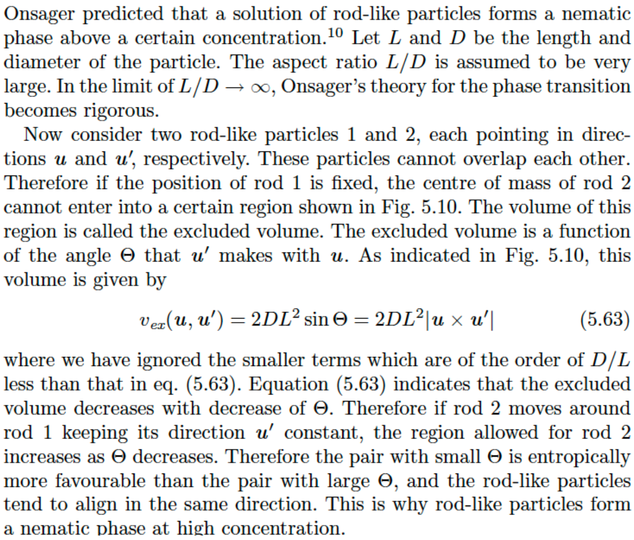
where K_1, K_2, K_3 are constants having dimension of [J/m], and are called the Frank elastic constants. Each constant represents the resistance of the nematics to the spatial variation of $\boldsymbol{n}$ shown in Fig. 5.8. The constants K_1, K_2, and K_3 are called the splay, twist, and bend constants, respectively.

Splay, Twist and Bend



Onsager



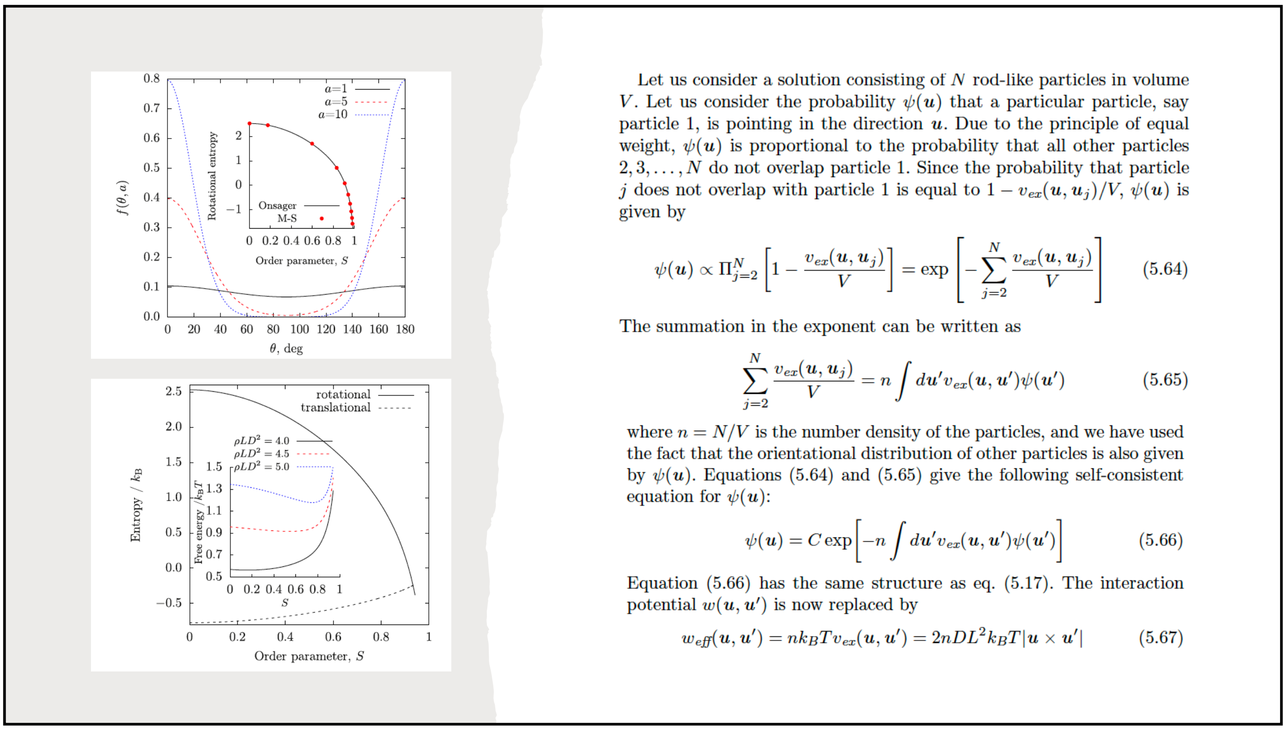


Onsager predicted that a solution of rod-like particles forms a nematic phase above a certain concentration.[10] Let L and D be the length and diameter of the particle. The aspect ratio L/D is assumed to be very large. In the limit of $L/D \to \infty$, Onsager's theory for the phase transition becomes rigorous.

