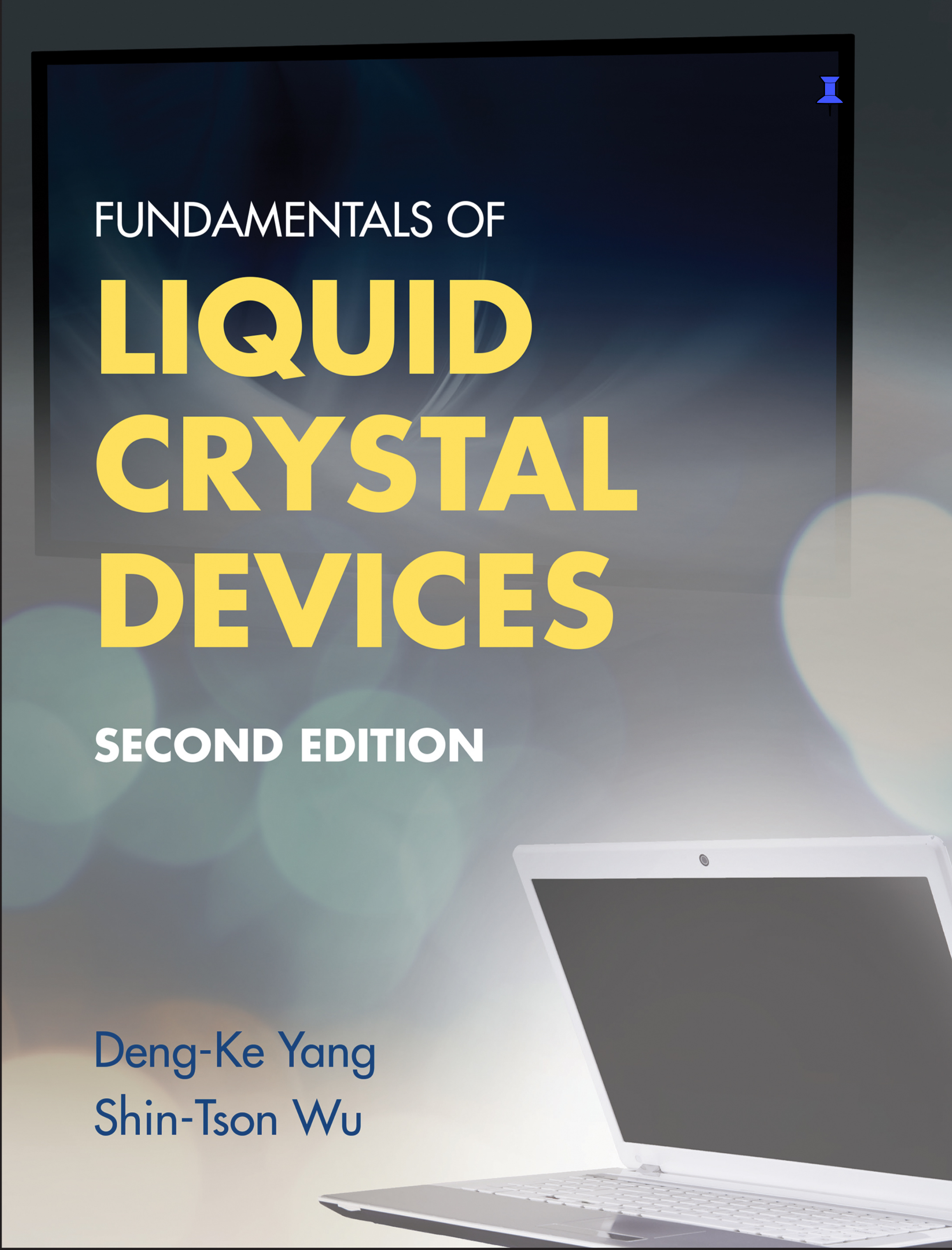

FUNDAMENTALS OF
LIQUID CRYSTAL DEVICES

SECOND EDITION

Deng-Ke Yang
Shin-Tson Wu

WILEY SID Series in **Display Technology**

FUNDAMENTALS OF LIQUID CRYSTAL DEVICES

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FUNDAMENTALS OF LIQUID CRYSTAL DEVICES

Second Edition

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Series Editor's Foreword

The first edition of this book marked a new departure for the Wiley-SID Series in Display Technology because it had been written primarily as a text for postgraduate and senior undergraduate students. It fulfilled that objective admirably, but the continuing advances in liquid crystal display technology over the intervening eight years have made necessary some additions to keep the book current.

