1

Liquid Crystal Physics

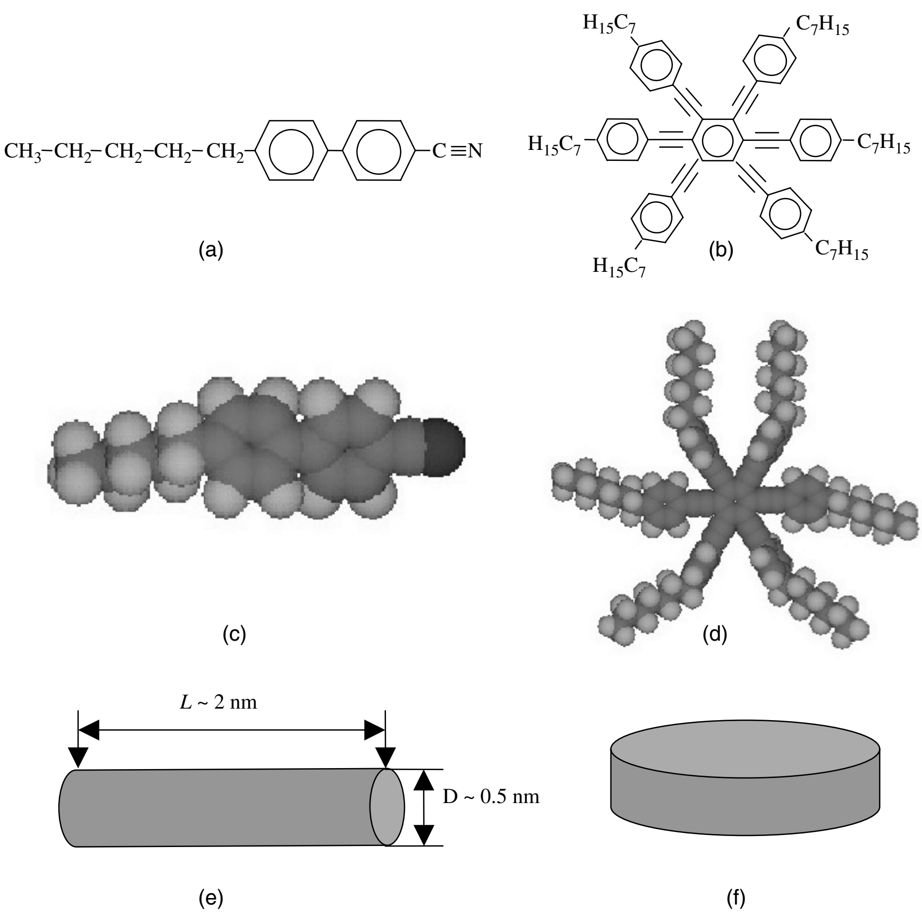
1.1 Introduction

Liquid crystals are mesophases between crystalline solids and isotropic liquids [1–3]. The constituents are elongated rod-like (calamitic) or disk-like (discotic) organic molecules as shown in Figure 1.1. The size of the molecules is typically a few nanometers (nm). The ratio between the length and the diameter of the rod-like molecules or the ratio between the diameter and the thickness of the disk-like molecules is about 5 or larger. Because the molecules are non-spherical, besides positional order, they may also possess orientational order.

Figure 1.1(a) shows a typical *calamitic* liquid crystal molecule. Its chemical name is 4′-*n*-pentyl-4-cyano-biphenyl and is abbreviated as 5CB [4,5]. It consists of a biphenyl, which is the rigid core, and a hydrocarbon chain, which is the flexible tail. The space-filling model of the molecule is shown in Figure 1.1(c). Although the molecule itself is not cylindrical, it can be regarded as a cylinder, as shown Figure 1.1(e), in considering its physical behavior because of the fast rotation (on the order of 10^{-9} s) around the long molecular axis due to thermal motion. The distance between two carbon atoms is about1.5 Å; therefore the length and the diameter of the molecule are about 2 nm and 0.5 nm, respectively. The molecule shown has a permanent dipole moment (from the CN head); however, it can still be represented by a cylinder whose head and tail are the same, because in non-ferroelectric liquid crystal phases, the dipole has equal probability of pointing up or down. It is necessary for a liquid crystal molecule to have a rigid core(s) and flexible tail(s). If the molecule is completely flexible, it will not have orientational order. If it is completely rigid, it will transform directly from the isotropic liquid phase at high temperature to the crystalline solid phase at low temperature. The rigid part favors both orientational and positional order while the flexible part does not. With balanced rigid and flexible parts, the molecule exhibits liquid crystal phases.

Figure 1.1(b) shows a typical *discotic* liquid crystal molecule [6]. It also has a rigid core and flexible tails. The branches are approximately on one plane. The space-filling model of the molecule is shown in Figure 1.1(d). If there is no permanent dipole moment perpendicular to the plane of the molecule, it can be regarded as a disk in considering its physical behavior as shown in Figure 1.1(f), because of the fast rotation around the axis which is at the center of the molecule and perpendicular to the plane of the molecule. If there is a permanent dipole moment perpendicular to the plane of the molecule, it is better to

Fundamentals of Liquid Crystal Devices D.-K. Yang and S.-T. Wu



(a) (b) (c) (d) (e) (f)

Figure 1.1 Calamitic liquid crystal: (a) chemical structure, (c) space-filling model, (e) physical model. Discostic liquid crystal: (b) chemical structure, (d) space-filling mode, (f) physical model

visualize the molecule as a bowl, because the reflection symmetry is broken and all the permanent dipoles may point in the same direction and spontaneous polarization occurs. The flexible tails are also necessary, otherwise the molecules form the crystal phase where there is positional order.

The variety of phases that may be exhibited by rod-like molecules are shown in Figure 1.2. At high temperature, the molecules are in the isotropic liquid state where they do not have either positional or orientational order. The molecules can easily move around and the material can flow like water. The translational viscosity is comparable to that of water. Both the long and short axes of the molecules can point in any direction.

When the temperature is decreased, the material transforms into the *nematic* phase, which is the most common and simplest liquid crystal phase, where the molecules have orientational order but still no positional order. The molecules can still diffuse around and the translational viscosity does not change much from that of the isotropic liquid state. The long axis of the molecules has preferred direction. Although the molecules still swivel due to thermal motion, the time-averaged direction of the long axis of a molecule is well defined and is the same for all the molecules at the macroscopic scale. The average

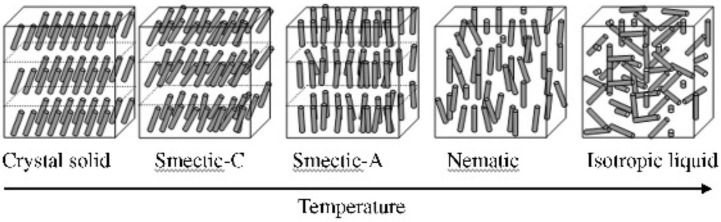


Figure 1.2 Schematic representation of the phases of rod-like molecules

direction of the long molecular axis is denoted by $\vec{n}$ which is a unit vector and called the liquid crystal director. The short axes of the molecules have no orientational order in a uniaxial nematic liquid crystal.

When the temperature is decreased further, the material may transform into the *smetic-A* phase where, besides the orientational order, the molecules have partial positional order, i.e., the molecules form a layered structure. The liquid crystal director is perpendicular to the layers. Smectic-A is a one-dimensional crystal where the molecules have positional order in the normal direction of the layer. The diagram shown in Figure 1.2 is schematic. In reality, the separation between neighboring layers is not as well defined as that shown in the figure. The molecular number density exhibits an undulation with the wavelength about the molecular length. Within a layer, it is a two-dimensional liquid in which there is no positional order and the molecules can move around. For a material in poly-domain smectic-A, the translational viscosity is significantly higher, and it behaves like a grease. When the temperature is decreased still futher, the material may transform into the *smectic-C* phase where the liquid crystal director is no longer perpendicular to the layer but tilted.

At low temperature, the material is in the crystal solid phase where there are both positional and orientational orders. The translational viscosity become infinite and the molecules (almost) no longer diffuse.

Liquid crystals get the 'crystal' part of their name because they exhibit optical birefringence like crystalline solids. They get the 'liquid' part of their name because they can flow and do not support shearing like regular liquids. Liquid crystal molecules are elongated and have different molecular polarizabilities along their long and short axes. Once the long axes of the molecules orient along a common direction, the refractive indices along and perpendicular to the common direction are different. It should be noted that not all rod-like molecules exhibit all the liquid crystal phases, but just some of them.

Some of the liquid crystal phases of disk-like molecules are shown in Figure 1.3. At high temperature, they are in the isotropic liquid state where there are no positional and orientational orders. The material behaves in the same way as a regular liquid. When the temperature is decreased, the material transforms

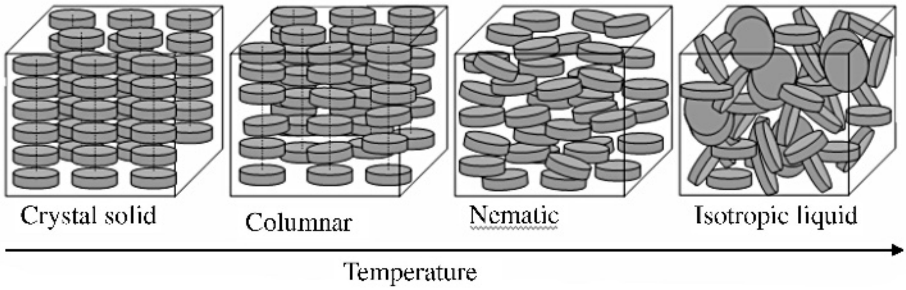


Figure 1.3 Schematic representation of the phases of disk-like molecules

into the nematic phase which has orientational order but not positional order. The average direction of the short axis perpendicular to the disk is oriented along a preferred direction which is also called the liquid crystal director and denoted by a unit vector $\vec{n}$. The molecules have different polarizabilities along a direction in the plane of the disk and along the short axis. Thus the discotic nematic phase also exhibits birefringence as crystals.

When the temperature is decreased further, the material transforms into the columnar phase where, besides orientational order, there is partial positional order. The molecules stack up to form columns. Within a column, the columnar phase is a liquid where the molecules have no positional order. The columns, however, are arranged periodically in the plane perpendicular to the columns. Hence the columnar phase is a two-dimensional crystal. At low temperature, the material transforms into the crystalline solid phase where the positional order along the columns is developed.

The liquid crystal phases discussed so far are called thermotropic liquid crystals and the transitions from one phase to another phase are driven by varying temperature. There is another type of liquid crystallinity, called lyotropic, exhibited by molecules when they are mixed with a solvent of some kind. The phase transitions from one phase to another phase are driven by varying the solvent concentration. Lyotropic liquid crystals usually consist of amphiphilic molecules which have a hydrophobic group at one end and a hydrophilic group at the other end, with water as the solvent. The common lyotropic liquid crystal phases are micelle phase and lamellar phase. Lyotropic liquid crystals are important in biology. They will not be discussed in this book because its scope concerns displays and photonic devices.

Liquid crystals have a history of more than 100 years. It is believed that the person who discovered liquid crystals was Friedrich Reinitzer, an Austrian botanist [7]. The liquid crystal phase observed by him in 1888 was a cholesteric phase. Since then liquid crystals have come a long way and become a major branch of interdisciplinary science. Scientifically, liquid crystals are important because of the richness of their structures and transitions. Technologically, they have gained tremendous success in display and photonic applications [8–10].

1.2 Thermodynamics and Statistical Physics

Liquid crystal physics is an interdisciplinary science, involving thermodynamics, statistical physics, electrodynamics, and optics. Here we give a brief introduction to thermodynamics and statistical physics.

1.2.1 Thermodynamic laws

One of the important quantities in thermodynamics is entropy. From the microscopic point of view, entropy is a measure of the number of quantum states accessible to a system. In order to define entropy quantitatively, we first consider the fundamental logical assumption that *for a closed system (in which no energy and particles exchange with other systems), quantum states are either accessible or inaccessible to the system, and the system is equally likely to be in any one of the accessible states as in any other accessible state* [11]. For a macroscopic system, the number of accessible quantum states g is a huge number ($\sim 10^{23}$). It is easier to deal with ln g, which is defined as the *entropy* σ:

$$\sigma = \ln g \tag{1.1}$$

If a closed system consists of subsystem 1 and subsystem 2, the numbers of accessible states of the subsystems are g_1 and g_2, respectively. The number of accessible quantum states of the whole system is $g = g_1 g_2$ and the entropy is $\sigma = \ln g = \ln(g_1 g_2) = \ln g_1 + \ln g_2 = \sigma_1 + \sigma_2$.

Entropy is a function of the energy u of the system $\sigma = \sigma(u)$. The second law of thermodynamics states that *for a closed system, the equilibrium state has maximum entropy*. Let us consider a closed system which contains two subsystems. When two subsystems are brought into thermal contact the energy exchange between them is allowed, the energy is allocated to maximize the number of accessible states; that is, the entropy is maximized. Subsystem 1 has energy u_1 and entropy σ_1; subsystem 2 has energy u_2 and entropy σ_2. For the whole system, $u = u_1 + u_2$ and $\sigma = \sigma_1 + \sigma_2$. The first law of thermodynamics states that *energy is conserved*, i.e., $u = u_1 + u_2 =$ constant. For any process inside the closed system, $\delta u = \delta u_1 + \delta u_2 = 0$. From the second law of thermodynamics, for any process we have $\delta\sigma = \delta\sigma_1 + \delta\sigma_2 \geq 0$. When the two subsystems are brought into thermal contact, at the beginning energy flows. For example, an amount of energy $|\delta u_1|$ flows from subsystem 1 to subsystem 2, $\delta u_1 < 0$ and $\delta u_2 = -\delta u_1 > 0$, and

$$\frac{\partial\sigma}{\partial u_2} = \frac{\partial\sigma_1}{\partial u_2} + \frac{\partial\sigma_2}{\partial u_2} = \frac{\partial\sigma_1}{\partial u_1}\frac{\partial u_1}{\partial u_2} + \frac{\partial\sigma_2}{\partial u_2} = -\frac{\partial\sigma_1}{\partial u_1} + \frac{\partial\sigma_2}{\partial u_2} \geq 0$$

When equilibrium is reached, the entropy is maximized and

$$\frac{\partial\sigma_1}{\partial u_1} - \frac{\partial\sigma_2}{\partial u_2} = 0 \quad \text{or} \quad \frac{\partial\sigma_1}{\partial u_1} = \frac{\partial\sigma_2}{\partial u_2}$$

