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Editors

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10

Bowlics

L. Lam

FIGURE 10.1. Sonal Mansingh in an almost C_2 pose.

10.1 Introduction

December 4, 1979, 6:30 p.m., Hotel Ashok, Bangalore, India. I was from Beijing, invited by S. Chandrasekhar of the Raman Research Institute to attend this wonderful conference on liquid crystals. Since India is a country with a long history, unlike most other international conferences, there was a cultural event almost every evening during this particular conference. And they were free! There was still half-an-hour to go before the performance by the very beautiful and renowned classical dancer, Sonal Mansingh (Fig. 10.1). (Sonal and I were born in the same year, but this is inconsequential to what was going to happen.)

I was sitting in a room, waiting for the performance to begin. Incidentally, this was the first international liquid crystal conference I ever attended in my life and there were no old acquaintances in that room. So I was sitting by myself, and having nothing more meaningful to do, I looked up to the ceiling. It was a ceiling decorated by some regular hexagons connected to each other in an irregular pattern, or so it seemed. Each one of these hexagons was like the convex cover of a fruit plate except that it was now attached upside down to the ceiling. In other words, it was a three-dimensional object.

Let me go back a little bit to that conference. As every liquid crystalist knows these days, the first discotic was hexagonal and was created in the laboratory by Chandrasekhar's group in 1977 [1], and many different varieties were immediately synthesized in other parts of the world. In this particular conference, organized by Chandrasekhar himself, a mere two years after the discovery, it was only natural that paper after paper on discotics was presented day after day. Discotics was hot! Working in Beijing in those two years was quite isolated and handicapped. (There was only one Chinese-made copying machine in the whole Institute of Physics where I worked, which broke down more often than not and was off limits to any scientist, Ph.D. or not. The machine was attended by two "specialists." In addition to that, the main library at the Academy of Sciences to which my Institute belonged, was *not* open-shelf.) Obviously, there was no way that I could play catch up in discotics. I got to leapfrog this hot topic and found something new to do.

When I was admiring these hexagons and their pattern of arrangement in the ceiling, the discotics came to mind. But wait a minute, these hexagons were different from the discotics! A discotic molecule is flat like a pancake (Fig. 10.2)—a two-dimensional object, while these hexagons on the ceiling were three dimensional, like a rice bowl. (Being an oriental, I use rice bowls three times a day. It is not surprising that rice bowls pop into the mind even when one is not actually hungry.) If pancakes can stack up in columns to form columnar discotics, shouldn't rice bowls be able to do the same? I saw them in the kitchens, no doubt about that! As they say, the rest is history.

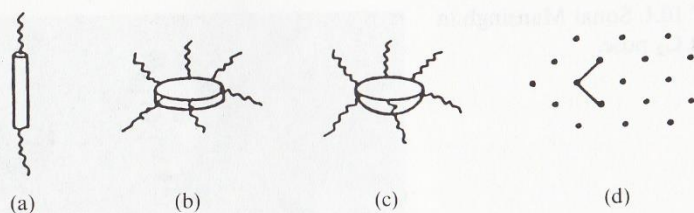I could not shake the thought of bowl-like liquid crystals out of my mind.

FIGURE 10.2. Shapes of molecules that form liquid crystal phases: (a) rodic (1D); (b) discotic (2D); (c) bowlic (3D); and (d) mass point (0D)—hexatic phase.

During one of the coffee hours after that fateful night I worked up my courage to tell it to the experts, in this case, Adriaan de Vries of Kent and Christian Destrade of Boudeaux. (By the way, Sonal's dance was splendid, and I promised myself that I would come back to every conference that Chandrasekhar organized in Bangalore. Which I did, almost. But that is another story.)

Back to Beijing. Even though I wanted very much to write up my thoughts on the bowl-like liquid crystals, it would have been very difficult, if not impossible, to get it published in China, or elsewhere. In China, you did not pay anything to the journal when your paper was accepted for publication; instead, they paid you! That was one of the two and only two ways for a Chinese scientist to supplement his or her low income; the other was to referee a paper. In other words, to get a paper published was not a purely academic matter. Since there was no experimental evidence to support the existence of bowl-like liquid crystals at that time, I did not think I stood a chance of getting my speculations published. Besides, I was busy with the nematic–isotropic phase transition [2] and other problems [3]. Yet, I did talk to a few chemists in Beijing and asked them to try the synthesis. They were not interested; they were interested in discotics!

The chance of getting my beloved speculations into print finally came in 1981. I was writing a review on the liquid crystal phases for the journal *Wuli*, which is the Chinese word for physics. (This journal is the Chinese equivalent of *Physics Today* minus the advertisements, except that it also has a section for original papers.) I was trying to give a systematic survey of the rodics (liquid crystals with long molecules), the discotics, and the less familiar hexatic phases [4], and I decided on a scheme of introducing them according to the "dimension" of their constituent molecules (Fig. 10.2). It then followed that we could have liquid crystal phases from molecules of dimension zero (hexatics), one (rodics), or two (discotics). Following this reasoning, the conjecture of the existence of liquid crystals with molecules of three dimensions (bowlics) was natural and almost irresistible. I was right. The paper [5], "Liquid Crystal Phases and the 'Dimensionality' of Molecules," got through the referee and the editor without a hitch.

Knowing that *Wuli* was not the most popular journal in the world, after its publication in 1982, I sent out an English translation (of the Introduction

and Section IV) of this paper to the major liquid crystal laboratories outside China. A year later, in an article [6] summarizing the development of liquid crystal research in China from 1970 to 1982, I devoted a whole paragraph to my predictions of the bowlics.

Nothing happened, not until 1985. In Halle (Saale), of the then German Democratic Republic, during the 6th Liquid Crystal Conference of Socialist Countries, August 26–30, 1985, I was informed by Christian Destrade that bowlics had been successfully synthesized, and Anne Levelut of Orsay had just finished doing an x ray study of them. I was more than excited. On my way home to New York after the conference, I stopped over at Orsay and talked to Levelut. She kindly provided me with a preprint of her work [7] and copies of the two papers announcing the synthesis [8,9].

Of course, none of these authors called these compounds bowlics. Neither did I. Zimmermann et al. [8] called them "pyramidics," and Malthête and Collet [9] called them "cone-shaped." After all, Egypt is closer to Europe than China is. In fact, I myself had been calling them bowl-likes, even though "pyramid or hemisphere shapes" were also mentioned earlier in my paper [5]. The word bowlic was formally introduced in my invited talk [10] at the 11th International Liquid Crystal Conference at Berkeley, July 2, 1986, ten years after America's Bicentennial and three years before the Tiananmen massacre in Beijing.

Since then, there have been more studies [11–27] of bowlics. The monomers do form the usual columnar liquid crystal phases as expected [5], and sometimes do possess some unique properties [11] not shared by the discotics. However, the predicted ferroelectricity and thermotropic nematic phases [5] have not yet been found. Bowlic Langmuir films have been studied [22,23]. Bowlic polymers have been discussed theoretically [24–27] and predicted to be capable of forming ultrahigh T_c superconductors [24,25]. These polymers remain to be synthesized. All these developments will be summarized in the rest of this chapter.

As will be emphasized below, there exist no fundamental obstacles for these exotic properties of bowlics to be realized in the laboratory, and hence their novel applications in industry. What is needed is more effort on the part of chemists and materials scientists.

10.2   The First Paper

The first paper predicting the existence of bowlics [5] contains an introductory section, outlining the systematics of the then existing liquid crystal phases and the motivation for the bowlics, and five other sections. The bowlics and their unique properties are discussed in Section IV, which is followed by the conclusions in Section V. In the following, the English translation of the relevant parts of this paper is presented.

Liquid Crystal Phases and the "Dimensionality" of Molecules

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Liquid crystal was first observed in cholesteryl benzoate by the Austrian botanist Reinitzer in 1888 and named by the German crystallographer Lehmann one year later. The two words "liquid crystal" represent a new state of matter intermediate between liquid and crystal, which is now very important in both basic research and applications.[1] The history of liquid crystal research in our country goes for 11 years already.[2]

In the 89 years span between the discovery of liquid crytals and 1977, the only known liquid crystals are found in compounds made up of long organic molecules. In these molecules there is usually a central part that is long and rigid of lathy shape with flexible end chains fixed at one or both ends.[3] Liquid crystal states (phases) of long organic molecules can be chiefly divided into three types, viz., nematics, cholesterics, and smectics (see Sec. I). The basic properties of these liquid crystal phases may be explained by treating the molecules as volumeless rod-like (1-dimensional) entities.