Accordingly, the following new sections have been added: elastic deformation of liquid crystals in Chapter 1, polarisation conversion with narrow and broadband quarter-wave plates in Chapter 3, and measurement of anchoring strength and pretilt angle in Chapter 5.

With each chapter is designed to be self-contained, the first chapters cover the basic physics of liquid crystals, their interaction with light and electric fields, and the means by which they can be modelled. Next are described the majority of the ways in which liquid crystals can be used in displays, and Chapter 12, the final chapter of the first edition, deals with photonic devices such as beam steerers, tunable-focus lenses and polarisation-independent devices. In this second edition, four new chapters have been added: two on blue phase and polymer stabilised blue phase liquid crystals, which are emerging from the realm of academic research to show promise for very fast response display and photonic devices, a chapter which discusses LCD componentry, and a final chapter on the use of LCDs in 3D display systems.

As with the first edition, and following a standard textbook format, each chapter concludes with a set of problems, the answers to which may be found on the Wiley web site.

New electro-optic technologies continue to be developed, and some of them make inroads into the LCD market. Nevertheless, liquid crystal technology – the first other than the CRT to make a significant breakthrough into the mass market and which made possible flat displays and transformed projection display technology – continues to hold a dominant position. This second edition of Fundamentals of Liquid Crystal Devices, with its additions which include references to some very recent work, will ensure that this volume will continue to provide students and other readers at the professional level with a most useful introduction to the subject.

Anthony C Lowe
Braishfield, UK 2014

Preface to the First Edition

Liquid crystal displays have become the leading technology in the information display industry. They are used in small-sized displays such as calculators, cellular phones, digital cameras, and head-mounted displays; in medium-sized displays such as laptop and desktop computers; and in large-sized displays such as direct-view TVs and projection TVs. They have the advantages of high resolution and high brightness, and, being flat paneled, are lightweight, energy saving, and even flexible in some cases. They can be operated in transmissive and reflective modes. Liquid crystals have also been used in photonic devices such as laser beam steering, variable optical attenuators, and tunable-focus lenses. There is no doubt that liquid crystals will continue to play an important role in the era of information technology.

There are many books on the physics and chemistry of liquid crystals and on liquid crystal devices. There are, however, few books covering both the basics and applications of liquid crystals. Our main goal, therefore, is to provide a textbook for senior undergraduate and graduate students. The book can be used for a one- or two-semester course. The instructors can selectively choose the chapters and sections according to the length of the course and the interest of the students. The book can also be used as a reference book by scientists and engineers who are interested in liquid crystal displays and photonics.

The book is organized in such a way that the first few chapters cover the basics of liquid crystals and the necessary techniques to study and design liquid crystal devices. The later chapters cover the principles, design, operation, and performance of liquid crystal devices. Because of limited space, we cannot cover every aspect of liquid crystal chemistry and physics and all liquid crystal devices, but we hope this book will introduce readers to liquid crystals and provide them with the basic knowledge and techniques for their careers in liquid crystals.

We are greatly indebted to Dr A. Lowe for his encouragement. We are also grateful to the reviewers of our book proposal for their useful suggestions and comments. Deng-Ke Yang would like to thank Ms E. Landry and Prof. J. Kelly for patiently proofreading his manuscript. He would also like to thank Dr Q. Li for providing drawings. Shin-Tson Wu would like to thank his research group members for generating the new knowledge included in this book, especially Drs Xinyu Zhu, Hongwen Ren, Yun-Hsing Fan, and Yi-Hsin Lin, and Mr Zhibing Ge for kind

help during manuscript preparation. He is also indebted to Dr Terry Dorschner of Raytheon, Dr Paul McManamon of the Air Force Research Lab, and Dr Hiroyuki Mori of Fuji Photo Film for sharing their latest results. We would like to thank our colleagues and friends for useful discussions and drawings and our funding agencies (DARPA, AFOSR, AFRL, and Toppoly) for providing financial support. Finally, we also would like to thank our families (Xiaojiang Li, Kevin Yang, Steven Yang, Cho-Yan Wu, Janet Wu, and Benjamin Wu) for their spiritual support, understanding, and constant encouragement.