We know that when two systems reach equilibrium, they have the same temperature. Accordingly the *fundamental temperature* τ is defined by

$$1/\tau = (\partial\sigma/\partial u)_{N,V} \tag{1.2}$$

where N is the number of particles and V the volume. Energy flows from a high temperature system to a low-temperature system. The *conventional temperature* (Kelvin temperature) is defined by

$$T = \tau/k_B \tag{1.3}$$

where $k_B = 1.81 \times 10^{-23}$ joules/kelvin is the Boltzmann constant. *Conventional entropy S* is defined by

$$1/T = \partial S/\partial u \tag{1.4}$$

Hence

$$S = k_B\sigma \tag{1.5}$$

1.2.2 Boltzmann distribution

Now we consider the thermodynamics of a system at a constant temperature, i.e., in thermal contact with a thermal reservoir. The temperature of the thermal reservoir (named B) is τ. The system under consideration (named A) has two states with energy 0 and ε, respectively. A and B form a closed system, and its total energy $u = u_A + u_B = u_o =$ constant. When A is in the state with energy 0, B has energy u_o, and the number of accessible states is $g_1 = g_A \times g_B = 1 \times g_B(u_o) = g_B(u_o)$. When A has energy ε, B has energy $u_o - \varepsilon$, and the number of accessible states is $g_2 = g_A \times g_B = 1 \times g_B(u_o - \varepsilon) = g_B(u_o - \varepsilon)$. For the whole system, the total number of accessible states is

$$G = g_1 + g_2 = g_B(u_o) + g_B(u_o - \varepsilon) \tag{1.6}$$

$(A + B)$ is a closed system, and the probability in any of the G states is the same. When the whole system is in one of the g_1 states, A has energy 0. When the whole system is in one of the g_2 states, A has energy ε. Therefore the probability that A is in the state with energy 0 is

$$P(0)=\frac{g_1}{g_1+g_2}=\frac{g_B(u_o)}{g_B(u_o)+g_B(u_o-\varepsilon)}$$

The probability that A is in the state energy ε is

$$P(\varepsilon)=\frac{g_2}{g_1+g_2}=\frac{g_B(u_o-\varepsilon)}{g_B(u_o)+g_B(u_o-\varepsilon)}$$

From the definition of entropy, we have $g_B(u_o)=e^{\sigma_B(u_o)}$ and $g_B(u_o-\varepsilon)=e^{\sigma_B(u_o-\varepsilon)}$. Because $\varepsilon \ll u_o$,

$$\sigma_B(u_o-\varepsilon)\approx\sigma_B(u_o)-\frac{\partial\sigma_B}{\partial u_B}\varepsilon=\sigma_B(u_o)-\frac{1}{\tau}\varepsilon$$

Therefore we have

$$P(0)=\frac{e^{\sigma_B(u_o)}}{e^{\sigma_B(u_o)}+e^{\sigma_B(u_o)-\varepsilon/\tau}}=\frac{1}{1+e^{-\varepsilon/\tau}}=\frac{1}{1+e^{-\varepsilon/k_BT}} \tag{1.7}$$

$$P(\varepsilon)=\frac{e^{\sigma_B(u_o)-\varepsilon/\tau}}{e^{\sigma_B(u_o)}+e^{\sigma_B(u_o)-\varepsilon/\tau}}=\frac{e^{-\varepsilon/\tau}}{1+e^{-\varepsilon/\tau}}=\frac{e^{-\varepsilon/k_BT}}{1+e^{-\varepsilon/k_BT}} \tag{1.8}$$

$$\equiv\frac{p(\varepsilon)}{P(0)}=e^{-\varepsilon/k_BT} \tag{1.9}$$

For a system having N states with energies $\varepsilon_1,\varepsilon_2,\ldots,\varepsilon_i,\ldots\varepsilon_{i+1},\ldots,\varepsilon_N$, the probability for the system in the state with energy ε_i is

$$P(\varepsilon_i)=e^{-\varepsilon_i/\tau}\Bigg/\sum_{j=1}^{N}e^{-e_j/k_BT} \tag{1.10}$$

The *partition function* of the system is defined as

$$Z=\sum_i e^{-\varepsilon_i/k_BT} \tag{1.11}$$

The *internal energy* (average energy) of the system is given by

$$U=\langle\varepsilon\rangle=\sum_i\varepsilon_iP(\varepsilon_i)=\frac{1}{Z}\sum_i\varepsilon_ie^{-\varepsilon_i/k_BT} \tag{1.12}$$

Because

$$\frac{\partial Z}{\partial T}=\sum_i\left(\frac{\varepsilon_i}{k_BT^2}\right)e^{-\varepsilon_i/K_BT}=\frac{1}{k_BT^2}\sum_i\varepsilon_ie^{-\varepsilon_i/k_BT}$$

then

$$U=\frac{k_BT^2}{Z}\frac{\partial Z}{\partial T}=k_BT^2\frac{\partial(\ln Z)}{\partial T} \tag{1.13}$$

1.2.3 Thermodynamic quantities

As energy is conserved, the change of the internal energy U of a system equals the heat dQ absorbed and the mechanical work dW done to the system, $dU = dQ + dW$. When the volume of the system changes by dV under the pressure P, the mechanical work done to the system is given by

$$dW = -PdV \tag{1.14}$$

When there is no mechanical work, the heat absorbed equals the change of internal energy. From the definition of temperature $1/T = (\partial S/\partial U)_V$, the heat absorbed in a reversible process at constant volume is

$$dU = dQ = TdS \tag{1.15}$$

When the volume is not constant, then

$$dU = TdS - PdV \tag{1.16}$$

The derivatives are

$$T = \left(\frac{\partial U}{\partial S}\right)_V \tag{1.17}$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_S \tag{1.18}$$

The internal energy U, entropy S, and volume V are extensive quantities, while temperature T and pressure P are intensive quantities. The *enthalpy* H of the system is defined by

$$H = U + PV \tag{1.19}$$

Its variation in a reversible process is given by

$$dH = dU + d(PV) = (TdS - PdV) + (PdV + VdP) = TdS + VdP \tag{1.20}$$

From this equation, it can be seen that the physical meaning of enthalpy is that in a process at constant pressure ($dP = 0$), the change of enthalpy dH is equal to the heat absorbed $dQ(= TdS)$. The derivatives of the enthalpy are

$$T = \left(\frac{\partial H}{\partial S}\right)_P \tag{1.21}$$

$$V = \left(\frac{\partial H}{\partial P}\right)_S \tag{1.22}$$

The *Helmholtz free energy* F of the system is defined by

$$F = U - TS \tag{1.23}$$

Its variation in a reversible process is given by

$$dF = dU - d(TS) = (TdS - PdV) - (TdS + SdT) = SdT - PdV \tag{1.24}$$

The physical meaning of Helmholtz free energy is that in a process at constant temperature, the change of Helmholtz free energy is equal to the work done to the system. The derivatives are

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \tag{1.25}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \tag{1.26}$$

The *Gibbs free energy G* of the system is defined by

$$G = U - TS + PV \tag{1.27}$$

The variation in a reversible process is given by

$$dG = dU - d(TS) - d(PV) = -SdT + VdP \tag{1.28}$$

In a process at constant temperature and pressure, the Gibbs free energy does not change. The derivatives are

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \tag{1.29}$$

$$V = \left(\frac{\partial G}{\partial P}\right)_T \tag{1.30}$$

The Helmholtz free energy can be derived from the partition function. From Equations (1.13) and (1.25),

$$F = U - TS = K_B T^2 \frac{\partial(\ln Z)}{\partial T} + T\left(\frac{\partial F}{\partial T}\right)_V$$

$$F - T\left(\frac{\partial F}{\partial T}\right)_V = -T^2\left\{\frac{1}{T}\left(\frac{\partial F}{\partial T}\right)_V + F\left[\frac{\partial(1/T)}{\partial T}\right]_V\right\} = -T^2\left[\frac{\partial(F/T)}{\partial T}\right]_V = K_B T^2 \frac{\partial(\ln Z)}{\partial T}$$

Hence

$$F = -k_B T \ln Z = -k_B T \ln\left(\sum_i e^{-\varepsilon_i/k_B T}\right) \tag{1.31}$$

From Equations (1.11), (1.25), and (1.31), the entropy of a system at constant temperature can be calculated as

$$S = -k_B\langle \ln \rho \rangle = -k_B \sum_i \rho_i \ln \rho_i \tag{1.32}$$

1.2.4 Criteria for thermodynamic equilibrium

Now we consider the criteria which can used to judge whether a system is in its equilibrium state under given conditions. We already know that for a closed system, as it changes from a non-equilibrium state to the equilibrium state, the entropy increases:

$$\delta S \geq 0 \tag{1.33}$$

It can be stated differently that, for a closed system, the entropy is maximized in the equilibrium state.

In considering the equilibrium state of a system at constant temperature and volume, we construct a closed system which consists of the system (subsystem 1) under consideration and a thermal reservoir (subsystem 2) with temperature T. When the two systems are brought into thermal contact, energy is exchanged between subsystem 1 and subsystem 2. Because the whole system is a closed system, $\delta S = \delta S_1 + \delta S_2 \geq 0$. For system 2, $1/T = (\partial S_2/\partial U_2)_V$, and therefore $\delta S_2 = \delta U_2/T$ (this is true when the volume of the subsystem is fixed, which also means the volume of subsystem 1 is fixed). Because of energy conservation, $\delta U_2 = -\delta U_1$. Hence $\delta S = \delta S_1 + \delta S_2 = \delta S_1 + \delta U_2/T = \delta S_1 - \delta U_1/T \geq 0$. Because the temperature and volume are constant for subsystem 1, $\delta S_1 - \delta U_1/T = (1/T)\delta(TS_1 - U) \geq 0$, and therefore

$$\delta(U_1 - TS_1) = \delta F_1 \leq 0 \tag{1.34}$$

At constant temperature and volume, the equilibrium state has minimum Helmholtz free energy.

Again, as above, in considering the equilibrium state of a system at constant temperature and pressure, we construct a closed system which consists of the system (subsystem 1) under consideration and a thermal reservoir (subsystem 2) with temperature T. When the two systems are brought into thermal contact, energy is exchanged between subsystem 1 and subsystem 2. Because the whole system is a closed system, $\delta S = \delta S_1 + \delta S_2 \geq 0$. But now, for system 2, because the volume is not fixed, and mechanical work is involved, $\delta U_2 = T\delta S_2 - P\delta V_2$, i.e., $\delta S_2 = (\delta U_2 + P\delta V_2)/T$. Because $\delta U_2 = -\delta U_1$ and $\delta V_2 = -\delta V_1$, then $\delta S = \delta S_1 + (\delta U_2 + P\delta V_2)/T = \delta S_1 - (\delta U_1 + P\delta V_1)/T = (1/T)\delta(TS_1 - U_2 - PV_1) \geq 0$. Therefore

$$\delta(U_1 + PV_1 - TS_1) = \delta G_1 \leq 0 \tag{1.35}$$

At constant temperature and pressure, the equilibrium state has minimum Gibbs free energy. If electric energy is involved, then we have to consider the electric work done to the system by external sources such as a battery. In a thermodynamic process, if the electric work done to the system is dW_e, then

$$\delta S \geq \frac{dQ}{T} = \frac{dU - dW_m - dW_e}{T} = \frac{dU + PdV - dW_e}{T}$$

Therefore at constant temperature and pressure

$$\delta(U - W_e + PV - TS) = \delta(G - W_e) \leq 0 \tag{1.36}$$

In the equilibrium state, $G - W_e$ is minimized.

1.3 Orientational Order

Orientational order is the most important feature of liquid crystals. The average directions of the long axes of the rod-like molecules are parallel to each other. Because of the orientational order, liquid crystals possess anisotropic physical properties; that is, in different directions, they have different responses to external fields such as an electric field, a magnetic field, and shear. In this section, we will discuss how to quantitatively specify orientational order and why rod-like molecules tend to be parallel to each other.

For a rigid elongated liquid crystal molecule, three axes can be attached to it to describe its orientation. One is the long molecular axis and the other two are perpendicular to the long molecular axis. Usually the molecule rotates rapidly around the long molecular axis. Although the molecule is not cylindrical, if there is no hindrance to the rotation in the nematic phase, the rapid rotation around the long molecular axis makes it behave like a cylinder. There is no preferred direction for the short axes and thus the nematic liquid crystal is usually uniaxial. If there is hindrance to the rotation, the liquid crystal is biaxial. A biaxial nematic liquid crystal is a long sought for material. The lyotropic biaxial nematic phase has been observed [12]. The existence of a thermotropic biaxial nematic phase is still under debate, and it may exist in bent-core molecules [13,14]. Here our discussion is on bulk liquid crystals. The rotational symmetry around the long molecular axis can be broken by confinement. In this book, we will deal with uniaxial liquid crystals consisting of rod-like molecules unless otherwise stated.

1.3.1 Orientational order parameter

In uniaxial liquid crystals, we have only to consider the orientation of the long molecular axis. The orientation of a rod-like molecule can be represented by a unit vector $\hat{a}$ which is attached to the molecule and parallel to the long molecular axis. In the nematic phase, the average directions of the long molecular axes are along a common direction: namely, the liquid crystal director denoted by the unit vector $\vec{n}$. The 3-D orientation of $\hat{a}$ can be specified by the polar angle θ and the azimuthal angle ϕ where the z axis is chosen parallel to $\vec{n}$ as shown in Figure 1.4. In general the orientational order of $\hat{a}$ is specified by an orientational distribution function $f(\theta, \phi)$. $f(\theta, \phi)d\Omega(d\Omega = \sin\theta d\theta d\phi)$ is the probability that $\hat{a}$ is oriented along the direction specified by θ and ϕ within the solid angle $d\Omega$. In the isotropic phase, $\hat{a}$ has equal probability of pointing in any direction and therefore $f(\theta, \phi) = \text{constant}$. For uniaxial liquid crystals, there is no preferred orientation in the azimuthal direction, and then $f = f(\theta)$ which depends only on the polar angle θ.

Rod-like liquid crystal molecules may have permanent dipole moments. If the dipole moment is perpendicular to the long molecular axis, the dipole has equal probability of pointing along any direction because of the rapid rotation around the long molecular axis in uniaxial liquid crystal phases. The dipoles of the molecules cannot generate spontaneous polarization. If the permanent dipole moment is along the

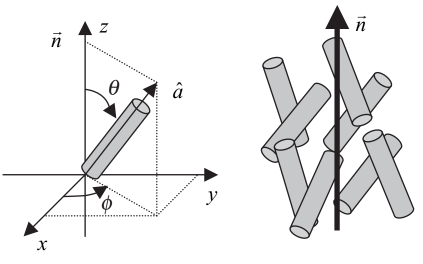


Figure 1.4 Schematic diagram showing the orientation of rod-like molecules

long molecular axis, the flip of the long molecular axis is much slower (of the order of 10^{-5} s), so the above argument does not hold. In order to see the orientation of the dipoles in this case, we consider the interaction between two dipoles [15]. When one dipole is on top of the other, if they are parallel, the interaction energy is low and thus parallel orientation is preferred. When two dipoles are side by side, if they are anti-parallel, the interaction energy is low and thus anti-parallel orientation is preferred. As we know, the molecules cannot penetrate each other. For elongated molecules, the distance between two dipoles when they are on top of each other is farther than that when they are side by side. The interaction energy between two dipoles is inversely proportional to the cubic power of the distance between them. Therefore anti-parallel orientation of dipoles is dominant in rod-like molecules. There are the same number of dipoles aligned parallel to the liquid crystal director $\vec{n}$ as there are aligned anti-parallel to $\vec{n}$. The permanent dipole along the long molecular axis cannot generate spontaneous polarization. Thus, even when the molecules have a permanent dipole moment along the long molecular axes, they can be regarded as cylinders whose top and bottom are the same. It can also be concluded that $\vec{n}$ and $-\vec{n}$ are equivalent.

