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Introduction

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1.1 Historical Background

Liquid crystals are so named because the original pioneers, particularly Friedrich Reinitzer and Otto Lehmann, observed fluids which exhibited what they interpreted as crystalline properties [1]. After some years it became clear that these materials were all optically anisotropic. Hitherto all optically anisotropic materials had indeed been crystalline, but nevertheless, in principle, the properties of anisotropy and of crystallinity could be regarded as distinct.

Until the discovery of liquid crystals, optical anisotropy had been regarded as a function of crystal structure, and was often regarded as part of the study of optical mineralogy. By anisotropy we mean that the velocities of light waves in a particular direction depend on the polarisation of the waves. An alternative way of considering this is to note that a light beam incident on an anisotropic material is usually split into two beams inside the material; the material is said to be doubly refracting or birefringent. From far away, the rather dramatic manifestation of this phenomenon is the appearance of two different images of the same object when viewed through a slab of such a material. When a beam is viewed through a smaller birefringent slab, the two beams may still overlap when they exit the sample. Then the two beams can interfere destructively after exiting the slab. In non-monochromatic beams (i.e. usually), the consequence will be bright interference fringes. Historically speaking, birefringent media were traditionally divided into two categories, known as uniaxial and biaxial, which we now briefly describe.

Of these the uniaxial media were rather simpler. The crystals exhibit trigonal, tetragonal or hexagonal symmetry [2]. All such materials possess a single optical axis, which is also an axis of symmetry for the

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crystal. The origin of the term uniaxial comes from this one axis. In general optical propagation in any given direction inside a uniaxial material divides itself into ordinary and extraordinary beams. The velocity of the ordinary waves is determined by components of the dielectric tensor in the plane perpendicular to the optical axis. Only the propagation of the extraordinary wave is affected by the dielectric component in the optical axis direction. The ordinary and extraordinary beams correspond to eigenmodes of Maxwell's equation for propagation in the direction in question. The key property of a uniaxial medium is that there is a single direction – the optical axis – along which the velocities of light with perpendicular polarisations are equal. In this case the two different optical eigenmodes become degenerate.

When we compare the optical properties of biaxial crystalline materials with uniaxial materials, we find that there are now two different axes along which the light velocity is polarisation independent. It is the existence of these two optical axes which is the origin of the term biaxial. This behaviour appears in crystal structures of monoclinic, triclinic and orthorhombic types [2–4]. The dielectric properties of the crystal structures do of course possess three distinct principal axes, which correspond to symmetry axes of the crystal, if they exist. But the optical axes do not lie along any of these principal axes, but rather lie in the plane of the largest and smallest relevant dielectric tensor component, with the principal axes bisecting the optical axes [5]. Thus, strangely, in the context of the fundamental tensor material properties, a uniaxial material has one special axis, whereas a biaxial material, notwithstanding its name, has three. We further note that even if a material is not crystalline, it will possess locally a dielectric tensor, with principal axes, and hence local optical axes.

To be mathematically precise, the existence of optical birefringence is associated with a dielectric constant $\boldsymbol{\epsilon}$ with principal axis form:

$$\boldsymbol{\epsilon} = \begin{pmatrix} \epsilon_{xx} & 0 & 0 \\ 0 & \epsilon_{yy} & 0 \\ 0 & 0 & \epsilon_{zz} \end{pmatrix}. \tag{1.1}$$

In an optically isotropic medium $\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz}$. In a uniaxial medium two of these are equal (conventionally $\epsilon_{xx} = \epsilon_{yy} \neq \epsilon_{zz}$), while in a biaxial medium all three components are different: $\epsilon_{xx} \neq \epsilon_{yy} \neq \epsilon_{zz}$.