Deng-Ke Yang
Shin-Tson Wu

Preface to the Second Edition

Liquid crystal displays have become the leading technology in the information display industry. They are used in small-sized displays such as calculators, smart phones, digital cameras, and wearable displays; medium-sized displays such as laptop and desktop computers; and large-sized displays such as direct view TVs and data projectors. They have the advantages of having high resolution and high brightness, and being flat paneled, lightweight, energy saving, and even flexible in some cases. They can be operated in transmissive and reflective modes. Liquid crystals have also been used in photonic devices such as switching windows, laser beam steering, variable optical attenuators, and tunable-focus lenses. There is no doubt that liquid crystals will continue to play an important role in information technology.

There are many books on the physics and chemistry of liquid crystals and on liquid crystal devices. There are, however, few books covering both the basics and the applications of liquid crystals. The main goal of this book is to provide a textbook for senior undergraduate and graduate students. This book can be used for a one- or two-semester course. The instructors can selectively choose the chapters and sections according to the length of the course and the interest of the students. It can also be used as a reference book for scientists and engineers who are interested in liquid crystal displays and photonics.

The book is organized in such a way that the first few chapters cover the basics of liquid crystals and the necessary techniques to study and design liquid crystal devices. The later chapters cover the principles, design, operation, and performance of liquid crystal devices. Because of limited space, we cannot cover every aspect of liquid crystal chemistry and physics and all the different liquid crystal devices. We hope that this book can introduce readers to liquid crystals and provide them with the basic knowledge and techniques for their career in liquid crystals.

Since the publication of the first edition, we have received a lot of feedback, suggestions, corrections, and encouragements. We appreciate them very much and have put them into the second edition. Also there are many new advances in liquid crystal technologies. We have added new chapters and sections to cover them.

We are greatly indebted to Dr A. Lowe for his encouragement. We are also grateful to the reviewers of our book proposal for their useful suggestions and comments. Deng-Ke Yang would like to thank Ms E. Landry, Prof. P. Crooker, his research group, and coworkers for patiently proofreading and preparing his sections of the book. He would also like to thanks Dr Q. Li for providing drawings. Shin-Tson Wu would like to thank his research group members for generating new knowledge included in this book, especially Drs Xinyu Zhu, Hongwen Ren, Yun-Hsing Fan, Yi-Hsin Lin, Zhibing Ge, Meizi Jiao, Linghui Rao, Hui-Chuan Cheng, Yan Li, and Jin Yan for their kind help during manuscript preparation. He is also indebted to Dr Terry Dorschner of Raytheon, Dr Paul McManamon of Air Force Research Lab, and Dr Hiroyuki Mori of Fuji Photo Film for sharing their latest results. We would like to thank our colleagues and friends for useful discussions and drawings and our funding agencies (DARPA, AFOSR, AFRL, ITRI, AUO, and Innolux) for providing financial support. We would also like to thank our family members (Xiaojiang Li, Kevin Yang, Steven Yang, Cho-Yan Wu, Janet Wu, and Benjamin Wu) for their spiritual support, understanding, and constant encouragement.

Deng-Ke Yang
Shin-Tson Wu

1

Liquid Crystal Physics

1.1 Introduction

Liquid crystals are mesophases between crystalline solid and isotropic liquid [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 disk-like molecules is about 5 or larger. Because the molecules are non-spherical, besides positional order, they may 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 in Figure 1.1(e), in considering its physical behavior, because of the fast rotation (on the order of 10^{-9} s) around the long molecule axis due to thermal motion. The distance between two carbon atoms is about 1.5 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), but it can still be represented by the 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 isotropic liquid phase at high temperature to crystalline solid phase at low temperature. The rigid part favors both orientational and positional order while the flexible part disfavors them. With balanced rigid and flexible parts, the molecule exhibits liquid crystal phases.