In 1977, Chandrasekhar et al. of India first observed liquid crystal phases in organic compounds of circular disc-like molecules. Later, liquid crystals were consecutively found in other compounds of rectangular or asymmetric disc-like molecules. All these molecules may be considered to be 2-dimensional in shape. In these mesophases of disc-like molecules there exist also nematics and cholesterics, but no smectics; on the other hand, there are columnar phases[1,4,5] not found in the case of long molecules.

One of the characteristics of liquid crystals is its optical anisotropy (with the exception of the D phase, see Sec. I below). In the cases of long and disc-like molecules mentioned above the anisotropy of the liquid crystal phases comes from the (1- or 2-dimensional) asymmetric shape of the molecules.

Halperin and Nelson[6,7] in 1978 considered a 2-dimensional lattice of mass-point molecules. They suggested that a hexatic liquid crystal phase may appear before the 2-dimensional crystal melts into liquid. Recently, this idea was generalized to a 3-dimensional lattice by Nelson and Toner[8] who proposed the possible existence of a cubic liquid crystal phase in this case. According to what we said above, the mass-point molecules forming hexatic and cubic liquid crystals are molecules of 0 dimension. Although there are no decisive experiments so far, the question of the existence of hexatic and cubic mesophases has already aroused wide attention and many research activities. From the standpoint of liquid crystal research, mesophases of 0-dimensional molecules break away from the traditional concept that the liquid crystal phases must come from organic molecules of asymmetric shape. This development is very important.

Rigorously speaking, all molecules in nature are of course 3-dimensional. The "dimension" of a molecule discussed here really means the dimension of "molecules" in the physical models used in the description of the liquid crystal phases. In other words, it means the minimal (or important) character of the molecular shape when mesophases are formed.

Since 1- and 2-dimensional moleclues have been proved to have liquid crystal phases and 0-dimensional molecules may probably have liquid crystal phases, it is then natural to ask: Do 3-dimensional molecules also possess liquid crystal phases? In our opinion, the answer is yes!

In recent years, there has been tremendous progress on the study of liquid crystal phases. The aim of this paper is to introduce and summarize, from the viewpoint of the "dimensionality" of molecules, what is known about: (1) the different structures of (thermotropic) liquid crystal phases, especially those of smectics and disc-like molecules; (2) the sequences of phase transitions between the different mesophases including reentrant phenomena; and (3) to discuss the possible existence and properties of mesophases made up of 3-dimensional molecules. The last part is obviously speculative in nature. It is our hope that there will be more investigations by theorists and experimentalists in this direction.

The headings of Sections I–III are: I. One-Dimensional Molecules. 1. Nematics. 2. Cholesterics. 3. Smectics. 4. D phase and blue phases. 5. Sequences of phase transitions. 6. Reentrant phenomena. II. Two-Dimensional Molecules. 1. Nematics and cholesterics. 2. Columnar phases. 3. Sequences of phase transitions. III. Zero-Dimensional Molecules. Here Sections I–III will be skipped, and the translation is continued with Sections IV and V.

IV. Three-Dimensional Molecules

Although many long molecules do carry with them strong electric dipoles[3] but the arrangement of these molecules in the mesophases is such that they always compensate each other (Fig. 13) resulting in vanishing net polarization. Consequently, in nematics, cholesterics, and most of smectics there is not ferro-electricity (see Sec. I). In the case of 3-dimensional molecules, e.g., the bowl-like molecules shown in Fig. 14, due to the special shape of the molecules, the cancellation of the dipoles of the molecules will be more difficult (the probability of the molecules lying toward a common direction is larger). It is then possible to observe ferroelectric nematic phases. The corresponding phase for chiral molecules will be cholesterics.

In this case, the physical quantities of the mesophase do not necessarily have
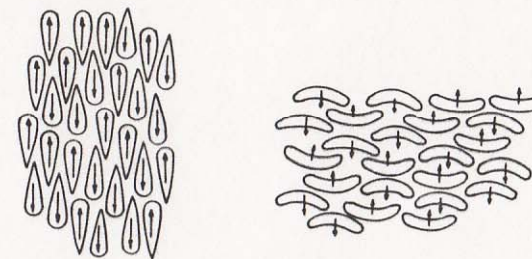

FIG. 13. Two cases in which the electric dipoles of rodic molecules cancel each other.
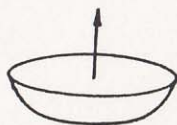
FIG. 14. A bowlic molecule. The arrow represents the electric dipole.

the $\mathbf{n} \to -\mathbf{n}$ symmetry, where $\mathbf{n}$ is the unit vector of the director (representing the average molecular orientation). For liquid crystal of bowl-like molecules, there is still the local symmetry of uniaxial rotations. The elastic energy of nematics is identical to the Frank free energy of 1-dimensional molecules (since the derivation[19] of the Frank free energy does not depend on the symmetry $\mathbf{n} \to -\mathbf{n}$). However, there are extra terms in the dissipation function in comparison with the case of long molecules [see (5.6) of Ref. 20], which lead to some new phenomena not found in nematics of 1-dimensional molecules. For example, thermal gradients can change the molecular orientations and vice versa.

It can be imagined that in the case of bowl-like molecules there will also be columnar phases, but no smectics. In addition, since it is easier for bowl-like molecules (in comparison with disc-like molecules) to pile up on each other, there may exist a new type of phase which is intermediate between nematic and columnar phases, viz., among the spatially separate individual molecules as in nematics there exist short columns of pile-up molecules.

Apart from bowl-like molecules, other 3-dimensional molecules of, for example, pyramid or hemisphere shapes may also be considered. But in these latter cases, the compensation of the dipoles is easier to achieve and the occurrence of ferroelectric mesophases are less likely. It should be pointed out that the term "bowl-like" used above is symbolic. In experiments, one only has to select those molecules which are slightly flat but asymmetric in the up and down directions. There should be some, but not too strong, piling capacity of the molecules; otherwise, once piled up the molecules may form crystals rather than liquid crystals.

Since mesophases of 3-dimensional molecules are ferroelectrics there should be many practical applications. Their properties are quite different from those of known mesophases.[21] Further investigations are worthwhile and most desirable.

V. Conclusions

These days the study of liquid crystal phases and their transitions is a hot topic[1] in condensed matter physics. It was only in the last few years that reentrant phenomena, ferroelectric liquid crystals, discotics, 2-dimensional hexatic and cubic phases, etc., were discovered or proposed. In this article, presented from the viewpoint of the "dimensionality" of molecules for the first time, these new developments are introduced; the existence and the unique properties of ferroelectric liquid crystals formed by 3-dimensional molecules are predicted.

10.3   Bowlic Monomers

All that is known about bowlic monomers will be summarized here. Theoretical studies of bowlic polymers will be presented in Section 10.4.

10.3.1   The Molecules

The three types of bowlic molecules synthesized so far are sketched in Fig. 10.3 and summarized in Table 10.1. Compounds I consist of a rigid bowl structure with three benzene rings, and six identical flexible side chains. In particular, I.1 is hexaalkyloxytribenzocylononene (nHETB), I.2 is hexaalkanoyloxytribenzocyclononene (nHATB), and I.4 is hexaalkoxybenzoyloxytribenzocyclononene (nHBTB). Compound II has a similar core but only three tails attached to the three benzene rings in the core; they are prepared in racemic and optically active forms. Both I and II are derivatives of the cyclotriveratrylenes [28], and the core is in the crown form. In contrast, III is formed from a core of four benzene rings and eight flexible tails; in the columnar phase the core is in the sofa form with C_{2h} symmetry [14,15].
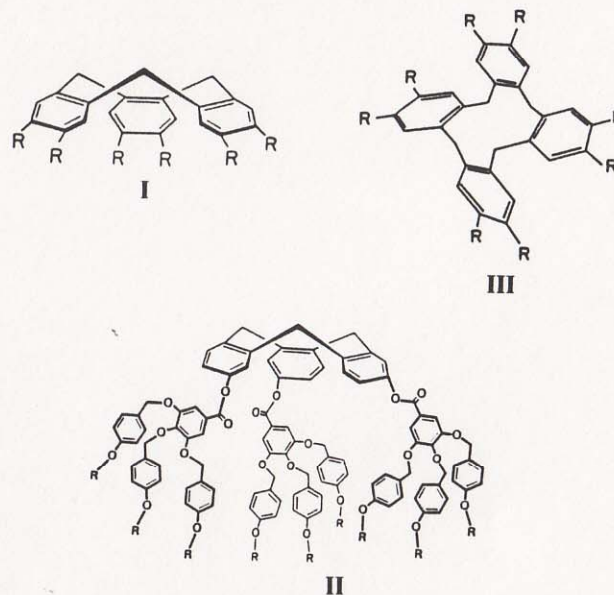

FIGURE 10.3. The three types of bowlic monomeric molecules synthesized: hexa-substituted cyclotricatechylene (I); a triester of cyclotriphenolene with a 3,4,5-trisubstituted benzoic acid (II); and octasubstituted tetrabenzocyclododecatetraene (III).