As a matter of observation, it appeared for many years that all liquid crystals were optically uniaxial. Of course, as fluids rather than solids, the symmetry of the system would be $D_{\infty h}$ rather than, for example, D_{6h} (in the case of a hexagonal crystal), but from an optical point of view this would not be crucial. Although liquid crystalline materials, in principle, exhibit relatively simple optical anisotropy properties, as is well-known, it is often difficult to prepare well-aligned samples. As a result, light passing through a liquid crystalline medium may undergo repeated scattering as the local dielectric tensor changes, leading to the characteristic turbid appearance of a liquid crystal. Alternatively, one may observe brightly coloured textures.

Phases have historically been recognised in the microscope by these characteristic textures. These textures are a consequence of the the patterns of the alignment discontinuities, which are themselves a statistical mechanical property of the phase in question. For example, the nature of the smectic C phase, first observed in 1959 by Arnold and Sackmann [6], excited much debate, for the textures included Schlieren textures characteristic of the nematic phase in addition to the focal conics and fans associated with the smectic layers. However, Arora, Fergason and Saupe [7] were able to align the smectic layers. It was then possible for Taylor, Fergason and Arora [8], using a conoscopic method that we will discuss further later in this chapter, to show that the resulting phase was optically biaxial.

This experiment was the key to understanding the smectic C phase as a layered phase with the director tilted with respect to the layer normal. The symmetry of this phase is such as to distinguish in an essential way three different axes, later conventionally labelled [9] as $\mathbf{a}$, the unit vector normal to the layers, $\mathbf{c}$, the projection of the director onto the plane perpendicular to the layers, and $\mathbf{b} = \mathbf{a} \times \mathbf{c}$.

However, the biaxiality of the smectic C liquid crystal phase is, in some sense, a derivative property, which arises as a consequence of the interaction between the layers and the tilt. Smectic C phases retain some one dimensional crystalline order. In crystalline phases the birefringence – whether uniaxial or biaxial – is

an orientational property which follows as a result of the crystalline order, rather than a primary property of the phase itself. By contrast, in the nematic liquid crystal phase the birefringence follows directly from the $D_{\infty h}$ point symmetry of the phase itself. Although the smectic C only exhibits, so to say, a secondary optical biaxiality, it does beg the question of whether materials exist which are at the same time homogeneous and optically biaxial. These would be the biaxial analogue of the uniaxial nematic phase. In the simplest case, the phase would possess D_{2h} point symmetry, and be the natural liquid crystalline analogue of orthorhombic crystals. This was the question posed in a pioneering paper by Marvin Freiser in 1970 [10].

In this book we shall follow the scientific narrative, and discuss the present state of play, of the search for the biaxial nematic phases whose existence was first conjectured by Freiser more than forty years ago. The topic is scientifically peculiar, in that more of the early running has been made by theorists rather than by experimentalists. The projected biaxial phase turned out to be of great interest to theorists of a variety of different backgrounds. This was surely, at least in part, because the mathematics provided a playground for methods developed and previously practised in simpler cases. But, in addition, experimentalists were attracted partly because of the challenges of synthesising molecules of sufficient complexity to sustain a biaxial phase, and partly because even the act of recognising a biaxial phase turned out to be a greater challenge than one might at first think. As a final touch, more recently it has also been proposed that biaxial phases might be employed in optoelectronic devices because such materials might switch quickly.

1.2 Freiser Theory

Freiser [10] was the first to try to extend ideas first introduced in the theory of uniaxial liquid crystal phases to study more complex phases. The standard molecular paradigm for the statistical physics of the uniaxial nematic liquid crystal phase is, of course, the Maier–Saupe theory [11]. This theory balances the entropically-induced free energy cost of an orientationally ordered phase against the energy gain following as a result of molecular order. Freiser noted that although the Maier–Saupe theory supposes cylindrical molecules, in fact most organic nematogens are formed from molecules which are elongated but flat. Formally speaking, the energy interaction would presumably be minimised if the molecules were fully aligned, and this would necessarily involve a degree of biaxial order. By interpolating rather hopefully between the high temperature isotropic and low temperature biaxial regimes, he suggested that, with decreasing temperature, we might see, successively, isotropic, uniaxial nematic and biaxial nematic phases (as well as possible biaxial smectic phases). The paper was more suggestive than definitive. The use of the theory developed by Saupe in his doctoral work was of some significance, for as it would turn out Alfred Saupe would make profound experimental contributions to the field.