An order parameter must be defined in order to quantitatively specify the orientational order. The order parameter is usually defined in such a way that it is zero in the high-temperature unordered phase and non-zero in the low-temperature ordered phase. By analogy with ferromagnetism, we may consider the average value of the projection of $\hat{a}$ along the director $\vec{n}$, i.e.,

$$\langle\cos\theta\rangle = \int_0^\pi \cos\theta f(\theta)\sin\theta d\theta \Big/ \int_0^\pi f(\theta)\sin\theta d\theta \tag{1.37}$$

where $\langle\rangle$ indicate the average (the temporal and spatial averages are the same) and $\cos\,\theta$ is the first-order Legendre polynomial. In the isotropic phase, the molecules are randomly oriented and $\langle\cos\theta\rangle = 0$. We also know that in the nematic phase the probability that a molecule will orient at angles θ and $\pi - \theta$ is the same, i.e., $f(\theta) = f(\pi - \theta)$; therefore $\langle\cos\theta\rangle = 0$, and so $\langle\cos\theta\rangle$ provides no information about the orientational order parameter. Next, let us consider the average value of the second-order Legendre polynomial for the order parameter:

$$S = \langle P_2(\cos\theta)\rangle = \left\langle \frac{1}{2}(3\cos^2\theta - 1)\right\rangle = \int_0^\pi \frac{1}{2}(3\cos^2\theta - 1) f(\theta)\sin\theta d\theta \Big/ \int_0^\pi f(\theta)\sin\theta d\theta \tag{1.38}$$

In the isotropic phase as shown in Figure 1.5(b), $f(\theta) = c$, a constant, and

$$\int_0^\pi \frac{1}{2}(3\cos^2\theta - 1) f(\theta)\sin\theta d\theta = \int_0^\pi \frac{1}{2}(3\cos^2\theta - 1) c\sin\theta d\theta = 0$$

In the nematic phase, $f(\theta)$ depends on θ. For a perfectly ordered nematic phase as shown in Figure 1.5(d), $f(\theta) = \delta(\theta)$, where $\sin\theta\delta(\theta) = \infty$ when $\theta = 0$, $\sin\theta\delta(\theta) = 0$ when $\theta \neq 0$, and $\int_0^\pi \delta(\theta)\sin\theta d\theta = 1$, and the order parameter is $S = \frac{1}{2}(3\cos^2\theta - 1) = 1$. It should be pointed out that the order parameter can be positive or negative. Two order parameters with the same absolute value but different signs correspond to different states. When the molecules all lie in a plane but are randomly oriented in the plane as shown in Figure 1.5(a), the distribution function is $f(\theta) = \delta(\theta - \pi/2)$, where $\delta(\theta - \pi/2) = \infty$ when $\theta = \pi/2$, $\delta(\theta - \pi/2) = 0$ when $\theta \neq \pi/2$, and $\int_0^\pi \delta(\theta - \pi/2)\sin\theta d\theta = 1$, and the order parameter is $S = \frac{1}{2}[3\cos^2(\pi/2) - 1)/1 = -0.5$. In this case, the average direction of the molecules

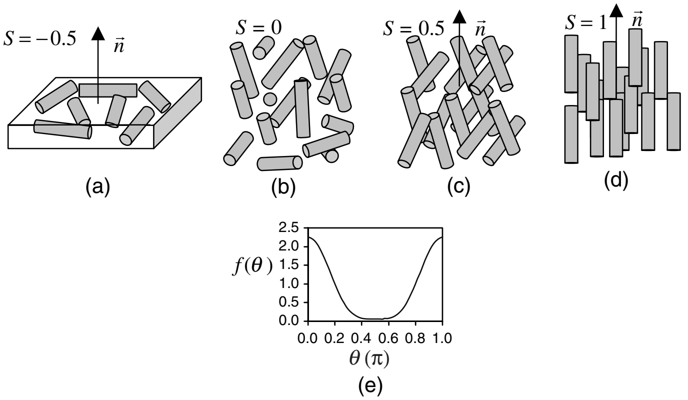


Figure 1.5 Schematic diagram showing the states with different orientational order parameters

is not well defined. The director $\vec{n}$ is defined by the direction of the uniaxial axis of the material. Figure 1.5(c) shows the state with the distribution function $f(\theta) = (35/16)[\cos^4\theta + (1/35)]$, which is plotted vs. θ in Figure 1.5(e). The order parameter is $S = 0.5$. Many anisotropies of physical properties are related to the order parameter and will be discussed later.

1.3.2 Landau–de Gennes theory of orientational order in the nematic phase

Landau developed a theory for second-order phase transitions [16], such as those from the diamagnetic phase to the ferromagnetic phase, in which the order parameter increases continuously from zero as the temperature is decreased across the transition temperature T_c from the high-temperature disordered phase to the low temperature ordered phase. For a temperature near T_c, the order is very small. The free energy of the system can be expanded in terms of the order parameter.

The transition from water to ice at 1 atmosphere pressure is a first-order transition and the latent heat is about 100 J/g. The isotropic–nematic transition is a weak first-order transition because the order parameter changes discontinuously across the transition but the latent heat is only about 10 J/g. De Gennes extended Landau's theory to the isotropic–nematic transition because it is a weak first-order transition [1, 17]. The free energy density f of the material can be expressed in terms of the order parameter S as

$$f = \frac{1}{2}a(T - T^*)S^2 - \frac{1}{3}bS^3 + \frac{1}{4}cS^4 + \frac{1}{2}L(\nabla S)^2 \tag{1.39}$$

where a, b, c and L are constants and T^* is the virtual second-order phase transition temperature. The last term is the energy cost when there is a variation of the order parameter in space, but here we will consider only the uniform order parameter case. There is no linear term of S, which would result in a non-zero order parameter at any temperature; a is positive, otherwise S will never be zero and the isotropic phase will not be stable at any temperature. A significant difference between the free energy here and that of a magnetic system is the cubic term. In a magnetic system, the magnetization m is the order parameter. For a given value of $|m|$, there is only one state, and the sign of m is decided by the choice of the coordinate. The free energy must be the same for a positive m and a negative m, and therefore the coefficient of the cubic term must be zero. For nematic liquid crystals, positive and negative values of the order parameter S correspond to two different states and the corresponding free energies can be different, and therefore b is not zero; b must be positive because at sufficiently low temperatures positive order parameters have global minimum free energies. We also know that the maximum value of S is 1. The quadratic term with a positive c prevents S from exploding. The values of the coefficients can be estimated in the following way: the energy of the intermolecular interaction between the molecules associated with orientation is about 0.1 eV and the molecular size is about 1 nm, f is the energy per unit volume, and therefore $Ta(\text{or } b \text{ or } c) \sim 0.1\ \text{eV/volume of 1 molecule} \sim 0.1 \times 10^{-19}\ \text{joules}/(10^{-9}\ \text{m})^3 \sim 10^7\ \text{J/m}^3$. For a given temperature, the order parameter S is found by minimizing f:

$$\frac{\partial f}{\partial S} = a(T - T^*)S - bS^2 + cS^3 = \left[a(T - T^*) - bS + cS^2\right]S = 0 \tag{1.40}$$

There are three solutions:

$$\begin{aligned} S_1 &= 0 \\ S_2 &= \frac{1}{2c}\left[b + \sqrt{b^2 - 4ac(T - T^*)}\right] \\ S_3 &= \frac{1}{2c}\left[b - \sqrt{b^2 - 4ac(T - T^*)}\right] \end{aligned}$$

$S_1 = 0$ corresponds to the isotropic phase and the free energy is $f_1 = 0$. The isotropic phase has global minimum free energy at a high temperature. It will be shown that at a low temperature S_2 has global minimum free energy

$$f_2 = \frac{1}{2}a(T - T^*)S_2^2 - \frac{1}{3}bS_2^3 + \frac{1}{4}cS_2^4$$

S_3 has a local minimum free energy. At the nematic–isotropic phase transition temperature T_{NI}, the order parameter is $S_c = S_{2c}$, and $f_2(S_2 = S_c) = f_1 = 0$; that is,

$$\frac{1}{2}a(T_{NI} - T^*)S_c^2 - \frac{1}{3}bS_c^3 + \frac{1}{4}cS_c^4 = 0 \tag{1.41}$$

From Equation (1.40), at this temperature, we also have

$$a(T_{NI} - T^*) - bS_c + cS_c^2 = 0 \tag{1.42}$$

From these two equations, we can obtain

$$a(T_{NI} - T^*) - \frac{1}{3}bS_c = 0$$

Therefore

$$S_c = \frac{3a}{b}(T_{NI} - T^*) \tag{1.43}$$

Substituting Equation (1.43) into Equation (1.42), we get the transition temperature

$$T_{NI} = T^* + \frac{2b^2}{9ac} \tag{1.44}$$

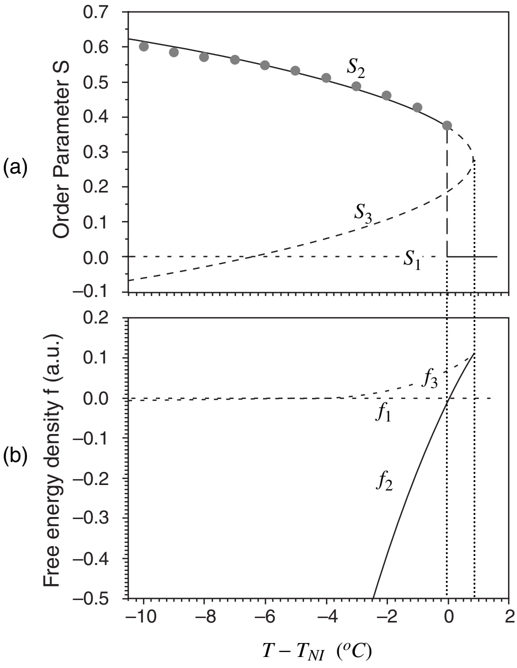


Figure 1.6 (a) The three solutions of order parameter as a function of temperature; (b) the corresponding free energies as a function of temperature, in Landau-de Gennes theory

and the order parameter at the transition temperature

$$S_c = \frac{2b}{3c} \tag{1.45}$$

For liquid crystal 5CB, the experimentally measured order parameter is shown by the solid circles in Figure 1.6(a) [6]. In fitting the data, the following parameters were used: $a = 0.023\sigma\,\mathrm{J/Km^3}$, $b = 1.2\sigma\,\mathrm{J/m^3}$, and $c = 2.2\sigma\,\mathrm{J/m^3}$, where σ is a constant which has to be determined by the latent heat of the nematic–isotropic transition.

Because S is a real number in the region from -0.5 to 1.0, when $T - T^* > b^2/4ac$, i.e., when $T - T_{NI} > b^2/4ac - 2b^2/9ac = b^2/36ac$, S_2 and S_3 are not real. The only real solution is $S = S_1 = 0$, corresponding to the isotropic phase. When $T - T_{NI} < b^2/36ac$, there are three solutions. However, when $0 < T - T_{NI} \leq b^2/36ac$, the isotropic phase is the stable state because its free energy is still the global minimum as shown in Figure 1.6(b). When $T - T_{NI} \leq 0$, the nematic phase with order parameter $S = S_2 = \left[b + \sqrt{b^2 - 4ac(T - T^*)}\right]/2c$ is the stable state because its free energy is the global minimum.

In order to see the physical meaning clearly, let us plot f vs. S at various temperatures as shown in Figure 1.7. At temperature $T_1 = T_{NI} + b^2/36ac + 1.0$°C, the curve has only one minimum at $S = 0$, which means that $S_1 = 0$ is the only solution and the corresponding isotropic phase is the stable state. At temperature $T_3 = T_{NI} + b^2/36ac - 0.5$°C, there are two local minima and one local maximum, where there are three solutions: $S_1 = 0, \quad S_2 > 0, \quad \text{and} \quad S_3 > 0$. $S_1 = 0$ corresponds to the global minimum free energy and the isotropic phase is still the stable state. At $T_4 = T_{NI}$, the free energies of the isotropic phase with order parameter S_1 and the nematic phase with order parameter S_2 become the same; phase

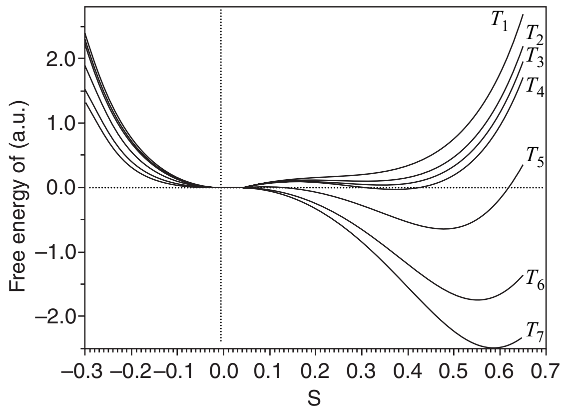


Figure 1.7 Free energy vs. order parameter at various temperatures in Landau-de Gennes theory

transition takes place and the order parameter changes discontinuously from 0 to $S_c = 2b/3c$. This is a first-order transition. It can be seen from the figure that at this temperature there is an energy barrier between S_1 and S_2. If the system is initially in the isotropic phase and there are no means to overcome the energy barrier, it will remain in the isotropic phase at this temperature. As the temperature is decreased, the energy barrier is lowered. At $T_5 = T_{NI} - 3°\text{C}$, the energy barrier is low. At $T_6 = T^*$, the second-order derivative of f with respect to S at $S_1 = 0$ is

$$\left.\frac{\partial^2 f}{\partial S^2}\right|_{S=0} = a(T - T^*) - 2bS + 3cS^2\Big|_{S=0} = a(T - T^*) = 0$$

S_1 is no longer a local minimum, and the energy barrier disappears. T^* is therefore the supercooling temperature below which the isotropic phase becomes absolutely unstable. At this temperature, $S_1 = S_3$. At $T_7 = T^* - 2°\text{C}$, there are two minima located at $S_2(>0)$ and $S_3(<0)$ (the minimum value is slightly below zero), and a maximum at $S_1 = 0$.

If initially the system is in the nematic phase, it will remain in this phase even at temperatures higher than T_{NI} and its free energy is higher than that of the isotropic phase because there is an energy barrier preventing the system from transforming from the nematic phase to the isotropic phase. The temperature T_2 (superheating temperature) at which the nematic phase becomes absolutely unstable can be found from

$$\left.\frac{\partial^2 f}{\partial S^2}\right|_{S_2} = a(T_2 - T^*) - 2bS_2 + 3cS_2^2 = 0 \tag{1.46}$$

Using $S_2 = (1/2c)[b + \sqrt{b^2 - 4ac(T_2 - T^*)}]$, we can get $T_2 = T_{NI} + b^2/36ac$.