TABLE 10.1. Summary of bowlic monomers synthesized. Molecules I, II, and III refer to those in Fig. 10.3.

Compound	Tail R	n	Year	Reference	Remarks
I.1	$C_nH_{2n+1}O$	4–12	1985	Zimmermann et al. [8]	Pressure study ($n = 7, 9, 10, 11$) [16]
I.2	$C_nH_{2n+1}CO_2$	7–14	1985	Zimmermann et al. [8]	x ray diffraction ($n = 8, 9, 10$) [17]
		9, 11, 15	1985	Malthête and Collet [9]	x ray diffraction ($n = 9, 11, 12, 14$) [17–19]
I.3	$C_nH_{2n+1}ØCO_2$	7, 8, 10	1986	Zimmermann et al. [11]	
I.4	$C_nH_{2n+1}OØCO_2$	12	1985	Malthête and Collet [9]	x ray diffraction [7]
		10	1986	Zimmermann et al. [11]	
I.5	$C_nH_{2n+1}CH=CHC_nH_{2n+1}CO_2$	8	1988	Wang and Pei [12]	See also [18]
		8	1988	Wang and Pei [12]	See also [18]
II	C_nH_{2n+1}	12	1987	Malthête and Collet [13]	
III.1	$C_nH_{2n+1}O$	8, 10	1988	Zimmermann et al. [14]	
III.2	$C_nH_{2n+1}CO_2$	11, 13	1988	Zimmermann et al. [14]	
III.3	$C_nH_{2n+1}ØCO_2$	10	1988	Zimmermann et al. [14]	
III.4	$CH_3O(CH_2CH_2O)_n$	1, 2, 3	1989	Zimmermann et al. [15]	

10.3.2   Mesophases and Phase Transitions

All bowlic compounds synthesized so far exhibit thermotropic columnar mesophases. In addition, methoxydiethyleneoxide and methoxytriethyleneoxide, **III.4** with $n = 2$ and 3, respectively, are also lyotropic and can sustain (at room temperature) up to 40 wt.% water. At a higher water content methoxydiethyleneoxide exhibits another lyomesophase M_F which is more fluid and *nematic-like* [15].
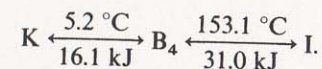
All the thermotropic bowlic mesophases discovered are columnar. There are at least five of them, denoted by $B_1–B_5$ here (corresponding to $P_A, \ldots, P_D$ in [8]). Tables or diagrams of phase transitions for the homologues and sometimes mixed bowlic compounds can be found in [8–11,14,15,18]. Compared with the tribenzos **I**, the tetrabenzos **III** have:

(i)   much less tendency for polymorphic mesomorphism;
(ii) an increase in the melting temperature; and, in most cases; and
(iii) a significant increase in the clearing temperatures and clearing enthalpies [14].
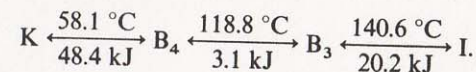
The tetrabenzos are therefore more highly ordered than the tribenzos.

Some typical transition sequences are listed here, where K(I) represents the crystal (isotropic liquid) phase:
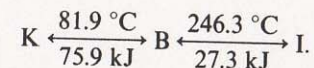
I.2, $n = 7$ (7HATB) [8]:

$$K \xleftrightarrow[16.1\ \text{kJ}]{5.2\ °C} B_4 \xleftrightarrow[31.0\ \text{kJ}]{153.1\ °C} I.$$

I.2, $n = 11$ (11HATB) [8]:

$$K \xleftrightarrow[48.4\ \text{kJ}]{58.1\ °C} B_4 \xleftrightarrow[3.1\ \text{kJ}]{118.8\ °C} B_3 \xleftrightarrow[20.2\ \text{kJ}]{140.6\ °C} I.$$

III.2, $n = 11$ [14]:

$$K \xleftrightarrow[75.9\ \text{kJ}]{81.9\ °C} B \xleftrightarrow[27.3\ \text{kJ}]{246.3\ °C} I.$$

All the phase transitions are first order; some of the transition enthalpies are extremely small. Note that 7HATB and 8HATB are both bowlic columnars at room temperature. When the tail R in **I** is too short, as is the case in the rodics, mesophases are not formed. In fact, 5HATB (6HATB) was found [18] to melt directly from the isotropic liquid phase at 152 °C (153 °C) to a "disordered crystalline phase" [20], in which the bowlic molecules stack in a triclinic system with space group $P\bar{1}$.

For the tetrabenzos **III.1**, **III.2**, and **III.3**, it was suggested [14] that the rapid interconversion between the two symmetry-related sofa conformations may result in an average planar four-fold symmetry for the molecules and

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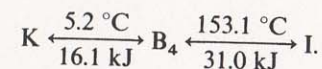
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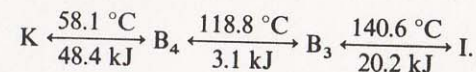
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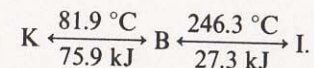
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hence nonpolar columns in the columnar phases. This remains to be confirmed by x ray diffraction studies.

The predicted thermotropic bowlic polar or nonpolar nematics [10] have not yet been found in the thermotropic bowlic compounds already synthesized. In principle, we do not see any basic difficulty for them to be realized. It seems that more effort in chemical synthesis is needed. In this regard, it should be emphasized that nematic-like lyotropic bowlics (the M_F mentioned above) already exist, which can even be readily and rapidly (~ 0.1 μs, in contrast to ~ 1 ms in thermotropic rodic nematics) aligned by a magnetic field [15]. The potential industrial applications of these lyotropics, as fast magnetooptic switches or displays, should be explored. No parallel results of electrical realignment on these compounds are available yet.

When the two R tails attached to each of the three benzene rings of I differ from each other, the molecule is chiral and bowlic cholesterics may be formed [10]. Compound II consists of exactly such molecules, in which a columnar but not cholesteric phase was found [13]. Of course, as in the case of the bowlic nematics, this result does not imply that bowlic cholesterics cannot exist.

In [10], other bowlic mesophases such as the "stringbean," the "donut," and the "onion" have been proposed (Fig. 10.4). It seems that the two-dimensional version of the donut or onion mesophase may have been observed in the bowlic Langmuir films (see Section 10.3.5).

The structures of the columnar phases have been found to be B_{ho}, B_{ro}, and B_{to} [7,17,18]. Here the subscripts "h" and "r" refer to vertical columns with two-dimensional hexagonal and rectangular structures, respectively; "t" refers to tilted columns; and "o" refers to ordered periodic arrangement of the molecules within a single column. There is no correlation among the molecules from different columns. (Of course, the opposite is true in the crystalline phases of 5HATB and 6HATB [20].) For example, the high (low) temperature B_3 (B_4) phase of 11HATB is B_{ho} (B_{to}) with a period of 4.82 Å along a column and a lattice constant of 49.38 Å [7]. A spiral structure exists for the low temperature columnar phase of 12HBTB in which the paraffinic medium, the external shell of each column, forms a helix [7]. This spiral structure is also found in discotics [29], and is not that uncommon in polymers [30].
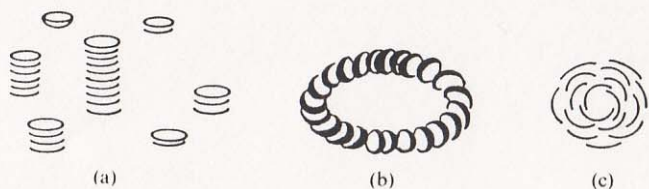

FIGURE 10.4. Three types of bowlic mesophases proposed in [10]: (a) stringbean; (b) donut; and (c) onion.

10.3.3 Physical Properties

The director $n \to -n$ symmetry is a mesoscopic or macroscopic symmetry which exists in the rodics and discotics but, because of the steric effect, may break down in the bowlics. Consequently, bowlics should be true ferroelectrics, or antiferroelectrics in other cases [5,10]. In the bowlic columnars it has not yet been found, for the obvious reason: Experimentally, the sample is not aligned before the columnars are formed. Once the columnar is formed the bowl shape of the molecular core leads to the lock-in of the bowls within the columns [9] with both up and down orientations coexisting in each column—the column is not polar and there is no ferroelectricity (or antiferroelectricity).