Now consider two rod-like particles 1 and 2, each pointing in directions $\boldsymbol{u}$ and $\boldsymbol{u}'$, respectively. These particles cannot overlap each other. Therefore if the position of rod 1 is fixed, the centre of mass of rod 2 cannot enter into a certain region shown in Fig. 5.10. The volume of this region is called the excluded volume. The excluded volume is a function of the angle Θ that $\boldsymbol{u}'$ makes with $\boldsymbol{u}$. As indicated in Fig. 5.10, this volume is given by

$$v_{ex}(\boldsymbol{u}, \boldsymbol{u}') = 2DL^2 \sin\Theta = 2DL^2 |\boldsymbol{u} \times \boldsymbol{u}'| \qquad (5.63)$$

where we have ignored the smaller terms which are of the order of D/L less than that in eq. (5.63). Equation (5.63) indicates that the excluded volume decreases with decrease of Θ. Therefore if rod 2 moves around rod 1 keeping its direction $\boldsymbol{u}'$ constant, the region allowed for rod 2 increases as Θ decreases. Therefore the pair with small Θ is entropically more favourable than the pair with large Θ, and the rod-like particles tend to align in the same direction. This is why rod-like particles form a nematic phase at high concentration.



Let us consider a solution consisting of N rod-like particles in volume V. Let us consider the probability $\psi(\boldsymbol{u})$ that a particular particle, say particle 1, is pointing in the direction $\boldsymbol{u}$. Due to the principle of equal weight, $\psi(\boldsymbol{u})$ is proportional to the probability that all other particles $2, 3, \ldots, N$ do not overlap particle 1. Since the probability that particle j does not overlap with particle 1 is equal to $1 - v_{ex}(\boldsymbol{u}, \boldsymbol{u}_j)/V$, $\psi(\boldsymbol{u})$ is given by

$$\psi(\boldsymbol{u}) \propto \Pi_{j=2}^{N}\left[1 - \frac{v_{ex}(\boldsymbol{u}, \boldsymbol{u}_j)}{V}\right] = \exp\left[-\sum_{j=2}^{N}\frac{v_{ex}(\boldsymbol{u}, \boldsymbol{u}_j)}{V}\right] \qquad (5.64)$$

The summation in the exponent can be written as

$$\sum_{j=2}^{N}\frac{v_{ex}(\boldsymbol{u}, \boldsymbol{u}_j)}{V} = n\int d\boldsymbol{u}' v_{ex}(\boldsymbol{u}, \boldsymbol{u}')\psi(\boldsymbol{u}') \qquad (5.65)$$

where $n = N/V$ is the number density of the particles, and we have used the fact that the orientational distribution of other particles is also given by $\psi(\boldsymbol{u})$. Equations (5.64) and (5.65) give the following self-consistent equation for $\psi(\boldsymbol{u})$:

$$\psi(\boldsymbol{u}) = C\exp\left[-n\int d\boldsymbol{u}' v_{ex}(\boldsymbol{u}, \boldsymbol{u}')\psi(\boldsymbol{u}')\right] \qquad (5.66)$$

Equation (5.66) has the same structure as eq. (5.17). The interaction potential $w(\boldsymbol{u}, \boldsymbol{u}')$ is now replaced by

$$w_{eff}(\boldsymbol{u}, \boldsymbol{u}') = nk_BTv_{ex}(\boldsymbol{u}, \boldsymbol{u}') = 2nDL^2k_BT|\boldsymbol{u} \times \boldsymbol{u}'| \qquad (5.67)$$