In reality, there are usually irregularities, such impurities and defects, which can reduce the energy barrier of nematic–isotropic transition. The phase transition takes place before the thermodynamic instability limits (the supercooling or superheating temperature). Under an optical microscope, it is usually observed that with decreasing temperature nematic ‘islands’ are initiated by irregularities and grow out of the isotropic ‘sea’, and with increasing temperature isotropic ‘lakes’ are produced by irregularities and grow on the nematic ‘land’. The irregularities are called nucleation seeds and the transition is a nucleation process. In summary, nematic–isotropic transition is a first-order transition and the order parameter changes discontinuously, there is an energy barrier in the transition, and the transition is a nucleation process; superheating and supercooling occur. In a second-order transition, there is no energy barrier and the transition occurs simultaneously everywhere at the transition temperature (the critical temperature).

There are a few points worth mentioning in Landau–de Gennes theory. First, the theory works well at temperatures near the transition temperature. At temperatures far below the transition temperature, however, the order parameter increases without limit with decreasing temperature, and the theory does not work well because the maximum order parameter should be 1. In Figure 1.6, the parameters are chosen in such a way that the fitting is good for a relatively wide temperatures region, $T_{NI} - T^* = 2b^2/9ac = 6.3°\mathrm{C}$, which is much larger than the value ($\sim 1°\mathrm{C}$) measured by light-scattering experiments in the isotropic phase [18]. There are fluctuations in orientational order in the isotropic phase, which results in a variation of refractive index in space and causes light scattering. The intensity of the scattered light is proportional to $1/(T - T^*)$.

1.3.3 Maier–Saupe theory

In the nematic phase, there are interactions, such as the van der Waals interaction, between the liquid crystal molecules. Because the molecular polarizability along the long molecular axis is larger than along the short transverse molecular axis, the interaction is anisotropic and results in the parallel alignment of the rod-like molecules. In the spirit of the mean field approximation, Maier and Saupe introduced an effective single molecule potential V to describe the intermolecular interaction [19, 20]. The potential has the following properties. (1) It must be a minimum when the molecule orients along the liquid crystal director (the average direction of the long molecular axis of the molecules). (2) Its strength is proportional to the order parameter $S = \langle P_2(\cos\theta)\rangle$ because the potential well is deep when the molecules are highly orientationally ordered and vanishes when the molecules are disordered. (3) It assures that the probabilities for the molecules pointing up and down are the same. The potential in Maier–Saupe theory is given by

$$V(\theta) = -\nu S\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right) \tag{1.47}$$

where ν is the orientational interaction constant of the order of 0.1 eV and θ is the angle between the long molecular axis and the liquid crystal director as shown in Figure 1.4. The probability f of the molecule orienting along the direction with polar angle θ is governed by the Boltzmann distribution:

$$f(\theta) = e^{-V(\theta)/k_BT} \Big/ \int_0^\pi e^{-V(\theta)/k_BT}\sin\theta d\theta \tag{1.48}$$

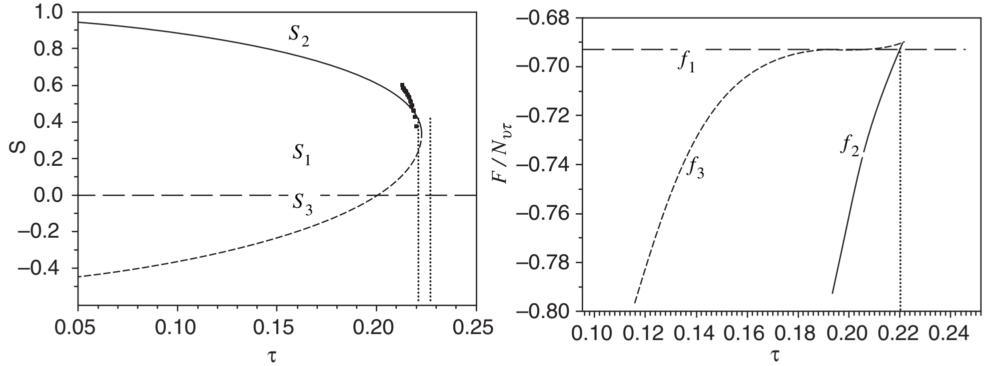
The single molecule partition function is

$$Z = \int_0^\pi e^{-V(\theta)/k_BT}\sin\theta d\theta \tag{1.49}$$

From the orientational distribution function we can calculate the order parameter:

$$S = \frac{1}{Z}\int_0^\pi P_2(\cos\theta)e^{-V(\theta)/k_BT}\sin\theta d\theta = \frac{1}{Z}\int_0^\pi P_2(\cos\theta)e^{\nu SP_2(\theta)/k_BT}\sin\theta d\theta \tag{1.50}$$

We introduce a normalized temperature $\tau = k_BT/\nu$. For a given value of τ, the order parameter S can be found by numerically solving Equation (1.50). An iteration method can be used for the numerical calculation of the order parameter: (1) choose an initial value for the order parameter, (2) substitute it



(a) (b)

Figure 1.8 (a) The three solutions of order parameter as a function of the normalized temperature in Maier–Saupe theory. The solid circles represent the experimental data. (b) The normalized free energies of the three solutions of the order parameter

into the right hand side of Equation (1.50), and (3) calculate the order parameter. Use the newly obtained order parameter to repeat the above process until a stable value is obtained. As shown in Figure 1.8(a), there are three solutions: S_1, S_2, and S_3. In order to determine which is the actual solution, we have to examine the corresponding free energies. The free energy F has two parts, $F = U - TE_n$, where U is the intermolecular interaction energy and E_n is the entropy. The single molecular potential describes the interaction energy between one liquid crystal molecule and the remaining molecules of the system. The interaction energy of the system with N molecules is given by

$$U = \frac{1}{2}N\langle V\rangle = \frac{N}{2Z}\int_0^\pi V(\theta)e^{-V(\theta)/k_BT}\sin\theta d\theta \tag{1.51}$$

where the factor $\frac{1}{2}$ avoids counting the intermolecular interaction twice. The entropy is calculated by using Equation (1.32):

$$En = -Nk_B\langle\ln f\rangle = -\frac{Nk_B}{Z}\int_0^\pi \ln[f(\theta)]e^{-V(\theta)/k_BT}\sin\theta d\theta \tag{1.52}$$

From Equation (1.48) we have $\ln[f(\theta)] = -V(\theta)/k_BT - \ln Z$; therefore $En = (N/T)\langle V\rangle + Nk_B\ln Z$ and the free energy is

$$F = U - TEn = -Nk_BT\ln Z - \frac{1}{2}N\langle V\rangle \tag{1.53}$$

From Equation (1.47) we have $\langle V\rangle = -vS^2$ and therefore

$$F = U - TEn = -Nk_BT\ln Z + \frac{1}{2}NvS^2 \tag{1.54}$$

Although the second term in this equation looks abnormal, this equation is correct and can be checked by calculating the derivative of F with respect to S:

$$\frac{\partial F}{\partial S} = -Nk_BT\frac{\partial\ln Z}{\partial S} - \frac{1}{2}N\frac{\partial\langle V\rangle}{\partial S} = -\frac{Nk_BT}{Z}\frac{\partial Z}{\partial S} + NvS$$

Letting $\partial F/\partial S = 0$, we have

$$S = \frac{k_BT}{vZ}\frac{\partial Z}{\partial S} = \frac{k_BT}{vZ}\int_0^{\pi} \frac{-1}{k_BT}\frac{\partial V}{\partial S} e^{-V(\theta)/k_BT}\sin\theta d\theta = \frac{1}{Z}\int_0^{\pi} P_2(\cos\theta) e^{vSP_2(\theta)/k_BT}\sin\theta d\theta$$

which is consistent with Equation (1.50). The free energies corresponding to the solutions are shown in Figure 1.8(b). The nematic–isotropic phase transition temperature is $\tau_{NI} = 0.22019$. For temperatures higher than τ_{NI}, the isotropic phase with order parameter $S = S_1 = 0$ has a lower free energy and thus is stable. For temperatures lower than τ_{NI}, the nematic phase with order parameter $S = S_2$ has a lower free energy and thus is stable. The order parameter jumps from 0 to $S_c = 0.4289$ at the transition.

In the Maier–Saupe theory there are no fitting parameters. The predicted order parameter as a function of temperature is universal, and agrees qualitatively, but not quantitatively, with experimental data. This indicates that higher order terms are needed in the single molecule potential, i.e.,

$$V(\theta) = \sum_i [-v_i \langle P_i(\cos\theta)\rangle P_i(\cos\theta)] \tag{1.55}$$

where $P_i(\cos\theta)$ $(i = 2, 4, 6, \ldots)$ are the ith-order Legendre polynomials. The fitting parameters are v_i. With higher order terms, better agreement with experimental results can be achieved.

Maier–Saupe theory is very useful in considering liquid crystal systems consisting of more than one type of molecule, such as mixtures of nematic liquid crystals and dichroic dyes. The interactions between different molecules are different and the constituent molecules have different order parameters.

All the theories discussed above do not predict well the orientational order parameter for temperatures far below T_{NI}. The order parameter as a function of temperature is better described by the empirical formula [21]

$$S = \left(1 - \frac{0.98TV^2}{T_{NI}V_{NI}^2}\right)^{0.22} \tag{1.56}$$

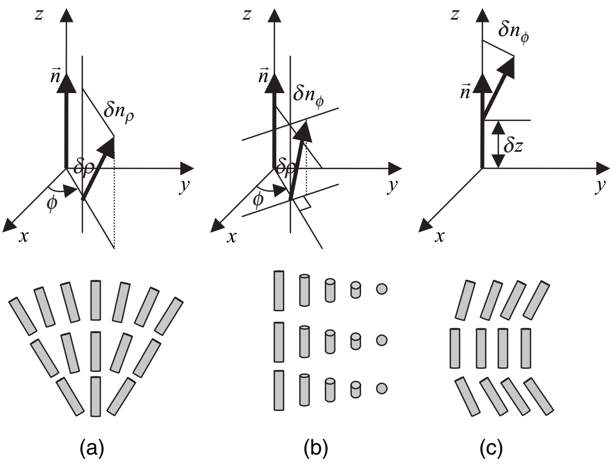
where V and V_{NI} are the molar volumes at T and T_{NI}, respectively.

1.4 Elastic Properties of Liquid Crystals

In the nematic phase, the liquid crystal director $\vec{n}$ is uniform in space in the ground state. In reality, the liquid crystal director $\vec{n}$ may vary spatially because of confinement or external fields. This spatial variation of the director, called the deformation of the director, costs energy. When the variation occurs over a distance much larger than the molecular size, the orientational order parameter does not change and the deformation can be described by a continuum theory analogous to the classic elastic theory of a solid. The elastic energy is proportional to the square of the spatial variation rate.

1.4.1 Elastic properties of nematic liquid crystals

There are three possible deformation modes of the liquid crystal director as shown in Figure 1.9. We choose the cylindrical coordinate such that the z axis is parallel to the director at the origin of the coordinate: $\vec{n}(0) = \hat{z}$. Consider the variation of the director at an infinitely small distance from the origin. When moving in the radial direction, there are two possible modes of variation: (1) the director tilts toward the radial direction $\hat{\rho}$ as shown in Figure 1.9(a), and (2) the director tilts toward the azimuthal



(a) (b) (c)

Figure 1.9 The three possible deformations of the liquid crystal director: (a) splay; (b) twist; and (c) bend

direction $\hat{\phi}$ as shown in Figure 1.9(b). The first mode is called splay, where the director at $(\delta\rho,\ \phi,\ z=0)$ is

$$\vec{n}(\delta\rho, z=0) = \delta n_\rho(\delta\rho)\hat{\rho} + [1+\delta n_z(\delta\rho)]\hat{z} \tag{1.57}$$

where $\delta n_\rho \ll 1$ and $\delta n_z \ll 1$. Because $|\vec{n}|^2 = n_\rho^2 + n_\phi^2 + n_z^2 = (\delta n_\rho)^2 + (1+\delta n_z)^2 = 1$, then $\delta n_z = -(\delta n_\rho)^2/2$, where δn_z is a higher order term and can be neglected. The spatial variation rate is $\partial n_\rho/\partial\rho$ and the corresponding elastic energy is

$$f_{splay} = (1/2)K_{11}(\partial n_\rho/\partial\rho)^2 \tag{1.58}$$

where K_{11} is the splay elastic constant.

The second mode is called twist, where the director at $(\delta\rho,\ \phi,\ z=0)$ is

$$\vec{n}(\delta\rho,\ \phi,\ z=0) = \delta n_\phi(\delta\rho)\hat{\phi} + [1+\delta n_z(\delta\rho)]\hat{z} \tag{1.59}$$

where $\delta n_\phi \ll 1$ and $\delta n_z = -(\delta n_\phi)^2/2$, a higher order term which can be neglected. The spatial variation rate is $\partial n_\phi/\partial\rho$ and the corresponding elastic energy is

$$f_{twist} = (1/2)K_{22}(\partial n_\phi/\partial\rho)^2 \tag{1.60}$$

where K_{22} is the twist elastic constant.

When moving in the z direction, there is only one possible mode of variation, as shown in Figure 1.9(c), which is called bend. The director at $(\rho=0,\ \phi,\ \delta z)$ is

$$\vec{n}(\rho=0,\ \phi,\ \delta z) = \delta n_\rho(\delta z)\hat{\rho} + [1+\delta n_z(\delta z)]\hat{z} \tag{1.61}$$

where $\delta n_\rho \ll 1$ and $\delta n_z = -(\delta n_\rho)^2/2$, a higher order term which can be neglected.