In this regard, it is encouraging to note that the half-life of the crown conformer is only ~ 4 min at 3° below the clearing temperature in II so that, in principle, the columns can be made polar by the crown inversion process under an electric field and the resulting ferroelectricity can be preserved at a lower temperature by quenching [13]. By the same reasoning, it should be easier to align electrically the bowlic molecules in the isotropic liquid phase where the crown half-life is even shorter (~ 0.1 s at 200 °C [9]) provided that the molecular polarization is large enough. This isotropic liquid is paraelectric and the lower mesophases obtained from cooling should be ferroelectric [10].

All previous experiments on bowlics were done with unaligned samples. However, some alignment methods have been tried. For example, 9HATB at 60 °C was put between two glass plates, with one coated with DMOAP and the other untreated. It seems that the coated surface was able to align the bowlic columns and some hexagonal structures were observed in the textures [31]. This approach of alignment is worth further pursuit. Also, some degree of orientation is possible when the mesophase is spread out on a glass plate with a spatula [18]—a method used before for the discotics.

For I.1 and I.2 the columnar mesophases B_1 and B_3 are optically uniaxial, and B_2 and B_4 are apparently biaxial [8]. The compounds III.1 and III.2 are optically uniaxial while III.4 could be optically biaxial; all these three compounds have a negative optical anisotropy [14]. A very interesting optical phenomenon was observed in I.3 and I.4, viz., the optical anisotropy reverses sign at some well-defined temperature within the mesophase region. This is interpreted as due to the conformational changes involving the side-chain benzene rings [11].

Many textures of the bowlics look like those in the discotics since both exhibit columnar phases. In particular, hexagonal dendrites are formed when the bowlics are slowly cooled from the isotropic liquid phase (see Plate 2 in [14] for bowlics and [32] for discotics). The growth of these dendrites can be easily controlled and could serve as very good candidates in the study of pattern formation [33]. Second harmonic generation studies of bowlics on a water film have been carried out. The effect is similar to those found in the case of the rodics [34].

Pressure studies for nHATB reveals that the transition temperatures increase monotonically with pressure, and there exists no reentrant phenomenon. Volume changes for the transitions and the ratio of the expansion and isothermal compressibility coefficients for the mesophases are reported [16].

Discussions on other physical properties such as elasticity, flexoelectricity, defects and textures, and hydrodynamics unique to bowlics are given in [5,10]. In particular, coupling between the molecular orientation and temperature gradient (like those in the Lehmann rotation phenomenon in the rodic cholesterics) is expected in bowlic nematics.

10.3.4   Bowlic Nematics in Electric Fields

Bowlic nematics may exist in the polar (i.e., ferroelectric) or nonpolar form [10,21]. The static and dynamic response of polar nematics to external electric fields [35] will be presented in this section. The results are relevant to a new type of fast-switching liquid crystal displays using these polar nematics [10].

Statics

The free energy density describing a polar nematic in the presence of an external electric field $\mathbf{E}$ is given by [10]

$$F = F_0 + K_0 \nabla \cdot \mathbf{n} - a\mathbf{n} \cdot \mathbf{E} - (\varepsilon_a/8\pi)(\mathbf{n} \cdot \mathbf{E})^2, \tag{10.1}$$

where F_0 is the Frank free energy given by $F_0 = \frac{1}{2}K_1(\nabla \cdot \mathbf{n})^2 + \frac{1}{2}K_2(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + \frac{1}{2}K_3(\mathbf{n} \times \nabla \times \mathbf{n})^2$.

We now consider a planar polar nematic in which the molecules are parallel to the two glass plates at $z = \pm d/2$. Here the z axis is along the cell normal, and d is the cell thickness. Under the action of a field $\mathbf{E}$ normal to the cell, the molecules will tend to align parallel to $\mathbf{E}$ (since $a > 0$). Let us first consider the case that the dielectric interaction is weak, i.e., $\varepsilon_a = 0$. F becomes

$$F = \frac{1}{2}(K_1 \cos^2 \theta + K_3 \sin^2 \theta)\left(\frac{d\theta}{dz}\right)^2 + K_0 \nabla \cdot \mathbf{n} - aE \sin \theta, \tag{10.2}$$

where θ is the angle between the director $\mathbf{n}$ and the horizontal x axis. The Lagrange equation of motion is given by

$$(K_1 \cos^2 \theta + K_3 \sin^2 \theta)\frac{d^2\theta}{dz^2} + (K_3 - K_1) \sin \theta \cos \theta \left(\frac{d\theta}{dz}\right)^2 + aE \cos \theta = 0, \tag{10.3}$$

resulting in

$$\frac{1}{2}(K_1 \cos^2 \theta + K_3 \sin^2 \theta)\left(\frac{d\theta}{dz}\right)^2 = -a \sin \theta + aE \sin \theta_m, \tag{10.4}$$

where θ_m is the maximum tilt angle at $z = 0$. Setting $\sin \theta_m \equiv k$ and $\sin \theta \equiv k \sin \lambda$, and following the usual procedure [36], we obtain

$$\sqrt{2aE}\left(\frac{d}{2}\right) = \int_0^{\pi/2} \left[\frac{K_1(1 - k^2 \sin^2 \lambda) + K_3 k^2 \sin^2 \lambda}{k - k \sin \lambda}\right]^{1/2} \frac{k \cos \lambda \, d\lambda}{(1 - k^2 \sin^2 \lambda)^{1/2}}. \tag{10.5}$$

The threshold field E_c is obtained by taking the limit $k \to 0$ on the right-hand side of (10.5). We then have

$$\sqrt{2aE_c}\left(\frac{d}{2}\right) = \lim_{k \to 0} \int_0^{\pi/2} \frac{\sqrt{K_1}k \cos \lambda \, d\lambda}{\sqrt{1 - \sin \lambda}}$$

$$= \lim_{k \to 0} \int_0^1 \frac{\sqrt{K_1}k \, dt}{\sqrt{1 - t}} = 0, \tag{10.6}$$

i.e., $E_c = 0$. In other words, there is no Freedericksz transition for polar nematics. The molecules reorient as soon as the electric field is turned on. This conclusion remains true even when the dielectric interaction is included and is independent of the magnitude of ε_a. Similar results are obtained for the other two kinds of Freedericksz transitions (i.e., $\mathbf{E}$ parallel to the glass plates for either planar or homeotropic cells).

For the case considered above, the variation of θ_m as a function of E obtained numerically is plotted in Fig. 10.5. Note that E_c remains zero for a twisted polar nematic cell with arbitrary twist angle. Consequently, many grey scales are possible in a liquid crystal display using polar nematics.
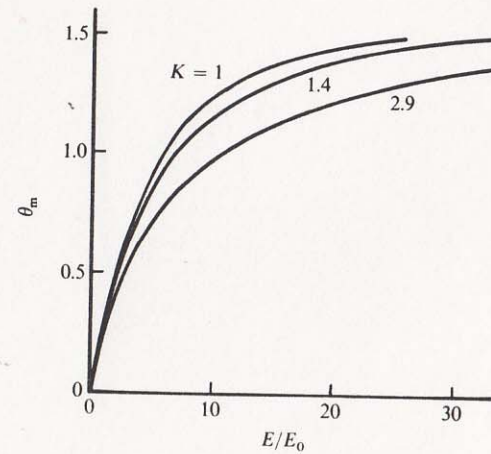

FIGURE 10.5. Variation of the maximum tilt angle θ_m as a function of electric field E in a planar polar nematic cell. $K \equiv K_3/K_1$ and $E_0 \equiv 2K_1/(ad)$.

Dynamics

The orientational motion of molecules in polar nematics may be described by

$$\gamma \frac{\partial \theta}{\partial t} = K\nabla^2\theta + aE\cos\theta, \qquad (10.7)$$

where γ is a viscosity coefficient, the one-elastic-constant approximation is assumed for simplicity, and the dielectric term is ignored. Equation (10.7) is the overdamped sine–Gordon equation, or the double sine–Gordon equation if the dielectric term is included [37]. Similar equations appear in the ferroelectric smectic C* case [38] and can be handled accordingly. In particular, soliton solutions are possible. Response time could be in the microsecond range and we have a very fast liquid crystal switch device [10].

10.3.5   Bowlic Langmuir Films

In a bowlic Langmuir film a monolayer of bowlic molecules can rest on a film of liquid. There are at least four possibilities as far as the orientation of the molecules with respect to the air–liquid interface is concerned, viz., the bowl-shaped core can be up, down, vertical, or tilted (Fig. 10.6).