Fundamentals of Liquid Crystal Devices, Second Edition. Deng-Ke Yang and Shin-Tson Wu.

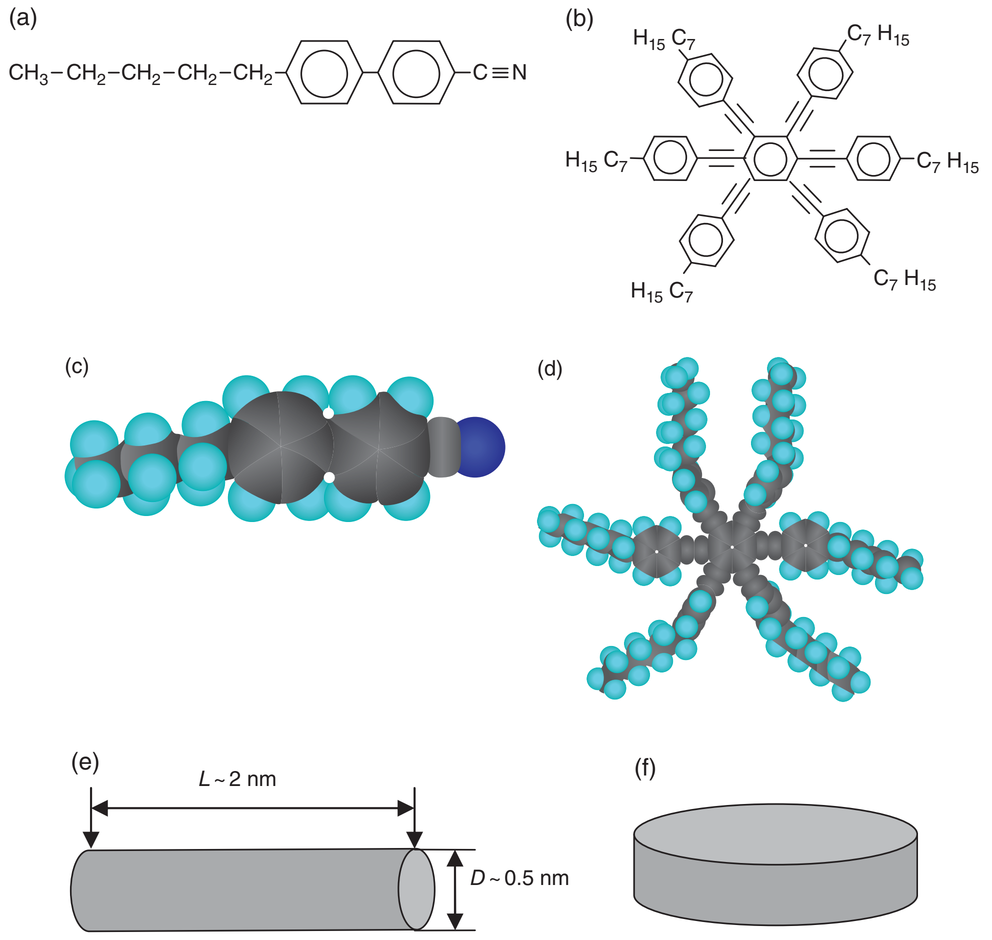

Figure 1.1 Calamitic liquid crystal: (a) chemical structure, (c) space-filling model, (e) physical model. Discostic liquid crystal: (b) chemical structure, (d) space-filling mode, (f) physical model.

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 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 a crystal phase where there is positional order.