Note that when $\rho = 0$, the azimuthal angle is not well defined and we can choose the coordinate such that the director tilts toward the radial direction. The corresponding elastic energy is

$$f_{bend} = (1/2)K_{33}(\partial n_\rho/\partial z)^2 \tag{1.62}$$

where K_{33} is the bend elastic constant. Because δn_z is a higher order term, $\partial n_z/\partial z \approx 0$ and $\partial n_z/\partial \rho \approx 0$. Recall that $\nabla \cdot \vec{n}|_{\rho=0,\,z=0} = (1/\rho)\partial(\rho n_\rho)/\partial\rho + (1/\rho)\partial n_\phi/\partial\phi + \partial n_z/\partial z = \partial n_\rho/\partial\rho + \delta n_\rho$. Because $\partial n_\rho/\partial\rho$ is finite and $\delta n_\rho \ll 1$, $\nabla \cdot \vec{n}|_{\rho=0,\,z=0} = \partial n_\rho/\partial\rho$. The splay elastic energy can be expressed as $f_{splay} = (1/2)K_{11}(\nabla \cdot \vec{n})^2$. Because $\vec{n} = \hat{z}$, at the origin $\vec{n} \cdot \nabla \times \vec{n}|_{\rho=0,\,z=0} = (\nabla \times \vec{n})_z = \partial n_\phi/\partial\rho$. The twist elastic energy can be expressed as $f_{twist} = (1/2)K_{22}(\vec{n} \cdot \nabla \times \vec{n})^2$. Because $\vec{n} \times \nabla \times \vec{n}|_{\rho=0,\,z=0} = (\nabla \times \vec{n})_\rho - (\nabla \times \vec{n})_\phi = \partial n_\rho/\partial z$, the bend elastic energy can be expressed as $f_{bend} = (1/2)K_{33}(\vec{n} \times \nabla \times \vec{n})^2$. Putting all the three terms together, we obtain the elastic energy density:

$$f_{ela} = \frac{1}{2}K_{11}(\nabla \cdot \vec{n})^2 + \frac{1}{2}K_{22}(\vec{n} \cdot \nabla \times \vec{n})^2 + \frac{1}{2}K_{33}(\vec{n} \times \nabla \times \vec{n})^2 \tag{1.63}$$

This elastic energy is often referred to as the *Oseen–Frank energy* and K_{11}, K_{22}, and K_{33} are referred to as the Frank elastic constants because of his pioneering work on the elastic continuum theory of liquid crystals [22]. The value of the elastic constants can be estimated in the following way. When a significant variation of the director occurs in a length L, the angle between the average directions of the long molecular axes of two neighboring molecules is (a/L), where a is the molecular size. When the average directions of the long molecular axes of two neighboring molecules are parallel, the intermolecular interaction energy between them is a minimum. When the average direction of their long molecular axes makes an angle of (a/L), the intermolecular interaction energy increases to $(a/L)^2u$, where u is the intermolecular interaction energy associated with orientation and is about 0.1 eV. The increase of the interaction energy is the elastic energy, i.e.,

$$\left(\frac{a}{L}\right)^2 u = K_{ii}(\nabla\vec{n})^2 \times \text{molecular volume} = K_{ii}\left(\frac{1}{L}\right)^2 a^3$$

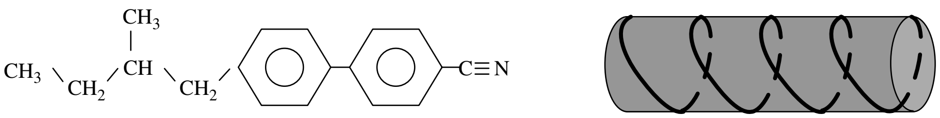
Therefore

$$K_{ii} = \frac{u}{a} \sim 0.1 \times 10^{-19}\frac{\text{J}}{1\,\text{nm}} = 10^{-11}\,\text{N}$$

Experiments show that usually the bend elastic constant K_{33} is the largest and the twist elastic constant K_{22} is the smallest. As an example, at room temperature the liquid crystal 5CB has these elastic constants: $K_{11} = 0.64 \times 10^{-11}$ N, $K_{22} = 0.3 \times 10^{-11}$ N, and $K_{33} = 1\times\ 10^{-11}$ N.

The elastic constants are temperature dependent. As shown in Maier–Saupe theory, the intermolecular interaction energy u (the averaged value of the potential given by Equation (1.47) is proportional to the square of the orientational order parameter S. Therefore the elastic constants are proportional to S^2.

It is usually sufficient to consider the splay, twist, and bend deformations of the liquid crystal director in determining the configuration of the director, except in some cases where the surface to volume ratio is high and another two terms, called divergence terms (or surface terms), may have to be considered. The elastic energy density of these terms is given by $f_{13} = K_{13}\nabla \cdot (\vec{n}\nabla \cdot \vec{n})$ and $f_{24} = -K_{24}\nabla \cdot (\vec{n}\nabla \cdot \vec{n} + \vec{n} \times \nabla \times \vec{n})$, respectively [23]. The volume integral of these two terms can be changed to a surface integral because of the Gauss theorem.



(a) (b)

Figure 1.10 (a) Chemical structure of a typical chiral liquid crystal molecule; (b) physical model of a chiral liquid crystal molecule

1.4.2 Elastic properties of cholesteric liquid crystals

So far we have considered liquid crystals consisting of molecules with reflectional symmetry. The molecules are the same as their mirror images, and are called *achiral* molecules. The liquid crystal 5CB shown in Figure 1.1(a) is an example of an achiral molecule. Now we consider liquid crystals consisting of molecules without reflectional symmetry. The molecules are different from their mirror images and are called *chiral* molecules. Such an example is CB15 shown in Figure 1.10(a). It can be regarded as a screw, instead of a rod, in considering its physical properties. After considering the symmetry where $\vec{n}$ and $-\vec{n}$ are equivalent, the generalized elastic energy density is

$$f_{ela}=\frac{1}{2}K_{11}(\nabla\cdot\vec{n})^2+\frac{1}{2}K_{22}(\vec{n}\cdot\nabla\times\vec{n}+q_o)^2+\frac{1}{2}K_{33}(\vec{n}\times\nabla\times\vec{n})^2 \tag{1.64}$$

where q_o is the *chirality* and its physical meaning will be discussed in a moment. Note that $\nabla\times\vec{n}$ is a pseudo-vector which does not change sign under reflectional symmetry while $\vec{n}\cdot\nabla\times\vec{n}$ is a pseudo-scalar which changes sign under reflectional symmetry operation. Under reflectional symmetry operation, the elastic energy changes to

$$f'_{ela}=\frac{1}{2}K_{11}(\nabla\cdot\vec{n})^2+\frac{1}{2}K_{22}(-\vec{n}\cdot\nabla\times\vec{n}+q_o)^2+\frac{1}{2}K_{33}(-\vec{n}\times\nabla\times\vec{n})^2 \tag{1.65}$$

If the liquid crystal molecule is achiral and thus has reflectional symmetry, the system does not change and the elastic energy does not change under reflectional symmetry operation. It is required that $f_{ela}=f'_{eta}$; then $q_o=0$. When the liquid crystal is in the ground state with minimum free energy, $f_{ela}=0$, which requires that $\nabla\cdot\vec{n}=0$, $\vec{n}\cdot\nabla\times\vec{n}=0$, and $\vec{n}\times\nabla\times\vec{n}=0$. This means that in the ground state, the liquid crystal director $\vec{n}$ is uniformly aligned along one direction.

If the liquid crystal molecule is chiral and thus has no reflectional symmetry, the system changes under reflectional symmetry operation. The elastic energy may change. It is no longer required that $f_{ela}=f'_{eta}$, and thus q_o may not be zero. When the liquid crystal is in the ground state with minimum free energy, $f_{ela}=0$, which requires that $\nabla\cdot\vec{n}=0$, $\vec{n}\cdot\nabla\times\vec{n}=-q_o$, and $\vec{n}\times\nabla\times\vec{n}=0$. A director configuration which satisfies the above conditions is

$$n_x=\cos(q_oz),\quad n_y=\sin(q_oz),\quad n_z=0 \tag{1.66}$$

and is schematically shown in Figure 1.11. The liquid crystal director twists in space. This type of liquid crystal is called a *cholesteric* liquid crystal. The axis around which the director twists is called the *helical axis* and is chosen to be parallel to z here. The distance P_o over which the director twists by 360° is called the *pitch* and is related to the chirality by

$$P_o=\frac{2\pi}{q_o} \tag{1.67}$$

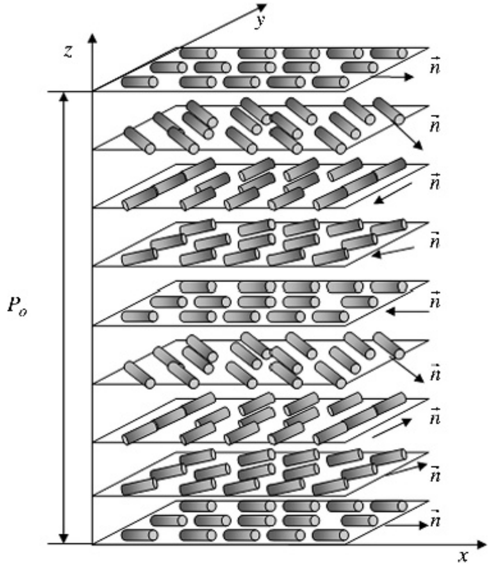


Figure 1.11 Schematic diagram of the director configuration of the cholesteric liquid crystal

Depending on the chemical structure, the pitch of a cholesteric liquid crystal could take any value in the region from a few tenths of a micron to infinitely long. The periodicity of a cholesteric liquid crystal with pitch P_o is $P_o/2$ because $\vec{n}$ and $-\vec{n}$ are equivalent. Cholesteric liquid crystals are also called *chiral nematic* liquid crystals and denoted as N*. Nematic liquid crystals can be considered as a special case of cholesteric liquid crystals with an infinitely long pitch.

In practice, a cholesteric liquid crystal is usually obtained by mixing a nematic host with a chiral dopant. The pitch of the mixture is given by

$$P = \frac{1}{(HTP) \cdot x} \tag{1.68}$$

where x is the concentration of the chiral dopant and (*HTP* is the *helical twisting power* of the chiral dopant, which is mainly determined by the chemical structure of the chiral dopant and depends only slightly on the nematic host.

1.4.3 Elastic properties of smectic liquid crystals

Smectic liquid crystals possess partial positional orders besides the orientational order exhibited in nematic and cholesteric liquid crystals. Here we only consider the simplest case: smectic-A. The elastic energy of the deformation of the liquid crystal director in smectic-A is the same as in the nematic liquid crystal. In addition, the dilatation (compression) of the smectic layer also costs energy which is given by [24]

$$f_{layer} = \frac{1}{2} B \left(\frac{d - d_o}{d_o} \right)^2 \tag{1.69}$$

where B is the elastic constant for the dilatation of the layer and is referred as to the Young modulus, d_o and d are the equilibrium layer thickness (the periodicity of the density undulation) and the actual layer

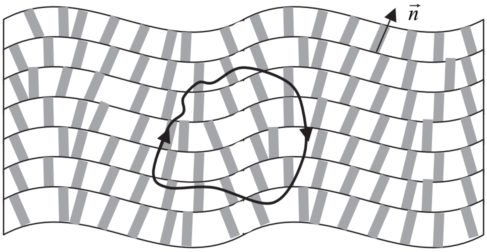


Figure 1.12 Schematic diagram showing the deformation of the liquid crystal director and the smectic layer in the smectic-A liquid crystal

thickness of the smectic layer, respectively. Typical values of B are about $10^6 - 10^7\ \mathrm{J/m^3}$, which are 10^3 to 10^4 smaller than those in a solid. In a slightly deformed smectic-A liquid crystal, we consider a closed loop as shown in Figure 1.12. The total number of layers traversed by the loop is zero, which can be mathematically expressed as $\oint \vec{n}\cdot dl = 0$. Using the Stokes theorem, we have $\int \nabla \times \vec{n}\cdot d\vec{s} = \oint \vec{n}\cdot dl = 0$. Therefore in smectic-A we have

$$\nabla \times \vec{n} = 0 \tag{1.70}$$

which assures that $\vec{n}\cdot\nabla\times\vec{n} = 0$ and $\vec{n}\times\nabla\times\vec{n} = 0$. The consequence is that twist and bend deformations of the director are not allowed (because they change the layer thickness and cost too much energy). The elastic energy in a smectic-A liquid crystal is

$$f_{elas} = \frac{1}{2}K_{11}(\nabla\cdot\vec{n})^2 + \frac{1}{2}B\left(\frac{d-d_o}{d_o}\right)^2 \tag{1.71}$$

Some chiral liquid crystals, as the temperature is decreased, exhibit the mesophases isotropic → cholesteric → smectic-A. Because of the property shown by Equation (1.70), there is no spontaneous twist in smectic-A. Expressed another way, the pitch in smectic-A is infinitely long. In the cholesteric phase, as the temperature is decreased toward the cholesteric–smectic-A transition, there is a pretransitional phenomenon where the smectic-A order forms in short space-scale and time-scale due to thermal fluctuations. This effect causes the pitch of the cholesteric liquid crystal to increase with decreasing temperature and diverge at the transition temperature as shown in Figure 1.13. As will be discussed later, a cholesteric liquid crystal with pitch P exhibits Bragg reflection at the wavelength $\lambda = \bar{n}P$, where $\bar{n}$ is the average refractive index of the material. If $\lambda = \bar{n}P$ is in the visible light region,

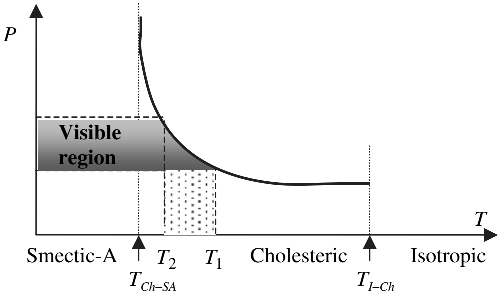


Figure 1.13 Schematic diagram showing how the pitch of a thermochromic cholesteric liquid crystal changes

the liquid crystal reflects colored light. When the temperature is varied, the color of the liquid crystal changes. These types of cholesteric liquid crystals are known as thermochromic cholesteric liquid crystals [24]. As shown in Figure 1.13, the reflected light is in the visible region for temperatures in the region from T_1 to T_2. There are liquid crystals with $\Delta T = T_1 - T_2 = 1^\circ$. If there are two thermochromic cholesteric liquid crystals with different cholesteric–smectic-A transition temperatures, mixtures with different concentrations of the two components will exhibit color reflections at different temperatures. This is how thermochromic cholesteric liquid crystals are used to make thermometers.

1.5 Response of Liquid Crystals to Electromagnetic Fields

Liquid crystals are anisotropic dielectric and diamagnetic media [1,25]. Their resistivities are very high ($\sim 10^{10}\,\Omega\,\text{cm}$). Dipole moments are induced in them by external fields. They have different dielectric permittivities and magnetic susceptibilities along the directions parallel and perpendicular to the liquid crystal director.