Experiments on Langmuir films with 8HATB (**I.2**) and 9HETB (**I.1**), respectively, on purified water or a NaOH solution were carried out recently by El Abed et al. [22,23]. In the bulk, these two bowlic compounds form columnars at room temperature. The surface pressure π versus molecular area A isotherms, with purified water as the subphase, show the existence of plateaus (Fig. 10.7). The location and height of the plateau change when water is replaced by the NaOH solution [22]. The nonplateau parts at high A are understood to correspond to a monolayer arrangement, even though it is not entirely clear whether the molecules are in the up or down orientations [39]. The nonplateau parts at low A are interpreted to be due to the formation of an upper layer by a "roll-over" collapse. The difference between the two isotherms is attributed to the difference of the polar groups (COO— and
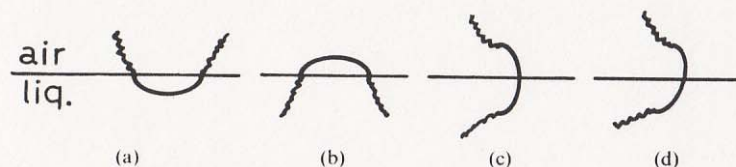
FIGURE 10.6. Four possible orientations of bowlic molecules with respect to the air–liquid interface: (a) up; (b) down; (c) vertical; and (d) tilted. Note that (a) and (b) are identical for a discotic molecule since there is no up–down asymmetry there.
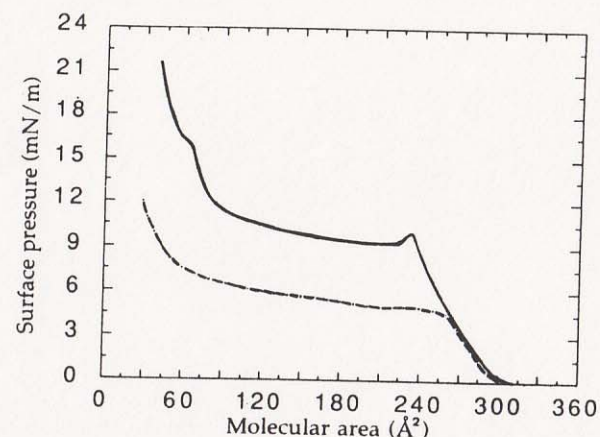
FIGURE 10.7. Surface pressure π versus molecular area A isotherms. The subphase is purified water (pH = 5.7); temperature is 21 °C. Solid curve, 8HATB; broken curve, 9HETB [22].

CO—), in that it takes more energy to remove the polar group and the whole molecule from the subphase for 8HATB than for 9HETB.

In the plateau region, anisotropic domains and an isotropic phase are found to coexist [23,40]. Within these domains, the molecules assume the vertical orientation similar to that found in some discotics [41]. Looking from the top of the film, the shape of the domains is needle-like and dot-like for 8HATB and 9HETB, respectively. From the light reflectivity study, both types of domains are found to be multilayered; the needle-like domains consist of molecules arranged in rectilinear rows; in the dot-like domains the molecules form concentric circles [40], with each circle like the donut mesophase first proposed by Lin [10]. This concentric-donut arrangement is partly deduced from the rate of domain growth [39]. In our opinion, both the concentric-donut and the (two-dimensional) onion phases are consistent with experimental data. It would be interesting to find out which one is the real arrangement. Or, maybe both phases are possible and can even coexist, i.e., there are actually two types of dot-like domains. Furthermore, if the concentric-donut arrangement is real then it may be possible to find the real donuts, or a concentric-donut with a hole in the middle. Similarly, the recti-linear rows in the needle-like domains may be understood as a set of parallel stringbeans [10], and we should look for single stringbeans in the Langmuir films. The possibility of finding single stringbeans or donuts should be higher at the high A region in which the concentration of the bowlic is lower.

Finally, it is worth pointing out that Langmuir films of simpler molecules have been shown to be fruitful ground in the study of pattern formation [42]. Similar and new phenomena can be expected when bowlic Langmuir films are used.

10.4   Bowlic Polymers

The bowlic monomers can be linked up to form main-chain, side-chain, or columnar bowlic polymers as shown in Fig. 10.8. These bowlic polymers have not been synthesized, but their counterparts using discotic monomers already exist [43]. Summarized below are theoretical studies on these very important materials, the bowlic polymers. Results in Sections 10.4.1 and 10.4.2 are equally applicable to the conventional polar polymers.

10.4.1   The Discrete Model for Dilute Solutions

In dilute polymer solutions of sufficiently low concentrations the polymers are separated from each other. We can then consider the conformations and behavior of a single main-chain bowlic (or polar) polymer in the presence of an electric field **E**. As proposed by Lam [24], a possible discrete model for this case is shown in Fig. 10.9. The description given below follows that of [24,26].

In the discrete model, the length of each monomer is b and the length of the chain is Lb. This model assumes a biased random walk of L steps, corresponding to L repeated monomers, such that the energy for a monomer parallel (antiparallel) to **E** causes energy $-\mu E$ (μE) where μ is the electric dipole moment of each monomer. A monomer perpendicular to **E** causes zero energy. Each bending from parallel to antiparallel, or vice versa, is called a hairpin which causes energy h. A pair of parallel (antiparallel) adjacent
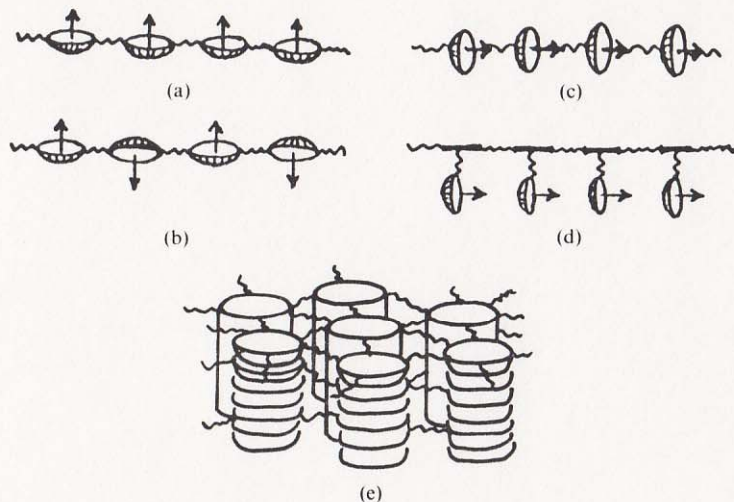
(a)

(b)

(c)

(d)

(e)

FIGURE 10.8. Three possible types of bowlic polymers: (a)–(c) main-chain; (d) side-chain; and (e) columnar. (a)–(d) are from [24].
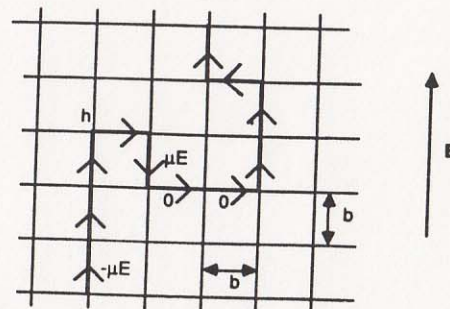
FIGURE 10.9. The discrete model of polar main-chain polymers in an external electric field **E**. The lattice may be one to three dimensions.

monomers have energy γ ($-\gamma'$). All μ, γ, γ', and h are positive. The lattice is three dimensional (3D) in general, but can be reduced to 2D or 1D for simplicity, or in special cases.

This model has not been solved analytically yet. However, it can be solved easily by computer simulation, e.g., by the Monte Carlo method. In the 1D continuum limit two special cases of this model have been solved exactly. First, for $E = 0$, the model reduces to that of Zwanzig and Lauritzen [44] which was solved exactly in the limit of $L \to \infty$. This solution shows a second-order phase transiton with the number of hairpins acting as the order parameter. Second, for $E \neq 0$ and $\gamma = \gamma' = 0$, the model reduces to that of Gunn and Warner [45] which was also solved exactly, but does not show any phase transition. As pointed out by Lauritzen and Zwanzig [46], the continuum version of a physically discrete model may contain spurious results.