Freiser's theory writes down a formal expression for the molecular field potential energy, and a further expression for the orientational entropy, thus enabling him to derive a Helmholtz free energy due to orientation. The theory uses only two order parameters, essentially denoting the ordering of the principal molecular direction. Freiser was not able to solve the molecular field theory he had formulated; at that time computational solution of self-consistent equations was still regarded as a tour de force! So he resorted to a Landau expansion of slightly questionable mathematical validity, and concluded that a biaxial nematic phase was, in principle, possible. The lack of rigour is not important; what is important is that the problem had been posed and some key concepts exposed.

In the years that followed Freiser's paper there was a large amount of effort to elucidate the properties of hypothetical biaxial phases. There were three complementary paradigms for the molecular statistical mechanics of uniaxial liquid crystal phases. The Maier–Saupe [11] theory focussed on an effective molecular field in thermotropic materials, the Onsager theory on rigid bodies in lyotropic materials [12], while the Flory

theory is a lattice theory of polymers [13]. Each of the viewpoints was extended to provide insight into biaxial nematic phases. In addition much insight into the isotropic-uniaxial nematic phase transition has been obtained using de Gennes's [14] Landau theory.

1.3 Nematic Order Parameters

Describing orientational order in a complex fluid phase, when the molecular symmetry and the phase symmetry are given (but not necessarily the same), is by necessity complicated. We need to specify, for each phase, not only how many order parameters are necessary for a complete description, but also what are their transformation properties under rotation of both molecular and laboratory frames. Then there is the question of the most convenient language in which to describe these quantities, as the transformations mean that the descriptions are not unique. In Chapter 2, Luckhurst gives an overview of this problem. Here we shall give a brief historical and heuristic introduction, which will serve to set the scene.

The first important theoretical advances were made by Alben and colleagues [15] and by Straley [16], who realised that in order to parameterise a biaxial phase correctly, at least four second-order scalar order parameters are necessary. We define these using molecular axes (x, y, z), and laboratory axes (X, Y, Z). The usual uniaxial nematic order parameter, in a phase with $D_{\infty h}$ symmetry, is

$$S = Q_{zz}^{ZZ}\,\langle P_2(\mathbf{Z}\cdot\mathbf{z})\rangle = \frac{1}{2}\langle(3(\mathbf{Z}\cdot\mathbf{z})^2 - 1)\rangle, \tag{1.2}$$

where $\mathbf{z}$ is a unit vector along the principal molecular axis, $\mathbf{Z}$ is a unit vector along the director (i.e the axis of symmetry for the phase), P_2 is the second Legendre polynomial, and angular brackets indicate taking mean values over molecules. In this phase the perpendicular laboratory axes (X, Y) are not distinguished.

The quantity Q_{zz}^{ZZ} may be regarded as an element of a *supertensor* [17], defined by

$$Q_{ij}^{KL} = \frac{1}{2}\langle(3(\mathbf{i}\cdot\mathbf{K})(\mathbf{j}\cdot\mathbf{L}) - \delta_{ij}\delta_{KL})\rangle, \tag{1.3}$$

where $\delta_{ij} = 1(i = j); 0\ (i \neq j)$ is the usual Kronecker delta.

If the molecules in the uniaxial phase also possess $D_{\infty h}$ (i.e. cylindrical) symmetry, as they do in simple models of uniaxial nematics, then in addition, the molecular axes (x, y) are not distinguished. The conditions of uniaxial molecules and phase, as well as the conditions of traceleness in both laboratory and molecular frames, constrain the supertensor elements considerably. For example, reflection symmetry implies that many off-diagonal terms are zero.