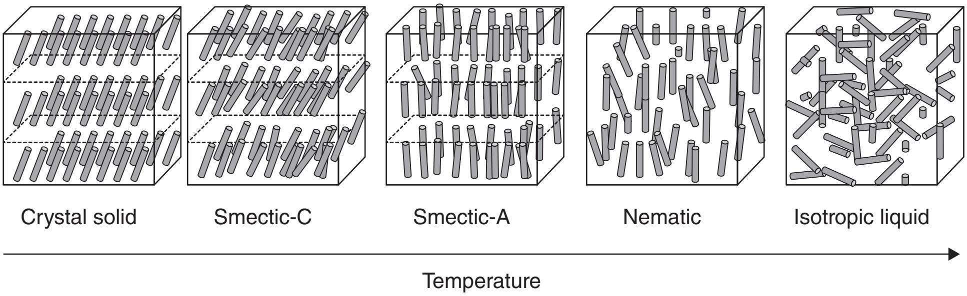

Figure 1.2 Schematic representation of the phases of rod-like molecules.

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 a 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 macroscopic scale. The average direction of the long molecular axis is denoted by $\vec{n}$ which is a unit vector 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 *Smectic-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 layer normal direction. The cartoon shown in Figure 1.2 is schematic. In reality, the separation between neighboring layers is not as well defined as that shown by the cartoon. The molecule number density exhibits an undulation with the wavelength about the molecular length. Within a layer, it is a two-dimensional liquid crystal 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 further, 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 becomes infinitely high and the molecules (almost) do not diffuse anymore.

Liquid crystals get the ‘crystal’ part of their name because they exhibit optical birefringence as crystalline solids. They get the ‘liquid’ part of their name because they can flow and do not support shearing as regular liquids. Liquid crystal molecules are elongated and have different

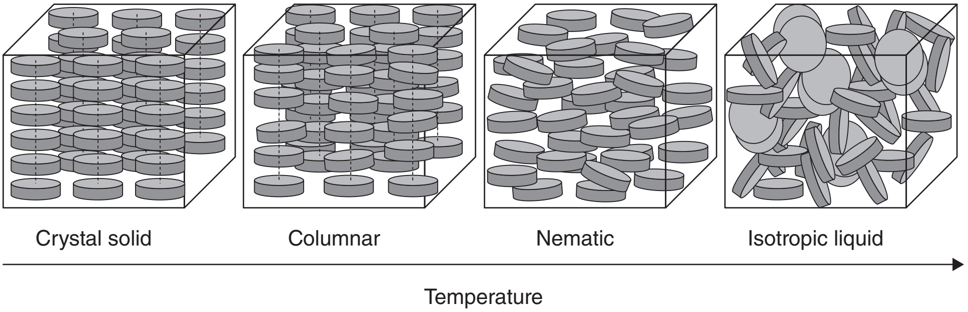

Figure 1.3 Schematic representation of the phases of disk-like molecules.

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. They may exhibit some of the liquid crystal phases.

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 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, it is a liquid where the molecules have no positional order. The columns, however, are arranged periodically in the plane perpendicular to the columns. Hence it 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 are driven by varying temperature. There is another type of liquid crystals, called lyotropic liquid crystals, 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 that have a hydrophobic group at one end and a hydrophilic group at the other end and the water is 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 the scope of this book is on displays and photonic devices.

Liquid crystals have a history of more than 100 years. It is believed that the person who discovered liquid crystals is 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 sciences. Scientifically, liquid crystals are important because of the richness of structures and transitions. Technologically, they have won tremendous success in display and photonic applications [8–10].

1.2 Thermodynamics and Statistical Physics

Liquid crystal physics is an interdisciplinary science: thermodynamics, statistical physics, electrodynamics, and optics are involved. 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 measurement 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 (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 the maximum entropy*. Let us consider a closed system which contains two subsystems. When two subsystems are brought into thermal contact (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 the energy u_1 and entropy σ_1; subsystem 2 has the 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*, that is, $u = u_1 + u_2 = \text{constant}$. 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 $\frac{\partial\sigma_1}{\partial u_1} - \frac{\partial\sigma_2}{\partial u_2} = 0$, that is, $\frac{\partial\sigma_1}{\partial u_1} = \frac{\partial\sigma_2}{\partial u_2}$. We know that when two systems reach equilibrium, they have the same temperature. Accordingly the *fundamental temperature* τ is defined by