The 2D Case

In order to solve the model analytically, the model is reduced to a simplified 2D (or 1D) version as shown in Fig. 10.10. This version allows the bending to
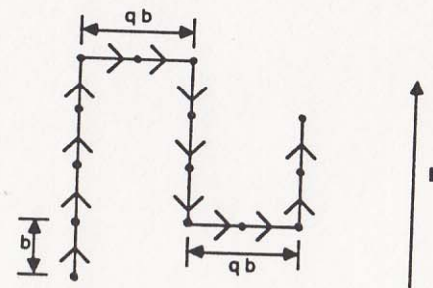
FIGURE 10.10. The simplified 2D (or 1D) model. q is a constant and $q = 0$ reduces the model to 1D. Here the horizontal bonds are in one direction only.
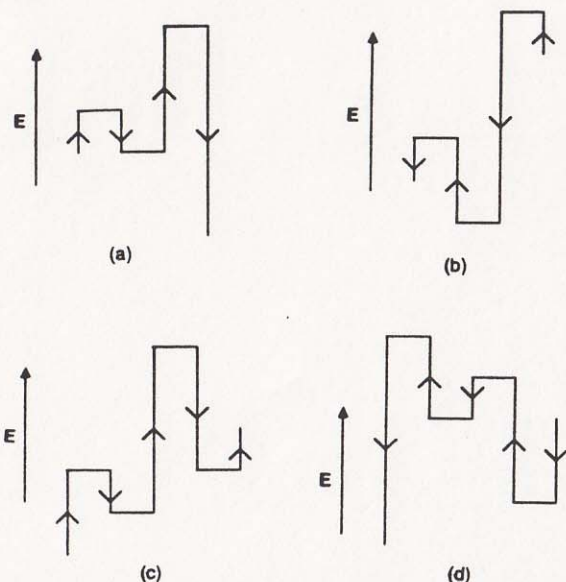
(a)   (b)

(c)   (d)

FIGURE 10.11. The four cases of the simplified 2D (or 1D) model of polar main-chain polymers. The diagram shown here corresponds to $N = 2$. (a) Case A: first monomer up, last monomer down. (b) Case B: first monomer down, last monomer up. (c) Case C: first monomer up, last monomer up. (d) Case D: first monomer down, last monomer down.

go in one direction only. To further simplify the model, the interaction between the monomers are assumed to be negligible, i.e., we assume $\gamma = \gamma' = 0$.

The partition function of the polar polymer is given by

$$Q(L, E) = Q_A(L, E) + Q_B(L, E) + Q_C(L, E) + Q_D(L, E), \qquad (10.8)$$

where Q_A, Q_B, Q_C, and Q_D are calculated from the four cases shown in Fig. 10.11, given by

$$Q_A(L, E) = \sum_{N=1}^{\infty} \sum_{X_1=1}^{\infty} \cdots \sum_{X_N=1}^{\infty} \sum_{Y_1=1}^{\infty} \cdots \sum_{Y_N=1}^{\infty} \delta_{L, \sum X_j + \sum Y_j + (2N-1)q} \exp(-\beta U_A),$$

$$Q_B(L, E) = \sum_{N=1}^{\infty} \sum_{X_1=1}^{\infty} \cdots \sum_{X_N=1}^{\infty} \sum_{Y_1=1}^{\infty} \cdots \sum_{Y_N=1}^{\infty} \delta_{L, \sum X_j + \sum Y_j + (2N-1)q} \exp(-\beta U_B),$$

$$Q_C(L, E) = \sum_{N=1}^{\infty} \sum_{X_1=1}^{\infty} \cdots \sum_{X_{N+1}=1}^{\infty} \sum_{Y_1=1}^{\infty} \cdots \sum_{Y_N=1}^{\infty} \delta_{L, \sum X_j + \sum Y_j + 2Nq} \exp(-\beta U_C),$$

$$Q_D(L, E) = \sum_{N=1}^{\infty} \sum_{X_1=1}^{\infty} \cdots \sum_{X_{N+1}=1}^{\infty} \sum_{Y_1=1}^{\infty} \cdots \sum_{Y_N=1}^{\infty} \delta_{L, \sum X_j + \sum Y_j + 2Nq} \exp(-\beta U_D),$$

$$(10.9)$$

with

$$U_A = (2N - 1)h - \mu E(\sum X_j - \sum Y_j),$$
$$U_B = (2N - 1)h - \mu E(-\sum X_j + \sum Y_j),$$
$$U_C = 2Nh - \mu E(\sum X_j - \sum Y_j),$$
$$U_D = 2Nh - \mu E(-\sum X_j + \sum Y_j).$$
$$(10.10)$$

Here X_i is the ith segment where the dipoles are pointing up, and Y_i is the ith segment where the dipoles are pointing down. In cases A and B, there are $N + 1$ segments that are pointing up and N segments that are pointing down; therefore, there are $2N - 1$ hairpins. In cases C and D, there are N equal segments pointing up and down; therefore there are $2N$ hairpins.

From (10.9) and (10.10), it is clear that

$$Q_B(L, E) = Q_A(L, -E), \qquad Q_D(L, E) = Q_C(L, -E). \qquad (10.11)$$

Consequently, (10.8) becomes

$$Q(L, E) = Q_A(L, E) + Q_A(L, -E) + Q_C(L, E) + Q_C(L, -E). \qquad (10.12)$$

Each term in (10.12) can be evaluated through the Z-transform (see [26] for details), resulting in

$$Q_A(L, E) = Q_A(L, -E) = \frac{f}{(L - q - 2)!} \lim_{z \to 0} \frac{d^{L-q-2}}{dz^{L-q-2}}\left[\frac{1}{F(z)}\right],$$

$$Q_C(L, E) = \frac{e^{u_0}}{(L - 1)!} \lim_{z \to 0} \frac{d^{L-1}}{dz^{L-1}}\left[\frac{1}{F(z)}\right] - \frac{1}{(L - 2)!} \lim_{z \to 0} \frac{d^{L-2}}{dz^{L-2}}\left[\frac{1}{F(z)}\right],$$
$$(10.13)$$

$$Q_C(L, -E) = \frac{e^{-u_0}}{(L - 1)!} \lim_{z \to 0} \frac{d^{L-1}}{dz^{L-1}}\left[\frac{1}{F(z)}\right] - \frac{1}{(L - 2)!} \lim_{z \to 0} \frac{d^{L-2}}{dz^{L-2}}\left[\frac{1}{F(z)}\right],$$

where

$$f \equiv e^{-\beta h}, \qquad u_0 \equiv \mu \beta E, \qquad (10.14)$$

and

$$F(z) \equiv z^2 - 2(\cosh u_0)z + 1 - f^2 z^{2(q+1)}. \qquad (10.15)$$

Therefore (10.12) can be written as

$$Q(L, E) = 2[H_L - (\cosh u_0)H_{L-1} + f H_{L-q-2}], \qquad (10.16)$$

where

$$H_m \equiv \lim_{z \to 0} \frac{d^m}{dz^m}\left[\frac{1}{F(z)}\right]. \qquad (10.17)$$

In general, $F(z) = 0$ is a $2(q + 1)$th-order algebraic equation which can be solved exactly if $2(q + 1) \leq 4$. Therefore, $F(z)$ can only be solved exactly, and $Q(L, E)$ can only be expressed analytically, for $q \leq 1$.

he 1D Case

q is set to zero, the 2D model reduces to a 1D model. The partition function r the 1D model is given by

$$Q = \frac{2}{(1-f^2)(z_2-z_1)}\left[(\cosh u_0)\left(\frac{1}{z_1^L}-\frac{1}{z_2^L}\right) + (f-1)\left(\frac{1}{z_1^{L-1}}-\frac{1}{z_2^{L-1}}\right)\right], \tag{10.18}$$

here

$$z_{2,1} = \frac{(\cosh u_0) \pm \sqrt{(\cosh^2 u_0)-(1-f^2)}}{1-f^2}. \tag{10.19}$$

or $E = 0$, the Helmholtz free energy A and the average number of hairpins are given by

$$A \equiv -\frac{1}{\beta}\ln Q = -\frac{1}{\beta}[\ln 2 + (L-1)\ln(1+f)], \tag{10.20}$$

$$\bar{n} = \frac{\partial A}{\partial h} = \frac{(L-1)f}{1+f}. \tag{10.21}$$

onsequently, $\bar{n}$ increases monotonically from 0 to $(L-1)/2$ as temperature increases from zero to infinity. This means that the polymer will bend more ten when the temperature increases.

The susceptibility χ is defined by $\partial P/\partial E$, where P is the polarization given

$$P \equiv -\frac{\partial A}{\partial E} = L\mu(\sinh u_0)[\sinh^2 u_0 + \exp(-2\beta h)]^{-1/2}. \tag{10.22}$$

/e then obtain

$$\chi = L\mu^2\beta(\cosh u_0)[\sinh^2 u_0 + \exp(-2\beta h)]^{-1/2}$$
$$- L\mu^2\beta(\cosh u_0)(\sinh^2 u_0)[\sinh^2 u_0 + \exp(-2\beta h)]^{-3/2}. \tag{10.23}$$

s $E \to 0$, we have $u_0 \to 0$, $\cosh u_0 \to 1$, and $\sinh u_0 \to 0$. This implies

$$\chi \to L\mu^2\beta \exp(\beta h), \tag{10.24}$$

hich is identical to Eq. (5) of [45] if l there is identified as b in our model.