However, if the molecules are biaxial and possess D_{2h} symmetry, for example, then even in a uniaxial nematic phase the molecular axes (x, y) will be inequivalent, implying (in general) the existence of a *molecular biaxiality*

$$D = Q_{xx}^{ZZ} - Q_{yy}^{ZZ} = \left\langle \frac{3}{2}\left((\mathbf{x}\cdot\mathbf{Z})^2 - (\mathbf{y}\cdot\mathbf{Z})^2\right)\right\rangle. \tag{1.4}$$

This order parameter is zero in the isotropic phase, and in the uniaxial nematic phase would be zero if the two molecular axes were identical. Interestingly, even without the benefit of a complex calculation it is clear that (at least in a sensible frame of reference) D will tend to zero at sufficiently low temperatures, for then the molecules will all be lined up with their z axes in the Z direction (i.e. $\langle(\mathbf{Z}\cdot\mathbf{z})^2\rangle \to 1$, and hence both $\langle(\mathbf{x}\cdot\mathbf{Z})^2\rangle, \langle(\mathbf{y}\cdot\mathbf{Z})^2\rangle \to 0$.

The biaxial phase, in which we may suppose, without loss of generality, that molecular x, y axes align respectively with laboratory X, Y axes, then requires two further order parameters. One of these, roughly speaking, characterises how the principal molecular $\mathbf{z}$ axis differentiates between the $\mathbf{X}$ and $\mathbf{Y}$ axes, and one

of which is more directly linked to the degree of orientational order of the minor axes. The *phase* biaxiality is then defined by:

$$P = \left(Q_{zz}^{XX} - Q_{zz}^{YY}\right) = \left\langle \frac{3}{2}\left((\mathbf{X}\cdot\mathbf{z})^2 - (\mathbf{Y}\cdot\mathbf{z})^2\right)\right\rangle . \tag{1.5}$$

This definition has some analogies to the definition of D, and in spherical harmonic language the analogy is closer because all that is required is the interchange of two Euler angles. But it is nevertheless clear that P is non-zero only in a biaxial phase. However, an important analogy with D holds good; the increasing molecular alignment at low temperatures also drives $P \to 0$ at low temperatures. So in some sense it must be regarded as an auxiliary order parameter for the biaxial phase. A more central order parameter, however, is the quantity C, defined by:

$$C = \frac{1}{3}\left(\left(Q_{xx}^{XX} + Q_{yy}^{YY}\right) - \left(Q_{yy}^{XX} + Q_{xx}^{YY}\right)\right) = \left\langle \left((\mathbf{X}\cdot\mathbf{x})^2 + (\mathbf{Y}\cdot\mathbf{y})^2 - (\mathbf{X}\cdot\mathbf{y})^2 - (\mathbf{Y}\cdot\mathbf{x})^2\right)\right\rangle . \tag{1.6}$$

This order parameter is zero in a uniaxial nematic phase, for then the laboratory X and Y axes are equivalent. It is always non-zero in a biaxial phase. In particular, when the system is perfectly ordered, we might suppose that the molecular x, y axes lie exactly along the laboratory X, Y axes respectively, and then at low temperatures $C \to 1$. Here we have introduced the apparently irrational factor of $\frac{1}{3}$, specifically in order to enforce this condition; perfect ordering often is associated with a unit order parameter in statistical mechanics.

Subsequent authors working in the field have agreed on the importance of the order parameters defined in eqs (1.2–1.6). However unfortunately they have approached the problem from a number of different viewpoints. The picture presented above uses a Cartesian point of view. But many authors have preferred a Wigner matrix representation, and indeed this is the natural extension of the traditional expansion of the nematic order parameter in terms of spherical harmonics. One consequence is that in the literature there has been no agreement on the nomenclature S, D, P, C, nor on the factors appearing in front of the analogous quantities. A comprehensive review has been made by Rosso [18].