1.5.1 Magnetic susceptibility

We first consider magnetic susceptibility. Because the magnetic interaction between the molecules is weak, the local magnetic field of the molecules is approximately the same as the externally applied magnetic field. For a uniaxial liquid crystal, a molecule can be regarded as a cylinder. When a magnetic field $\vec{H}$ is applied to the liquid crystal, it has different responses to the applied field, depending on the angle between the long molecular axis $\vec{a}$ and the field $\vec{H}$. The magnetic field can be decomposed into a parallel component and a perpendicular component as shown in Figure 1.14. The magnetization $\vec{M}$ is given by

$$\begin{aligned}\vec{M} &= N\kappa_{\parallel}(\vec{a}\cdot\vec{H})\vec{a} + N\kappa_{\perp}[\vec{H} - (\vec{a}\cdot\vec{H})\vec{a}] \\ &= N\kappa_{\perp}\vec{H} + N\Delta\kappa(\vec{a}\cdot\vec{H})\vec{a} \\ &= N\kappa_{\perp}\vec{H} + N\Delta\kappa(\vec{a}\vec{a})\cdot\vec{H}\end{aligned} \tag{1.72}$$

where N is the molecular number density, $\kappa_{\parallel}$ and $\kappa_{\perp}$ are molecular magnetic polarizabilities parallel and perpendicular to the long molecular axis, respectively, and $\Delta\kappa = \kappa_{\parallel} - \kappa_{\perp}$. Expressed in matrix form, Equation (1.72) becomes

$$\vec{M} = N\begin{pmatrix} \kappa_{\perp} + \Delta\kappa a_x a_x & \Delta\kappa a_x a_y & \Delta\kappa a_x a_z \\ \Delta\kappa a_y a_x & \kappa_{\perp} + \Delta\kappa a_y a_y & \Delta\kappa a_y a_z \\ \Delta\kappa a_z a_x & \Delta\kappa a_z a_y & \kappa_{\perp} + \Delta\kappa a_z a_z \end{pmatrix}\cdot\vec{H} = N\overleftrightarrow{\kappa}\cdot\vec{H} \tag{1.73}$$

where $a_i\ (i = x,\ y,\ z)$ are the projections of $\vec{a}$ in the x, y, and z directions in the lab frame whose z axis is parallel to the liquid crystal director: $a_z = \cos\theta$, $a_x = \sin\theta\cos\phi$, and $a_y = \sin\theta\sin\phi$. The molecule swivels because of thermal motion. The averaged magnetization is $\vec{M} = N\langle\overleftrightarrow{\kappa}\rangle\cdot\vec{H}$. For a uniaxial liquid crystal, recall that $\langle\cos^2\theta\rangle = (2S+1)/3$, $\langle\sin^2\theta\rangle = (2-2S)/3$, $\langle\sin^2\phi\rangle = \langle\cos^2\phi\rangle = 1/2$, and $\langle\sin\phi\cos\phi\rangle = 0$. Therefore

$$\langle\overleftrightarrow{\kappa}\rangle = \begin{pmatrix} \kappa_{\perp} + \frac{1}{3}(1-S)\Delta\kappa & 0 & 0 \\ 0 & \kappa_{\perp} + \frac{1}{3}(1-S)\Delta\kappa & 0 \\ 0 & 0 & \kappa_{\perp} + \frac{1}{3}(2S+1)\Delta\kappa \end{pmatrix} \tag{1.74}$$

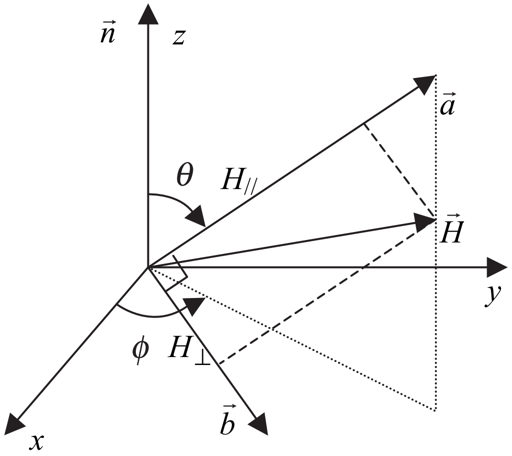


Figure 1.14 Schematic diagram showing the field decomposed into components parallel and perpendicular to the long molecular axis: $\vec{a}$, unit vector parallel to the long molecular axis; $\vec{b}$, unit vector perpendicular to the long molecular axis

Because $\vec{M} = \overleftrightarrow{\chi} \cdot \vec{H}$, the magnetic susceptibility tensor is

$$\overleftrightarrow{\chi} = \begin{pmatrix} \chi_\perp & 0 & 0 \\ 0 & \chi_\perp & 0 \\ 0 & 0 & \chi_\parallel \end{pmatrix} = N \begin{pmatrix} \kappa_\perp + \frac{1}{3}(1-S)\Delta\kappa & 0 & 0 \\ 0 & \kappa_\perp + \frac{1}{3}(1-S)\Delta\kappa & 0 \\ 0 & 0 & \kappa_\perp + \frac{1}{3}(2S+1)\Delta\kappa \end{pmatrix} \tag{1.75}$$

The anisotropy is

$$\Delta\chi = \chi_\parallel - \chi_\perp = N\Delta\kappa S \tag{1.76}$$

where $\chi_\parallel$ and $\chi_\perp$ are negative and small ($\sim 10^{-5}$ in SI units) and $\Delta\chi$ is usually positive. From Equation (1.75) it can be seen that $(2\chi_\perp + \chi_\parallel)/3 = N(3\kappa_\perp + \Delta\kappa)/3 = N(2\kappa_\perp + \kappa_\parallel)/3$, which is independent of the order parameter. The quantity $(2\chi_\perp + \chi_\parallel)/3N$ does not change discontinuously when crossing the nematic–isotropic transition.

1.5.2 Dielectric permittivity and refractive index

When an electric field is applied to a liquid crystal, it will induce dipole moments in the liquid crystal. For a uniaxial liquid crystal, the molecule can be regarded as a cylinder, and it has different molecular polarizabilities parallel and perpendicular to the long molecular axis $\vec{a}$. Similar to the magnetic case, when a local electric field $\vec{E}_{loc}$ (also called an internal field) is applied to the liquid crystal, the polarization (dipole moment per unit volume) is given by

$$\begin{aligned} \vec{P} &= N\alpha_\parallel(\vec{a}\cdot\vec{E}_{loc})\vec{a} + N\alpha_\perp[\vec{E}_{loc} - (\vec{a}\cdot\vec{E}_{loc})\vec{a}] \\ &= N\alpha_\perp\vec{E}_{loc} + N\Delta\alpha(\vec{a}\cdot\vec{E}_{loc})\vec{a} \\ &= N\alpha_\perp\vec{E}_{loc} + N\Delta\alpha(\vec{a}\vec{a})\cdot\vec{E}_{loc} \end{aligned} \tag{1.77}$$

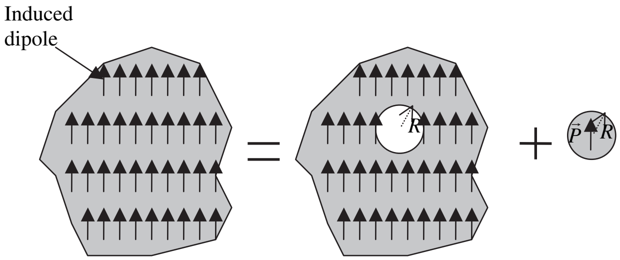


Figure 1.15 Schematic diagram showing how a macroscopic field is produced in a medium

where N is the molecular density, $\alpha_{\|}$ and $\alpha_{\perp}$ are the molecular polarizabilities parallel and perpendicular to the long molecular axis, respectively, and $\Delta\alpha = \alpha_{\|} - \alpha_{\perp}$. Different from the magnetic case, the dipole–dipole interactions between the molecules are strong, or, stated in another way, the local electric field on a molecule is the sum of the externally applied electric field and the electric field produced by the dipole moments of other molecules. We can approach this problem in the following way. Imagine a cavity created by removing the molecule under consideration, as shown in Figure 1.15. The macroscopic field $\vec{E}$ is the sum of the field $\vec{E}_{self}$ produced by the molecule itself and the field $\vec{E}_{else}$, which is the local field $\vec{E}_{local}$ produced by the external source and the rest of the molecules of the system:

$$\vec{E} = \vec{E}_{self} + \vec{E}_{else} = \vec{E}_{self} + \vec{E}_{local} \tag{1.78}$$

In order to illustrate the principle, let us first consider an isotropic medium. The cavity can be regarded as a sphere. The field $\vec{E}_{self}$ is produced by the dipole moment inside the sphere, which can be calculated in the following way. In the calculation of the field, the dipole moment can be replaced by the surface charge produced by the dipole moment on the surface of the sphere. The surface charge density is $\sigma = \vec{P} \cdot \vec{m}$. The field produced by the surface charge is $\vec{E}_{self} = -\vec{P}/3\varepsilon_o$. The local field is $\vec{E}_{local} = \vec{E} + \vec{P}/3\varepsilon_o$. Hence the polarizability is

$$\vec{P} = N\alpha\vec{E}_{loc} = N\alpha(\vec{E} + \vec{P}/3\varepsilon_o) \tag{1.79}$$

$$\vec{P} = \frac{N\alpha\vec{E}}{1 - N\alpha/3\varepsilon_o} \tag{1.80}$$

The electric displacement $\vec{D} = \varepsilon_o\varepsilon\vec{E} = \varepsilon_o\vec{E} + \vec{P}$, where $\varepsilon_o = 8.85 \times 10^{12}\,\mathrm{N/V^2}$ is the permittivity of vacuum, and ε is the (relative) dielectric constant which is given by

$$\varepsilon = 1 + \frac{\vec{P}}{\varepsilon_o\vec{E}} = 1 + \frac{N\alpha/\varepsilon_o}{1 - N\alpha/3\varepsilon_o} \tag{1.81}$$

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{1}{3\varepsilon_o}N\alpha \tag{1.82}$$

which is called the Clausius–Mossotti relation. At optical frequencies, the refractive index n is given by $n^2 = \varepsilon$, and therefore

$$\frac{n^2 - 1}{n^2 + 2} = \frac{1}{3\varepsilon_o} N\alpha \tag{1.83}$$

which is called the Lorentz–Lorenz relation. The local field is related to the macroscopic field by

$$\vec{E}_{local} = \vec{E} + \vec{P}/3\varepsilon_o = \vec{E} + \frac{N\alpha/3\varepsilon_o}{1 - N\alpha/3\varepsilon_o}\vec{E} = \frac{1}{1 - N\alpha/3\varepsilon_o}\vec{E} = K\vec{E} \tag{1.84}$$

where the defined $K = 1/(1 - N\alpha/3\varepsilon_o)$ is called the internal field constant.

Liquid crystals are anisotropic. The local field $\vec{E}_{local}$ in them depends on the macroscopic field $\vec{E}$ as well as the angles between $\vec{E}$ and the long molecular axis $\vec{a}$ and the liquid crystal director $\vec{n}$. They are related to each other by

$$\vec{E}_{local} = \overleftrightarrow{K} \cdot \vec{E} \tag{1.85}$$

where $\overleftrightarrow{K}$ is the internal field tensor which is a second-rank tensor. Taking account of the internal field tensor and the thermal motion of the molecules, the polarization is

$$\vec{P} = N\alpha_\perp \langle \vec{K} \rangle \cdot \vec{E} + N\Delta\alpha \langle [\vec{K} \cdot (\vec{a}\vec{a})] \rangle \cdot \vec{E} \tag{1.86}$$

The macroscopic dielectric tensor is

$$\overleftrightarrow{\varepsilon} = \overleftrightarrow{I} + \frac{N}{\varepsilon_o}[\alpha_\perp \langle \overleftrightarrow{K} \rangle + \Delta\alpha \langle \overleftrightarrow{K} \cdot (\vec{a}\vec{a}) \rangle] \tag{1.87}$$

In a material consisting of non-polar molecules, the induced polarization consist of two parts: (1) the electronic polarization $P_{electronic}$ which comes from the deformation of the electron clouds of the constituting atoms of the molecule, and (2) the ionic polarization P_{ionic} which comes from the relative displacement of the atoms constituting the molecule. For a material consisting of polar molecules, there is a third contribution, namely the dipolar polarization $P_{dipolar}$, which comes from the reorientation of the dipole. These contributions to the molecular polarizability depend on the frequency of the applied field. The rotation of the molecule is slow and therefore the dipole-orientation polarization can only contribute up to a frequency of megahertz. The vibration of atoms in molecules is faster and the ionic polarization can contribute up to the frequency of infrared light. The motion of electrons is the fastest and the electronic polarization can contribute up to the frequency of ultraviolet light. In relation to the magnitudes, the order is $P_{electronic} < P_{ionic} < P_{dipolar}$.

At optical frequencies, only the electronic polarization contributes to the molecular polarizability, which is small, and the electric field is usually low. De Jeu and Bordewijk showed experimentally that (1) $(2\varepsilon_\perp + \varepsilon_\parallel)/3\rho$ is a constant through the nematic and isotropic phases [25, 26], where ρ is the mass density, and (2) the dielectric anisotropy $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$ is directly proportional to the anisotropy of the magnetic susceptibility. Based on these results, it was concluded that $\overleftrightarrow{K}$ is a molecular tensor independent of the macroscopic dielectric anisotropy. In the molecular principal frame $\eta\zeta\xi$ with the ξ axis parallel to the long molecular axis $\vec{a}$, $\vec{K}$ has the form

$$\vec{K} = \begin{pmatrix} K_\perp & 0 & 0 \\ 0 & K_\perp & 0 \\ 0 & 0 & K_\parallel \end{pmatrix} \tag{1.88}$$

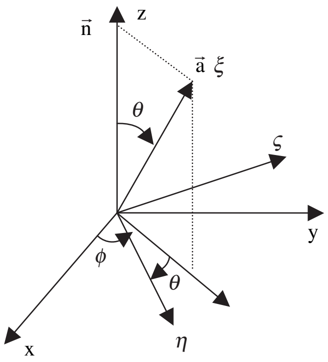


Figure 1.16 Schematic diagram showing the transformation between the molecular principal frame $\eta\zeta\xi$ and the lab frame *xyz*

Next we need to find the form of $\overleftrightarrow{K}$ in the lab frame *xyz* with the *z* axis parallel to the liquid crystal director $\vec{n}$. Because of the axial symmetry around $\vec{a}$, we only need to consider the transformation of the matrix between the two frames as shown in Figure 1.16. The frame $\eta\zeta\xi$ is achieved by first rotating the frame *xyz* around the *z* axis through the angle ϕ and then rotating the frame around the ζ axis through the angle θ. The rotation matrix is

$$\overleftrightarrow{R} = \begin{pmatrix} \cos\theta\cos\phi & -\sin\phi & \sin\theta\cos\phi \\ \cos\theta\sin\phi & \cos\phi & \sin\theta\sin\phi \\ -\sin\theta & 0 & \cos\theta \end{pmatrix} \tag{1.89}$$

and the reverse rotation matrix is

$$\overleftrightarrow{R}^{-1} = \begin{pmatrix} \cos\theta\cos\phi & \cos\theta\sin\phi & -\sin\theta \\ -\sin\phi & \cos\phi & 0 \\ \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \end{pmatrix} \tag{1.90}$$