The 1D model result can also be obtained directly by mapping the model) the 1D Ising model with nearest neighbor interactions. This can be seen isily by stretching the chain in Fig. 10.10 into a straight line (with $q = 0$) and lentifying the up (down) polarization in each monomer as an up (down))in. Note that parallel adjacent spins have energy zero and antiparallel ljacent spins have energy h. Mathematically, the partition function $Q(L, E)$ given by

$$Q(L, E) = \sum_{\sigma_1=-1}^{1}\sum_{\sigma_2=-1}^{1}\cdots\sum_{\sigma_L=-1}^{1}\exp(\beta\xi), \tag{10.25}$$

where

$$\xi = -\frac{h}{2}\sum_{j=1}^{L-1}(\sigma_j\sigma_{j+1}-1) - \mu E\sum_{j=1}^{L}\sigma_j. \tag{10.26}$$

Comparing (10.25) and (10.26) with the corresponding expressions in [47], the partition function here is seen to be equivalent to the free boundary partition function of the 1D Ising model with the following substitutions:

$$\exp\left(-\frac{\beta h}{2}(L-1)\right)Z_{1,N}^F \to Q(L, E), \qquad N \to L,$$

$$E_1 \to \frac{h}{2}, \qquad H \to \mu E \equiv \frac{u_0}{\beta}. \tag{10.27}$$

Applying these substitutions and from Eq. (2.14) of [47], we obtain

$$Q(L, E) = \exp\left(-\frac{\beta h}{2}(L-1)\right)Z_{1,N}^F$$
$$= f^{(L-1)/2}[\lambda_+^{L-1}\{\cosh u_0 + (\sinh^2 u_0 + f)(\sinh^2 u_0 + f^2)^{-1/2}\}$$
$$+ \lambda_-^{L-1}\{\cosh u_0 - (\sinh^2 u_0 + f)(\sinh^2 u_0 + f^2)^{-1/2}\}], \tag{10.28}$$

where $f \equiv \exp(-\beta h)$, and

$$\lambda_\pm \equiv f^{-1/2}[\cosh u_0 \pm \sqrt{\sinh^2 u_0 + f^2}],$$
$$= f^{-1/2}[\cosh u_0 \pm \sqrt{\cosh^2 u_0 - (1-f^2)}]. \tag{10.29}$$

Substituting (10.29) into (10.28) results in the same expression of (10.18) for $Q(L, E)$.

Discussions

In principle, analytical solutions for the simplified discrete model given by (10.16) can also be evaluated explicitly for the 2D ($q = 1$) case—a task that remains to be done. Other physical quantities such as $\bar{n}$ and χ can then be calculated from the partition function as is done in the 1D case.

The assumption that $\gamma = \gamma' = 0$ means that the interactions among molecules are ignored and the result shows no phase transition. If necessary, the influence of the other molecules on a single molecule can be treated using the mean field approximation. For this purpose, the same formulation described above can be used; we simply replace E by $E + aP$, where a is a proportional constant and P is the polarization, the order parameter. The existence of phase transitions can indeed be obtained this way, or by an alternative approach which maps the problem to a quantum mechanical differential equation [27] (see Section 10.4.2).

10.4.2 The Worm-Like Model for Bowlic Nematic Polymers

In the worm-like model [27], the main-chain polar polymer molecule is assumed to be like a worm, influenced by other molecules through a self-consistent mean field. The functional integral technique is used to describe the orientational distribution of the tangent to the polymer, and the problem is mapped into a diffusion equation of a particle on the surface of a unit sphere in a dipolar mean field.

Specifically, the bending of the chain will cost an energy

$$\int_0^L \frac{\varepsilon}{2}\left[\frac{d\mathbf{u}(s)}{ds}\right]^2 ds, \tag{10.30}$$

where ε is the bending constant, L is the length of the polymer, and $\mathbf{u}$ is the tangent unit vector along the chain at arclength s. The interaction in the polar polymer is assumed to be dominated by the first rank $P_1(\cos\theta)$-type potential, instead of the second rank $P_2(\cos\theta)$-type as in conventional liquid crystal polymers [48,49]. Here θ is the angle between a polymer segment and the director in the nematic phase. Let us assume that the semiflexible chains in the polymer favor a long-range order of parallel alignment. After summing along the chain, the dipolar potential in the mean field approximation is given by

$$U_q = -\int_0^L b\bar{P}_1 P_1(\cos\theta)\, ds, \tag{10.31}$$

where b is the coupling constant and is positive in this case, P_1 is the first Legendre polynomial, and $\bar{P}_1$ is the polar nematic order parameter given by

$$\bar{P}_1 = \frac{1}{L}\left\langle \int_0^L ds\, P_1(z)\right\rangle. \tag{10.32}$$

As shown in [27], for a uniaxial system, $\bar{P}_1$ can be calculated from the Green function G such that

$$\bar{P}_1 = \int_0^L \frac{ds}{L} \frac{\iiint dz\, dz'\, dz''\, G(z', z; L, s)G(z, z''; s, 0)P_1(z)}{\iiint dz\, dz'\, dz''\, G(z', z; L, s)G(z, z''; s, 0)}, \tag{10.33}$$

where $z = \cos\theta$, and

$$G(\theta, \theta'; s, s') = \sum_{n=0}^{\infty} \psi_n(\theta)\psi_n(\theta')\exp(-\lambda_n D|s - s'|), \tag{10.34}$$

where the eigenfunction $\psi_n(\theta)$ is given by

$$\left[\lambda_n + \frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right) + gP_1(\cos\theta)\right]\psi_n(\theta) = 0, \tag{10.35}$$

with $g \equiv \beta b\bar{P}_1/D = 2P_1/\tilde{T}^2$; the reduced temperature $\tilde{T} \equiv kT/(b\varepsilon)^{1/2}$ and $\beta \equiv 1/kT$. Here λ_n is the eigenvalue and D^{-1} is the persistence length.

A perturbation calculation near the polar nematic–isotropic phase transi-

tion gives

$$\bar{P}_1 = \alpha\tilde{T}^2(1 - \tfrac{3}{2}\tilde{T}^2)^{1/2}, \tag{10.36}$$

where $\alpha = (\tfrac{45}{2})^{1/2}$, and the transition temperature for an infinite chain $\tilde{T}_c = (\tfrac{2}{3})^{1/2} = 0.816$. For a finite chain of length L

$$\tilde{T}_c(L) = \tilde{T}_c\left[1 - \frac{1}{2LD}(1 - \exp(-2LD))\right]. \tag{10.37}$$

The term in square brackets is actually equal to $\langle R^2\rangle/(LD^{-1})$, the ratio of the mean square dimension of the polymer to its value when L is infinite in the isotropic state.

In the strong nematic limit, either at low temperature or with a strong polar potential, an asymptotic calculation gives

$$\bar{P}_1 = \tfrac{4}{3}\cos^2\left[\tfrac{1}{3}\cos^{-1}\left(-\frac{3\sqrt{3}}{4}\tilde{T}\right)\right]. \tag{10.38}$$

Equations (10.37) and (10.38) compare pretty well with the numerical results [27], as shown in Fig. 10.12.

For a 2D system such as in thin polymer films or in Langmuir films, the problem can be solved exactly [50]. In 2D, (10.35) becomes

$$\left(\frac{d^2}{d\theta^2} + g\cos\theta + \lambda_n\right)\psi_n(\theta) = 0. \tag{10.39}$$

Under the transformations $\Lambda_n = 4\lambda_n$, $q = 2g$, and $\xi = (\pi - \theta)/2$, (10.39) be-
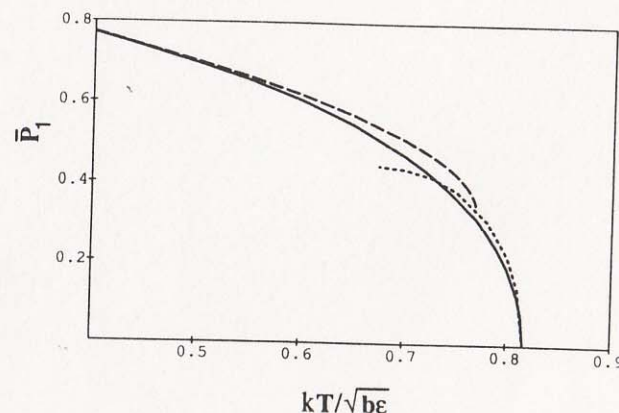

FIGURE 10.12. The order parameter $\bar{P}_1$ as a function of the reduced temperature $\tilde{T}$. The dotted and dashed lines represent the perturbation and asymptotic results, respectively. The solid line is the numerical result [27].