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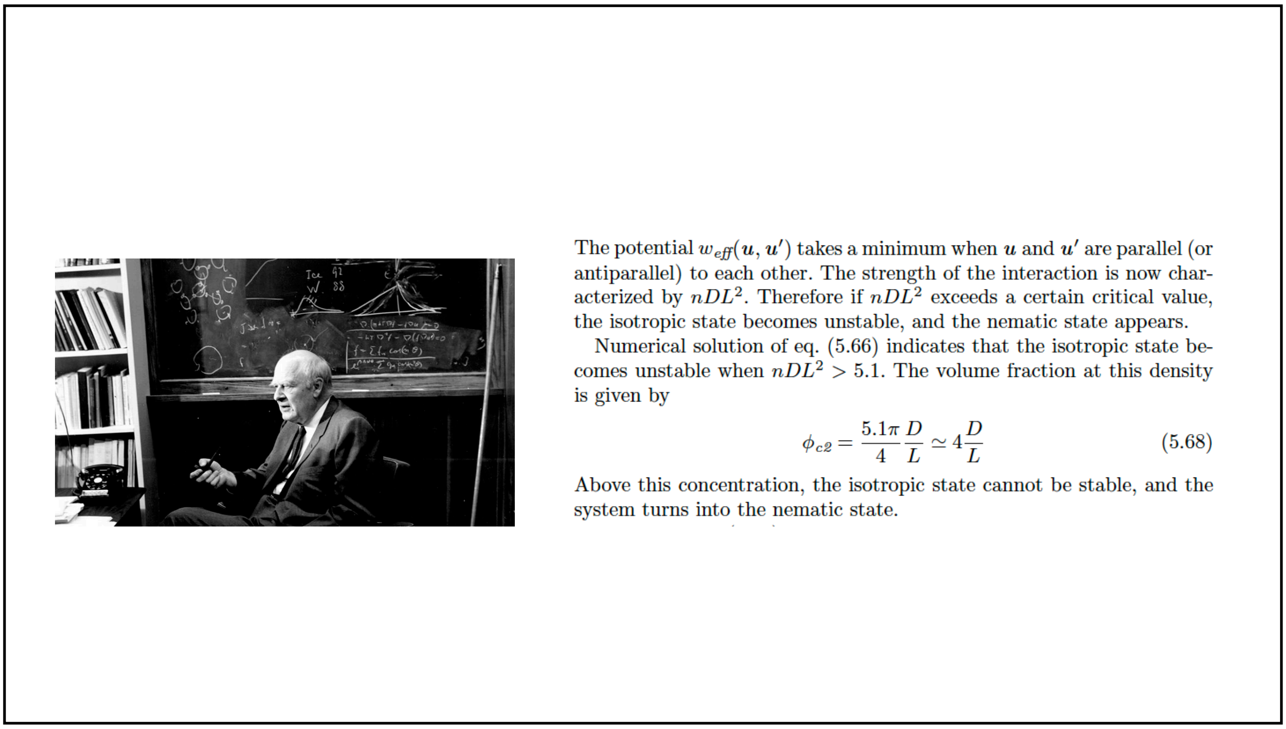

The potential $w_{eff}(\boldsymbol{u}, \boldsymbol{u}')$ takes a minimum when $\boldsymbol{u}$ and $\boldsymbol{u}'$ are parallel (or antiparallel) to each other. The strength of the interaction is now characterized by nDL^2. Therefore if nDL^2 exceeds a certain critical value, the isotropic state becomes unstable, and the nematic state appears.

Numerical solution of eq. (5.66) indicates that the isotropic state becomes unstable when $nDL^2 > 5.1$. The volume fraction at this density is given by

$$\phi_{c2} = \frac{5.1\pi}{4}\frac{D}{L} \simeq 4\frac{D}{L} \qquad (5.68)$$

Above this concentration, the isotropic state cannot be stable, and the system turns into the nematic state.

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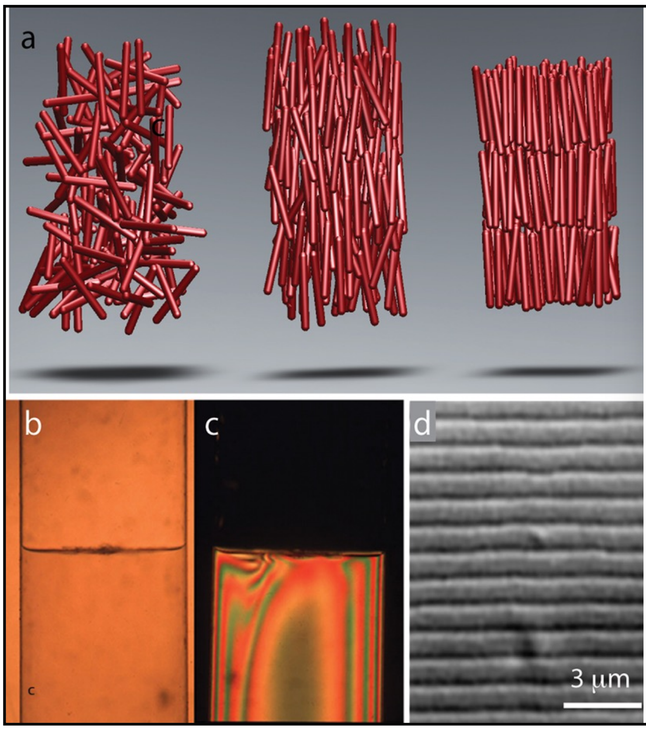
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