In the lab frame $\overleftrightarrow{K}$ has the form

$$\begin{aligned} \vec{K} = \overleftrightarrow{R} \cdot \begin{pmatrix} K_\perp & 0 & 0 \\ 0 & K_\perp & 0 \\ 0 & 0 & K_{//} \end{pmatrix} \cdot \overleftrightarrow{R}^{-1} \\ = \begin{pmatrix} K_\perp + \Delta K\sin^2\theta\cos^2\phi & \Delta K\sin^2\theta\sin\phi\cos\phi & \Delta K\sin\theta\cos\theta\cos\phi \\ \Delta K\sin^2\theta\sin\phi\cos\phi & K_\perp + \Delta K\sin^2\theta\sin^2\phi & \Delta K\sin\theta\cos\theta\sin\phi \\ \Delta K\sin\theta\cos\theta\cos\phi & \Delta K\sin\theta\cos\theta\sin\phi & K_\perp + \Delta K\cos^2\theta \end{pmatrix} \end{aligned} \tag{1.91}$$

where $\Delta K = K_\parallel - K_\perp$, and $\vec{a}\vec{a}$ has the form

$$\begin{aligned}
\vec{a}\vec{a} &= \begin{pmatrix} \sin\theta\cos\phi \\ \sin\theta\sin\phi \\ \cos\theta \end{pmatrix} \begin{pmatrix} \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \end{pmatrix} \\
&= \begin{pmatrix} \sin^2\theta\cos^2\phi & \sin^2\theta\sin\phi\cos\phi & \sin\theta\cos\theta\cos\phi \\ \sin^2\theta\sin\phi\cos\phi & \sin^2\theta\sin^2\phi & \sin\theta\cos\theta\sin\phi \\ \sin\theta\cos\theta\cos\phi & \sin\theta\cos\theta\sin\phi & \cos^2\theta \end{pmatrix}
\end{aligned} \tag{1.92}$$

and $\vec{a}\vec{a}\cdot\overleftrightarrow{K}$ has the form

$$\vec{a}\vec{a}\cdot\overleftrightarrow{K} = \begin{pmatrix} K_\parallel\sin^2\theta\cos^2\phi & K_\parallel\sin^2\theta\sin\phi\cos\phi & K_\parallel\sin\theta\cos\theta\cos\phi \\ K_\parallel\sin^2\theta\sin\phi\cos\phi & K_\parallel\sin^2\theta\sin^2\phi & K_\parallel\sin\theta\cos\theta\sin\phi \\ K_\parallel\sin\theta\cos\theta\cos\phi & K_\parallel\sin\theta\cos\theta\sin\phi & K_\parallel\cos^2\theta \end{pmatrix} \tag{1.93}$$

Recall that $\langle\cos^2\theta\rangle = (2S+1)/3$, $\langle\sin^2\theta\rangle = (2-2S)/3$, $\langle\sin^2\phi\rangle = \langle\cos^2\phi\rangle = 1/2$, and $\langle\cos\theta\rangle = \langle\sin\phi\rangle = \langle\cos\phi\rangle = \langle\sin\phi\cos\phi\rangle = 0$; therefore their averaged values are

$$\langle\overleftrightarrow{K}\rangle = \begin{pmatrix} K_\perp + \Delta K(1-S)/3 & 0 & 0 \\ 0 & K_\perp + \Delta K(1-S)/3 & 0 \\ 0 & 0 & K_\perp + \Delta K(2S+1)/3 \end{pmatrix} \tag{1.94}$$

$$\langle\vec{a}\vec{a}\cdot\overleftrightarrow{K}\rangle = \begin{pmatrix} K_\parallel(1-S)/3 & 0 & 0 \\ 0 & K_\parallel(1-S)/3 & 0 \\ 0 & 0 & K_\parallel(2S+1)/3 \end{pmatrix} \tag{1.95}$$

$$\overleftrightarrow{\varepsilon} = \overleftrightarrow{I} + \frac{N}{\varepsilon_o}[\alpha_\perp\langle\overleftrightarrow{K}\rangle + \Delta\alpha\langle\overleftrightarrow{K}\cdot(\vec{a}\vec{a})\rangle]$$

Therefore

$$\overleftrightarrow{\varepsilon} = \begin{pmatrix} \begin{array}{l} 1+\dfrac{N}{3\varepsilon_o}[\alpha_\perp K_\perp(2+S) \\ +\alpha_\parallel K_\parallel(1-S)] \end{array} & 0 & 0 \\ 0 & \begin{array}{l} 1+\dfrac{N}{3\varepsilon_o}[\alpha_\perp K_\perp(2+S) \\ +\alpha_\parallel K_\parallel(1-S)] \end{array} & 0 \\ 0 & 0 & \begin{array}{l} 1+\dfrac{N}{3\varepsilon_o}[\alpha_\perp K_\perp(2-2S) \\ +\alpha_\parallel K_\parallel(1+2S)] \end{array} \end{pmatrix} \tag{1.96}$$

The anisotropy is

$$\Delta\varepsilon = \varepsilon_{\|} - \varepsilon_{\perp} = \frac{N}{\varepsilon_o}(\alpha_{\|}K_{\|} - \alpha_{\perp}K_{\perp})S \tag{1.97}$$

which is linearly proportional to the order parameter S. In terms of the refractive indices, Equation (1.97) becomes

$$n_{\|}^2 - n_{\perp}^2 = 2\bar{n}\Delta n = \frac{N}{\varepsilon_o}(\alpha_{\|}K_{\|} - \alpha_{\perp}K_{\perp})S$$

where $\bar{n} = (n_{\|} + n_{\perp})/2$ and $\Delta n = (n_{\|} - n_{\perp})$. Approximately, the birefringence Δn is linearly proportional to the order parameter. For most liquid crystals, $\bar{n} \sim 1.5-2.0$ and $\Delta n \sim 0.05-0.3$.

The electronic polarization may be treated by using classical mechanics where the system is regarded as a simple harmonic oscillator. There are three forces acting on the electron: (1) the elastic restoring force $-Kx$, where K is the elastic constant and x is the displacement of the electron from its equilibrium position; (2) the viscosity force $-\gamma\partial x/\partial t$; and (3) the electric force $-eE_oe^{i\omega t}$, where E_o and ω are the amplitude and frequency of the applied electric field, respectively. The dynamic equation is

$$m\frac{d^2x}{dt^2} = -kx - eE_oe^{i\omega t} - \gamma\frac{\partial x}{\partial t} \tag{1.98}$$

The solution is $x = x_oe^{i\omega t}$ and the amplitude of the oscillation is

$$x_o = \frac{-eE_o}{m(\omega^2 - \omega_o^2) + i\gamma\omega} \tag{1.99}$$

where $\omega_o = \sqrt{k/m}$ is the frequency of the oscillator (the frequency of the transition dipole moment in quantum mechanics). The induced dipole moment is $p = -ex_o$. The molecule polarizability is

$$\alpha = p/E_{loc} = \frac{e^2}{m}\frac{(\omega_o^2 - \omega^2)}{(\omega_o^2 - \omega^2)^2 + (\gamma\omega/m)^2} - i\frac{e^2}{m}\frac{\gamma\omega/m}{(\omega_o^2 - \omega^2)^2 + (\gamma\omega/m)^2} \tag{1.100}$$

which is a complex number and the imaginary part corresponds to absorption. When the frequency of the light is far from the absorption frequency ω_o or the viscosity is small, the absorption is negligible, $\alpha = p/E_{loc} = (e^2/m)/(\omega_o^2 - \omega^2)$. The refractive index is

$$n^2 \propto \alpha \propto \frac{1}{(\omega_o^2 - \omega^2)} = \frac{1}{[(2\pi/C\lambda_o)^2 - (2\pi/C\lambda)^2]} = \frac{C^2\lambda_o^2}{4\pi^2}\frac{\lambda^2}{\lambda^2 - \lambda_o^2}$$

as expressed in Sellmeier's equation

$$n^2 = 1 + \frac{H\lambda^2}{\lambda^2 - \lambda_o^2} \tag{1.101}$$

where H is a constant. When λ is much longer than λ_o, expanding the above equation we have

$$n \approx A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \tag{1.102}$$

This is Cauchy's equation. The refractive index increases with decreasing wavelength. For liquid crystals, along different directions with respect to the long molecular axis, the molecular polarizabilities are different. Also along different directions, the frequencies of the transition dipole moments are different, which results in *dichroic absorption*: that is, when the electric field is parallel to the transition dipole moment, the light is absorbed; when the electric field is perpendicular to the transition moment, the light is not absorbed. Positive dichroic dyes have transition dipole moments parallel to the long molecular axis, while negative dichroic dyes have transition dipole moments perpendicular to the long molecular axis.

Under DC or low-frequency applied electric fields, for liquid crystals of polar molecules, the dipolar polarization is dominant. For a liquid crystal with a permanent dipole moment $\vec{p}$, the polarization is given by

$$\vec{P} = N\alpha_\perp \langle \vec{K} \rangle \cdot \vec{E} + N\Delta\alpha\langle [\vec{K} \cdot (\vec{a}\vec{a})] \rangle \cdot \vec{E} + N\langle \vec{p} \rangle \tag{1.103}$$

The macroscopic dielectric tensor is

$$\overleftrightarrow{\varepsilon} = \overleftrightarrow{I} + \frac{N}{\varepsilon_o}[\alpha_\perp \langle \overleftrightarrow{K} \rangle + \Delta\alpha\langle \overleftrightarrow{K} \cdot (\vec{a}\vec{a}) \rangle + \langle \vec{p} \rangle \vec{E}/E^2] \tag{1.104}$$

The energy of the dipole in the directing electric field $\vec{E}_d$ is $u = -\vec{p} \cdot \vec{E}_d$. The directing field $\vec{E}_d$ is different from the local field $\vec{E}_{loc}$ because the dipole polarizes its surroundings, which in turn results in a reaction field $\vec{E}_r$ at the position of the dipole. As $\vec{E}_r$ is always parallel to the dipole, it cannot affect the orientation of the dipole. As an approximation, it is assumed that $\vec{E}_d = d \cdot \vec{E}$, where d is a constant. Usually the dipole moment p is about $1e \times 1A^\circ = 1.6 \times 10^{-19}\,\mathrm{C} \times 10^{-10}\,\mathrm{m} = 1.6 \times 10^{-29}\,\mathrm{mC}$. At room temperature ($T \sim 300\,\mathrm{K}$) and under the normal strength field $E \sim 1\,\mathrm{V/\mu m} = 10^6\,\mathrm{V/m}$, $pE/3k_BT \ll 1$. Consider a liquid crystal molecule with a permanent dipole moment making an angle β with the long molecular axis. In the molecular frame $\eta\zeta\xi$, the components of $\vec{p}$ are $(p\sin\beta\cos\psi,\ p\sin\beta\sin\psi,\ p\cos\beta)$, as shown in Figure 1.17. Using the rotation matrix given by Equation (1.90), we can calculate the components of $\vec{p}$ in the lab frame xyz:

$$\begin{aligned}
\vec{p} &= \begin{pmatrix} \cos\phi & -\cos\theta\sin\phi & -\sin\theta\sin\phi \\ \sin\phi & \cos\theta\cos\phi & \sin\theta\cos\phi \\ 0 & -\sin\theta & \cos\theta \end{pmatrix} \cdot p \begin{pmatrix} \sin\beta\cos\psi \\ \sin\beta\sin\psi \\ \cos\beta \end{pmatrix} \\
&= p \begin{pmatrix} \sin\beta\cos\psi\cos\phi - \sin\beta\sin\psi\cos\theta\sin\phi - \cos\beta\sin\theta\sin\phi \\ \sin\beta\sin\psi\sin\phi + \sin\beta\sin\psi\cos\theta\cos\phi + \cos\beta\sin\theta\cos\phi \\ -\sin\theta\sin\beta\sin\psi + \cos\theta\cos\beta \end{pmatrix}
\end{aligned} \tag{1.105}$$

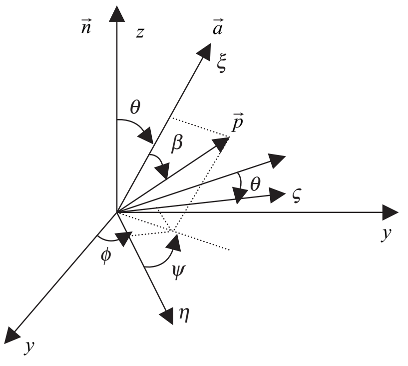


Figure 1.17 Schematic diagram showing the orientation of the dipole $\vec{p}$ in the molecular principal frame $\eta\zeta\xi$ and the lab frame xyz

When the applied field is parallel to $\vec{n}$, $\vec{E} = E_{\|}\vec{z}$, the projection of the dipole along the applied field is

$$p_{\|} = -p(\sin\beta \sin\psi \sin\theta + \cos\beta \cos\theta) \tag{1.106}$$

and the energy is

$$u = -dp(\cos\beta \cos\theta - \sin\beta \sin\psi \sin\theta)E_{\|} \tag{1.107}$$

The average value of the projection is

$$\langle p_{\|}\rangle = \frac{\int (p\cos\beta\cos\theta - p\sin\beta\sin\psi\sin\theta)e^{-u/k_BT - V(\theta)/k_BT}\sin\theta d\theta d\phi d\psi}{\int e^{-u/k_BT - V(\theta)/k_BT}\sin\theta d\theta d\phi d\psi} \tag{1.108}$$

Because $-u \ll k_BT$, $e^{-u/k_BT} \approx (1 - u/k_BT)$, then

$$\begin{aligned}\langle p_{\|}\rangle &= \frac{dE_{\|}}{k_BT}\frac{\int (p\cos\beta\cos\theta - p\sin\beta\sin\psi\sin\theta)^2 e^{-V(\theta)/k_BT}\sin\theta d\theta d\phi d\psi}{\int e^{-u/k_BT - V(\theta)/k_BT}\sin\theta d\theta d\phi d\psi}\\ &= \frac{dE_{\|}p^2}{k_BT}\langle(\cos^2\beta\cos^2\theta + \sin^2\beta\sin^2\theta\sin^2\psi - \sin\beta\cos\beta\sin\theta\cos\theta\sin\psi)\rangle\end{aligned}$$

Because $\langle\sin^2\psi\rangle = 1/2$, $\langle\sin\psi\rangle = 0$, $\langle\cos^2\theta\rangle = (2S+1)/3$, and $\langle\sin^2\theta\rangle = (2-2S)/3$,

$$\langle p_{\|}\rangle = \frac{dE_{\|}p^2}{3k_BT}[\cos^2\beta(2S+1) + \sin^2\beta(1-S)] = \frac{dE_{\|}p^2}{3k_BT}[1 - (1 - 3\cos^2\beta)S] \tag{1.109}$$

From Equations (1.96), (1.104), and (1.109), we have

$$\varepsilon_{\|} = 1 + \frac{N}{3\varepsilon_o}\left\{\alpha_{\perp}K_{\perp}(2-2S) + \alpha_{\|}K_{\|}(1+2S) + \frac{dp^2}{k_BT}[1 - (1 - 3\cos^2\beta)S]\right\} \tag{1.110}$$

Note that $\alpha_{\|}$ and $\alpha_{\perp}$ are the molecular polarizabilities contributed by the electronic and ionic polarizations.