comes the Mathieu equation

$$\left\{\frac{d^2}{d\xi^2} + [\Lambda_n - 2q\cos(2\xi)]\right\}\psi_n(\xi) = 0. \tag{10.40}$$

The lowest eigenvalue Λ_0, in a power series of q, is approximately given by

$$\Lambda_0 = -\frac{1}{8}q^2 + \frac{7}{512}q^4, \tag{10.41}$$

which contributes to the free energy for the long chain

$$F/(kTLD) = \lambda_0 + \frac{\bar{P}^2}{\tilde{T}^2}, \tag{10.42}$$

where the second term on the right-hand side arises from the mean field theory. Consequently, we obtain a Landau form of the free energy

$$F/(kTLD) = \frac{1}{16}(\tilde{T}^2 - 2)q^2 + \frac{7}{512}q^4$$
$$= (\tilde{T}^2 - 2)\frac{\bar{P}_1^2}{\tilde{T}^4} + \frac{7}{2}\frac{\bar{P}_1^4}{\tilde{T}^8}, \tag{10.43}$$

where k is the Boltzmann constant. Note that there is no cubic term. Conse-
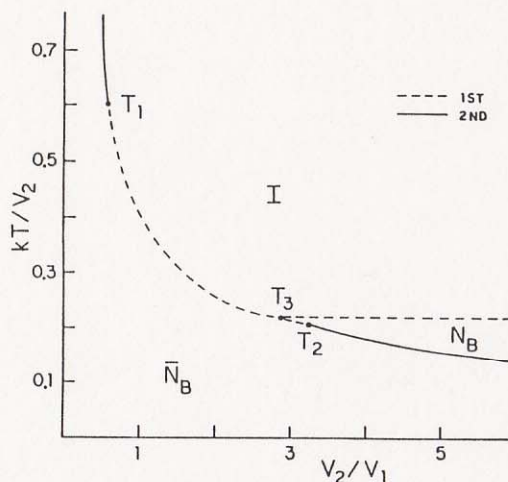

FIGURE 10.13. Phase diagram of bowlic monomers. I represents the isotropic liquid phase, N_B the nonpolar nematic phase, and $\bar{N}_B$ the polar nematic phase. T_1 and T_2 are tricritical points and T_3 is a triple point. The intermolecular interaction potential is given by $V_{ij} = -V_1 P_1(\cos\theta_{ij}) - V_2 P_2(\cos\theta_{ij})$, with $V_1 > 0$ and $V_2 > 0$. Columnar phases are not included [21]. A similar phase diagram is expected for bowlic polymers.

quently, the polar nematic–isotropic phase transition, in 2D here as in 3D above, is second order. The temperature dependence of the coefficient of the $\bar{P}_1$ terms gives the transition temperature $T_c = \sqrt{2}$. Minimizing F with respect to $\bar{P}_1$ gives

$$\bar{P}_1 = \sqrt{2/7}\,\tilde{T}^2(1 - \tilde{T}^2/2)^{1/2}. \tag{10.44}$$

Electric field effects are also discussed in [27]. Expressions for the susceptibility χ are obtained; the critical exponent γ equals 1, as expected for a mean field theory; and the order parameter is given numerically. For a polar polymer, giant dielectric response is possible. Finally, when both P_1 and P_2 interactions are allowed, we expect a phase diagram similar to that given by Leung and Lin [21] for bowlic monomers. The phase diagram contains two tricritical points and one triple point, and two types of bowlic nematics (polar and nonpolar) in addition to the isotropic liquid phase (Fig. 10.13). See [27] for further discussion.

10.4.3 Ultrahigh T_c Bowlic Superconductors

In the past few years there has been tremendous progress in raising the transition temperature T_c of superconductors [51] (see Fig. 10.14). The discovery of the high T_c superconducting copper oxides [52] was followed by that of the superconducting fullerenes [53].

As shown in Fig. 10.14, while the highest T_c of the molecular superconductors is still behind that of the cuprates, the rate of progress of the two categories are comparable. Historically, development of organic superconductors was prompted by the theoretical study of Little [54]. With the con-
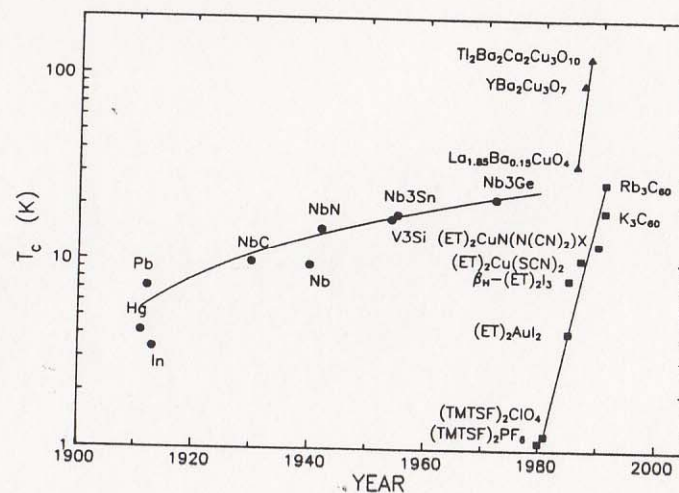

FIGURE 10.14. Progress of superconductivity over the century in metallic, cuprate, and molecular superconductors [51].

ventional phonon-mediated mechanism replaced by the excitonic mechanism, Little predicted that the superconducting T_c can be raised to greater than 1000 K (see [25]). The problem with this scheme is that the proposed molecules are very difficult, if not impossible, to synthesize; more importantly, even if they were synthesized there is no guarantee that they will stack up to form a 1D or a quasi-1D filament, as required by the theory.

To overcome these problems and with the excitonic mechanism in mind, ultrahigh T_c bowlic superconductors were proposed by Lam [24]. (The scheme should also work for the discotics, but the chance is higher in the bowlics [24,25]. See also [55].) The idea is that in the bowlic columnar phase, the columns are already there and they are empty tubes. We can then add metal (e.g., Cu) or transition metal atoms into the tubes by doping. Alternatively, we may actually attach such atoms to the centers of the bowlic molecules (as has been done successfully in the rodics and discotics). Either way, when the conditions are right we will have conducting or superconducting bowlic mesophases or crystals [25]. In the case of bowlic polymers shown in Fig. 10.8(e), the addition of metal or transition metal into the tubes will turn the polymer into a system with an infinite number of useful layers, which tends to raise further the superconducting T_c as demonstrated recently in the case of $(Sr_{1-x}Ca_x)_{1-y}CuO_2$ with a T_c of 110 K [56]. See [24,25] for more specific discussion.

10.5   Conclusions

Since the prediction of bowlics [5] three types of bowlic monomers have already been synthesized (see Table 10.1). The existence of the sign change of optical anisotropy with temperature [11] is a property unique to the bowlics but not to the discotics. On the other hand, when nematic and cholesteric discotics are found experimentally the same cannot be said for the bowlics. Maybe what is needed is new bowlic molecules with shallower bowls; this will lessen the tendency of the molecules to form columns, and encourage them to be separated from each other as required in the nematic or cholesteric phases. Note that lyotropic nematics bowlics seem to exist [15].

Ordinary polar molecules tend to form dimers due to the dipole–dipole interaction, but in the case of bowlics the steric effect will be able to overcome this. Consequently, bowlic (polar) nematics may be the *only* kind of ferroelectric liquid possible. And once existing, these bowlic nematics can be used for very fast electrooptical displays or switches. In view of these very important basic and applied interests, there is no doubt in our mind that further synthesizing effort is worthwhile.

Compared to the search for bowlic nematics, the task of synthesizing bowlic polymers is much more straightforward—the monomers are already there. Bowlic nematic polymers are in fact easier to form [27], and they could be stronger than the Kevlar.

It should be emphasized that, apart from the great interest in their liquid crystalline properties, the bowlics in bulk or as a Langmuir film can serve as a useful and novel physical system in the study of dynamical instabilities and pattern formation [10], such as those found in ferromagnetic liquids [57]. Hollow cage molecules, with or without foreign atoms inside the cages, can be formed with bowlic molecules as the building blocks, similar to the speleands and cryptophanes formed with one or two cyclotriveratrylenes [28].

Finally, unlike the rodics and discotics which were actually found or studied well before 1888 and 1977, the official dates of discoveries, respectively [58], we believe that bowlics are completely new and modern. In fact, they are so new that the measurement of their physical properties—be it viscosity, density, acoustical, optical, dielectric, or magnetic—has hardly started. Very exciting work in bowlics, including the search for ultrahigh T_c superconductors, awaits the experimentalists in physics, chemistry, and materials science. Furthermore, as happened in the case of bowlic monomers, theory is once again ahead of experiment in the study of bowlic polymers.

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