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

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 $k_B = 1.381 \times 10^{-23}$ *Joule/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, that is, 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 the energy u_o, the number of accessible states: $g_1 = g_A \times g_B = 1 \times g_B(u_o) = g_B(u_o)$. When A has the energy ε, B has the energy $u_o - \varepsilon$, 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 the energy 0. When the whole system is in one of the g_2 states, A has the energy ε. Therefore the probability for A in the state with energy 0 is $P(0) = \dfrac{g_1}{g_1 + g_2} = \dfrac{g_B(u_o)}{g_B(u_o) + g_B(u_o - \varepsilon)}$. The probability for A in the state with energy ε is $P(\varepsilon) = \dfrac{g_2}{g_1 + g_2} = \dfrac{g_B(u_o - \varepsilon)}{g_B(u_o) + g_B(u_o - \varepsilon)}$. 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 $\varepsilon \ll u_o$, $\sigma_B(u_o - \varepsilon) \approx \sigma_B(u_o) - \dfrac{\partial \sigma_B}{\partial u_B}\varepsilon = \sigma_B(u_o) - \frac{1}{\tau}\varepsilon$. Therefore we have

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

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

$$\frac{p(\varepsilon)}{P(0)} = e^{-\varepsilon/k_B T}. \tag{1.9}$$

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

$$P(\varepsilon_i) = e^{-\varepsilon_i/\tau} / \sum_{j=1}^{N} e^{-\varepsilon_j/k_B T}. \tag{1.10}$$

The *partition function* of the system is defined as

$$Z = \sum_{i=1}^{N} \mathrm{e}^{-\varepsilon_i/k_B T}. \tag{1.11}$$

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

$$U = <\varepsilon> = \sum_i \varepsilon_i P(\varepsilon_i) = \frac{1}{Z}\sum_i \varepsilon_i \mathrm{e}^{-\varepsilon_i/k_B T}. \tag{1.12}$$

Because $\frac{\partial Z}{\partial T} = \sum_i \left(\frac{\varepsilon_i}{k_B T^2}\right)\mathrm{e}^{-\varepsilon_i/k_B T} = \frac{1}{k_B T^2}\sum_i \varepsilon_i \mathrm{e}^{-\varepsilon_i/k_B T}$,

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

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 $1/T = \left(\frac{\partial S}{\partial U}\right)_V$, 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 ($dT = 0$), 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, 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. Because of Equations (1.13) and (1.25),

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

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

Hence

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

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

$$S = -k_B < \ln\rho > = -k_B \sum_i \rho_i \ln\rho_i \tag{1.32}$$

1.2.4 Criteria for thermodynamical 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 in a different way 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 the 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, $1/T = \left(\frac{\partial S_2}{\partial U_2}\right)_V$, and therefore $\delta S_2 = \delta U_2/T$ (this is true when the volume of subsystem is fixed, which also means that 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, $\delta S_1 - \delta U_1/T = (1/T)\delta(TS_1 - U_1) \geq 0$, and therefore

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

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

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 the 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, because the volume is not fixed, and mechanical work is involved. $\delta U_2 = T\delta S_2 - P\delta V_2$, that is, $\delta S_2 = (\delta U_2 + P\delta V_2)/T$. Because $\delta U_2 = -\delta U_1$ and $\delta V_2 = -\delta V_1$, $\delta S = \delta S_1 + (\delta U_2 + P\delta V_2)/T = \delta S_1 - (\delta U_1 + P\delta V_1)/T = (1/T)\delta(TS_1 - U_1 - PV_1) \geq 0$. 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 the 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, $\delta S \geq \frac{dQ}{T} = \frac{dU - dW_m - dW_e}{T} = \frac{dU + PdV - dW_e}{T}$. 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 electric field, magnetic field and shear. In this section, we will discuss how to specify quantitatively orientational order and why rod-like molecules tend to parallel 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 axes are perpendicular to the long molecular axis. Usually the molecule rotates fast around the long molecular axis. Although the molecule is not cylindrical, if there is no hindrance in the rotation in nematic phase, the fast rotation around the long molecular axis makes it behave as a cylinder. There is no preferred direction for the short axes and thus the nematic liquid crystal is usually uniaxial. If there is