When the applied field is perpendicular to $\vec{n}$, say $\vec{E} = E_{\perp}\hat{x}$, the projection of the dipole along the applied field is

$$p_{\perp} = p(\sin\beta\cos\psi\cos\phi - \sin\beta\sin\psi\cos\theta\sin\phi - \cos\beta\sin\theta\sin\phi) \tag{1.111}$$

and the energy is

$$u = -dp(\sin\beta\cos\psi\cos\phi - \sin\beta\sin\psi\cos\theta\sin\phi - \cos\beta\sin\theta\sin\phi)E_{\perp} \tag{1.112}$$

The average value of the projection is

$$\begin{aligned}\langle p_{\perp}\rangle &= \frac{dE_{\perp}p^2}{k_BT}\left[\frac{1}{4}\sin^2\beta + \frac{1}{4}\sin^2\beta\frac{(2S+1)}{3} + \cos^2\beta\frac{(1-S)}{3}\right]\\ &= \frac{dE_{\perp}p^2}{3k_BT}\left[1 + \frac{1}{2}(1 - 3\cos^2\beta)S\right]\end{aligned}$$

From Equations (1.96), (1.104), and (1.112), we have

$$\varepsilon_\perp = 1 + \frac{N}{3\varepsilon_o}\left\{\alpha_\perp K_\perp(2+S) + \alpha_\| K_\|(1-S) + \frac{dp^2}{k_B T}\left[1 + \frac{1}{2}(1 - 3\cos^2\beta)S\right]\right\} \tag{1.113}$$

The dielectric anisotropy is

$$\Delta\varepsilon = \varepsilon_\| - \varepsilon_\perp = \frac{N}{\varepsilon_o}\left[(\alpha_\| K_\| - \alpha_\perp K_\perp) - \frac{dp^2}{2k_B T}(1 - 3\cos^2\beta)\right]S \tag{1.114}$$

which is proportional to the order parameter S. The contribution of induced polarization (electronic and ionic polarizations) changes with temperature like S, while the contribution of the orientation polarization changes with temperature like S/T. When the angle between the permanent dipole and the long molecular axis is $\beta = 55°$, $(1 - 3\cos^2\beta) = 0$, the orientation polarization of the permanent dipole does not contribute to $\Delta\varepsilon$.

The permanent dipole moment is fixed on the molecule. Thus the molecule has to reorient in order to contribute to the dielectric constants. Qualitatively speaking, only when the frequency of the applied field is lower than a characteristic frequency ω_c can the molecule rotate to follow the oscillation of the applied field and therefore to contribute to the dielectric constants. For rod-like liquid crystal molecules, it is easier to spin around the long molecular axis than to rotate around a short molecular axis. Therefore the characteristic frequency $\omega_{\perp c}$ for $\varepsilon_\perp$ is higher than the characteristic frequency $\omega_{\| c}$ for $\varepsilon_\|$. For molecules for which the angle β between the permanent dipole and the long molecular axis is very small, $\Delta\varepsilon$ is always positive at all frequencies. For molecules with large permanent dipole moment p and large β, $\Delta\varepsilon$ is negative at low frequencies. For molecules with large permanent dipole moment p and intermediate β, $\Delta\varepsilon$ is positive at low frequencies, then changes to negative when the frequency is increased above a crossover frequency ω_o. The cross over frequency is in the region from a few kilohertz to a few tens of kilohertz. At infrared light or higher frequencies, the dipolar polarization no longer contributes, and $\Delta\varepsilon$ is always positive.

1.6 Anchoring Effects of Nematic Liquid Crystals at Surfaces

In most liquid crystal devices, the liquid crystals are sandwiched between two substrates coated with alignment layers. In the absence of externally applied fields, the orientation of the liquid crystal in the cell is determined by the anchoring condition of the alignment layer [26–28].

1.6.1 Anchoring energy

Consider an interface between a liquid crystal ($z > 0$) and an alignment layer ($z < 0$) as shown in Figure 1.18. For a liquid crystal molecule on the interface, some of the surrounding molecules are liquid crystal molecules and other surrounding molecules are alignment layer molecules. The potential for the molecule's orientation is different from that of the liquid crystal in the bulk, where all the surrounding molecules are liquid crystal molecules. At the interface, the orientational and positional orders may be different from those in the bulk. Here we only discuss the anisotropic part of the interaction between the liquid crystal molecule and the alignment layer molecule. The liquid crystal is anisotropic. If the alignment layer is also anisotropic, then there is a preferred direction, referred to as the easy axis, for the liquid crystal director at the interface, as shown in Figure 1.18. The interaction energy is a minimum when the liquid crystal director is along the easy axis. The z axis is perpendicular to the interface and pointing toward the liquid crystal side. The polar angle and the azimuthal angle of the easy axis are θ_o and ϕ_o, respectively. If $\theta_o = 0^\circ$, the anchoring is referred to as homeotropic. If $\theta_o = 90^\circ$ and ϕ_o is well

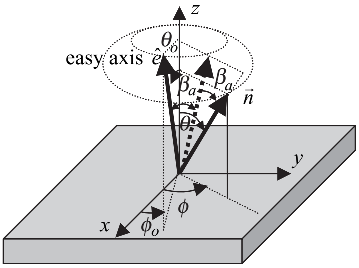


Figure 1.18 Schematic diagram showing the easy axis of the anchoring and the liquid crystal director

defined, the anchoring is termed homogeneous. If $\theta_o = 90^\circ$ and there is no preferred azimuthal angle, the anchoring is called planar. If $0 < \theta_o < 90^\circ$, the anchoring is referred to as tilted.

When the liquid crystal director $\vec{n}$ is aligned along the direction specified by the polar angle θ and the azimuthal angle ϕ, the anisotropic part of the surface energy, referred to as the anchoring energy function, of the liquid crystal is $f_s = f_s(\theta, \phi)$. When $\theta = \theta_o$ and $\phi = \phi_o$, f_s has a minimum value of 0, and thus $\partial f_s/\partial\theta|_{\theta=\theta_o} = 0$ and $\partial f_s/\partial\phi|_{\phi=\phi_o} = 0$. The materials above and below the interface are different and there is no reflectional symmetry about the interface. If $\theta_o \neq 0$, the anchoring energy does not have azimuthal rotational symmetry around the easy direction. Therefore the anchoring energies are different for deviations in polar angle and azimuthal angle. For small deviations, in the Rapini–Papoular model [29,30], the anchoring energy function can be expressed as

$$f_s = \frac{1}{2} W_p \sin^2 \beta_p + \frac{1}{2} W_a \sin^2 \beta_a \tag{1.115}$$

where β_p and β_a are the angles between $\vec{n}$ and the easy axis when $\vec{n}$ deviates from the easy axis in the polar angle direction and azimuthal angle direction, respectively; W_p and W_a are the polar and azimuthal anchoring strengths, respectively. For small $\theta - \theta_o$ and $\phi - \phi_o$, we have the approximations $\sin^2 \beta_p = \sin^2 (\theta - \theta_o)$ and $\sin^2 \beta_a = \sin^2 (\phi - \phi_o) \sin^2 \theta_o$. Therefore the anchoring energy function is

$$f_s = \frac{1}{2} W_p \sin^2 (\theta - \theta_o) + \frac{1}{2} W_a \sin^2 \theta_o \sin^2 (\phi - \phi_o) \tag{1.116}$$

1.6.2 Alignment layers

Homogeneous anchoring can be achieved by mechanically rubbing the surface of the substrate, such as glass, of the liquid crystal cell with a cotton ball or cloth. The rubbing creates micro-grooves along the rubbing direction in the form of ridges and troughs, as shown in Figure 1.19(a). When the liquid crystal is aligned parallel to the grooves, there is no orientational deformation. If the liquid crystal were perpendicular to the groves, there would be orientational deformation, which costs elastic energy. Therefore the liquid crystal will be homogeneously aligned along the grooves (the rubbing direction). The problem with alignment created in this way is that the anchoring strength ($\sim 10^{-5}$ J/m^2) is weak. Widely used for the homogeneous alignment layer are rubbed polyimides. The rubbing not only creates the micro-grooves but also aligns the polymer chains. The intermolecular interaction between the liquid crystal and the aligned polymer chains also favors parallel alignment and thus increases the anchoring energy. The anchoring strength can become as high as 10^{-3} J/m^2. Furthermore, pretilt angles of a few

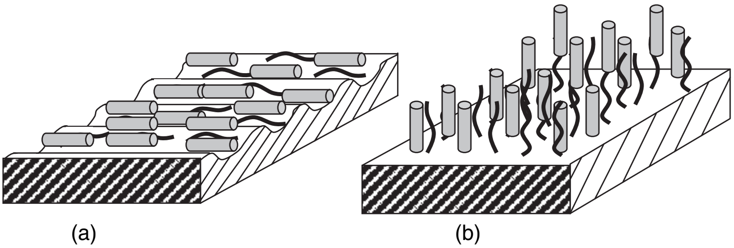


Figure 1.19 (a) Schematic diagram showing the liquid crystal aligned parallel to the grooves, (b)

degrees can be generated. Homogeneous anchoring can also be achieved by using obliquely evaporated SiO film.

Homeotropic anchoring can be achieved using monolayer surfactants such as lecithin and silane. The polar head of the surfactant is chemically attached to the glass substrate and the hydrocarbon tail points out and perpendicular to the surface, as shown in Figure 1.19(b). The intermolecular interaction between the surfactant and the liquid crystal promotes the homeotropic alignment.

Homework Problems

1.1 Consider a nematic liquid crystal. The molecule can be regarded as a cylinder with a length of 2 nm and diameter of 0.5 nm. The molecule has a permanent dipole moment of 10^{-29} mC at the center of the molecule. The interaction between the molecules comes from the interactions between the permanent dipoles. Calculate the interaction between two molecules in the following cases: (1) one molecule is on top of the other molecule and the dipoles are parallel, (2) one molecule is on top of the other molecule and the dipoles are anti-parallel, (3) the molecules are side by side and the dipoles are parallel, and (4) the molecules are side by side and the dipoles are anti-parallel.

1.2 Using Equations (1.11), (1.25), and (1.31), prove that the entropy of a system at a constant temperature is

$$S = -k_B\langle \ln \rho\rangle = -k_B \sum_i \rho_i \ln \rho_i$$

1.3 Calculate the orientational order parameter in the following two cases. (1) The orientational distribution function is $f(\theta) = \cos^2\theta$. (2) The orientational distribution function is $f(\theta) = \sin^2\theta$. θ is the angle between the long molecular axis and the liquid crystal director.

1.4 *Landau–de Gennes theory*. For a liquid crystal with parameters $a = 0.1319\times\ 10^5\,\mathrm{J/Km^3}$, $b = -1.836\times 10^5\,\mathrm{J/m^3}$, and $c = 4.05\times 10^5\,\mathrm{J/m^3}$, numerically calculate the free energy as a function of the order parameter and identify the order parameters corresponding to the maximum and minimum free energy at the following temperatures: (1) $T - T^* = 4.0\,^\circ\mathrm{C}$, (2) $T - T^* = 3.0\,^\circ\mathrm{C}$, (3) $T - T^* = 2.0\,^\circ\mathrm{C}$, (4) $T - T^* = 1.0\,^\circ\mathrm{C}$, (5) $T - T^* = 0.0\,^\circ\mathrm{C}$, (6) $T - T^* = -10.0\,^\circ\mathrm{C}$.

1.5 *Maier–Saupe theory*. Use Equation (1.50) to numerically calculate all the possible order parameters as a function of the normalized temperature $\tau = k_B T/v$, and use Equation (1.54) to calculate the corresponding free energy.

1.6 Use Maier–Saupe theory to study the isotropic–nematic phase transition of a binary mixture consisting of two components A and B. For molecule A, when its long molecular axis makes an angle θ_A with respect to the liquid crystal director, the single molecular potential is

$$V_A(\theta) = -v_{AA}(1-x)S_A\left(\frac{3}{2}\cos^2\theta_A - \frac{1}{2}\right) - v_{AB}xS_B\left(\frac{3}{2}\cos^2\theta_A - \frac{1}{2}\right)$$

For molecule B, when its long molecular axis makes an angle θ_B with respect to the liquid crystal director, the single molecular potential is

$$V_B(\theta) = -v_{AB}(1-x)S_A\left(\frac{3}{2}\cos^2\theta_B - \frac{1}{2}\right) - v_{BB}xS_B\left(\frac{3}{2}\cos^2\theta_B - \frac{1}{2}\right)$$

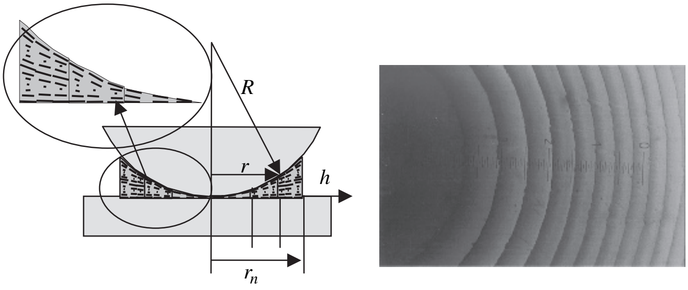
where x is the molar fraction of component B. The interaction constants are $v_{BB} = 1.05v_{AA}$ and $v_{AB} = 0.95v_{AA}$. Express the normalized temperature by $\tau = k_BT/v_{AA}$. Assume that the two components are miscible at any fraction. Numerically calculate the transition temperature as a function of the molar fraction x.

1.7 Consider a nematic liquid crystal cell with a thickness of 10 μm. On the bottom surface the liquid crystal is aligned parallel to the cell surface, and on top of the top surface the liquid crystal is aligned perpendicular to the cell surface. Assume the tilt angle of the liquid crystal director changes linearly with the coordinate z which is in the cell normal direction. Calculate the total elastic energy per unit area. The elastic constants of the liquid crystal are $K_{11} = 6 \times 10^{-12}$ N, $K_{22} = 3 \times 10^{-12}$ N, and $K_{33} = 10 \times 10^{-12}$ N.

1.8 The Cano-wedge method is an experimental technique to measure the pitch of cholesteric liquid crystals. It consists of a flat substrate and a hemisphere with a cholesteric liquid crystal sandwiched between them as shown Figure 1.20(a). At the center, the spherical surface touches the flat surface. On both the flat and spherical surfaces there is a homogeneous alignment layer. The intrinsic pitch of the liquid crystal is P_o. Because of the boundary condition, the pitch of the liquid crystal is quantized to match the boundary condition. In region n, $h = n(P/2)$. In each region, on the inner side, the pitch is compressed, i.e., $P < P_o$ while on the outer side, the pitch is stretched, i.e., $P > P_o$. Between region $(n-1)$ and region n there is a disclination ring as shown in Figure 1.20(b). Find the square of the radius of the nth disclination ring r_n^2 as a function of the intrinsic pitch P_o, the radius R of the hemisphere, and the ring number n. $R \gg P_o$ and for small r only twist elastic energy has to be considered. Hint: r_n^2 vs. n is a straight line with a slope dependent on P_o and R.

1.9 Consider a sphere of radius R. The polarization inside the sphere is $\vec{P}$. Calculate the electric field at the center of the sphere produced by the polarization. Hint: the polarization can be replaced by a surface charge whose density is given by $\vec{P} \cdot \vec{n}$, where $\vec{n}$ is the unit vector along the surface normal direction.

1.10 Using Equations (1.87), (1.91), and (1.93), calculate the dielectric tensor $\overleftrightarrow{\varepsilon}$ in terms of the order parameter S.



(a) (b)

Figure 1.20

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