1.4 Nematic Tensor Order Parameters

The viewpoint taken in the last section has emphasised the quadratic scalar order parameters, which may be regarded as key figures of merit in a discussion of biaxial nematic phases. But, of course, the true order parameter is a tensor quantity. For any given symmetry, we can use either a Wigner (i.e. spherical harmonic) or a Cartesian language to develop the invariance properties correctly.

The classical Landau–de Gennes theory [14] uses an expansion of the free energy in terms of a nematic Cartesian tensor Q_{ij}. From a macroscopic point of view this can be identified with an observable, and related, for example, to the dielectric tensor:

$$Q_{ij} = c\left(\epsilon_{ij} - \frac{1}{3}\mathrm{Tr}(\boldsymbol{\varepsilon})\delta_{ij}\right), \tag{1.7}$$

where c is some constant whose magnitude is unimportant. If we suppose that the molecules are more or less rigid (more often the case in theoretical models than in real life!), as well as cylindrically symmetric about a molecular axis, then the tensor Q_{ij} can be identified with a orientational order parameter:

$$Q_{ij} = \frac{1}{2}\langle 3l_i l_j - \delta_{ij}\rangle, \tag{1.8}$$

where $\mathbf{l}$ is a unit vector pointing along the (unique) molecular axis, and which we can identify with the z axis of the more complex biaxial molecule. In a principal axis frame, we can rewrite this symmetric

traceless object as

$$\mathbf{Q} = \begin{pmatrix} -\frac{1}{2}S + \frac{3}{4}U & 0 & 0 \\ 0 & -\frac{1}{2}S - \frac{3}{4}U & 0 \\ 0 & 0 & S \end{pmatrix}. \tag{1.9}$$

In a general frame of reference the five independent components of $\mathbf{Q}$ can be thought of as equivalent to three Euler angles (i.e. numbers which define the required rotation to the principal axis frame) and the two independent scalars which appear in eq. (1.9).

A biaxial liquid crystal indeed possesses a tensor with three different eigenvalues, and hence is specifically associated with a biaxial $\boldsymbol{\epsilon}$. However, the description in terms of the tensor Q_{ij} is incomplete, because D, C do not appear. Thus restricting the treatment to the tensor Q_{ij} clearly omits some crucial physics, notwithstanding de Gennes's insistence that he is following the Landau tradition and using "measurable" quantities. In fact it turns out that there is another tensor associated with the orientation of the X and Y molecular axes, which contains D and C, and which completes the picture [19].

A more general picture might wish not only not to favour any laboratory axes, but also not to favour any molecular axes either, for in general the molecules under consideration will surely only approximately possess D_{2h} symmetry. The proper definition of the molecular x, y, z axes will be a matter of convention. The normal convention is that $Q_{zz}^{ZZ} > Q_{xx}^{XX} > Q_{yy}^{YY}$, for the z axis will be the major axis carrying the strongest intermolecular orientational ordering.

This point of view requires the definition of the ordering *supertensor*:

$$Q_{ij}^{IJ} = \frac{1}{2}\langle 3(I \cdot i)(J \cdot j) - \delta_{IJ}\delta_{ij}\rangle, \tag{1.10}$$

where I, J are laboratory axis labels, i, j are molecular axis labels, and these labels double as unit vectors in the appropriate direction. The supertensor can be freely rotated (independently) in the laboratory and molecular frames. This object in principle contains 81 elements, which under suitable circumstances will reduce to the S, D, P, C set discussed above. However, the advantages conferred by the generality – necessary in a system lacking molecular symmetry – may be weighed against the cumbersome formalism.

Order parameters can also be defined in terms of elements of the Wigner matrix:

$$D_{mn}^{L}(\Omega) = e^{-m\alpha} d_{mn}^{L}(\beta) e^{-n\gamma}, \tag{1.11}$$

where Ω is an angular rotation from a fixed frame of reference defined by Euler angles (α, β, γ) [20–22],and the quantities $d_{mn}^{L}(\beta)$ are the so-called reduced or small Wigner matrices. The order parameters S, D, P, C can then be expressed in terms of $\langle D_{mn}^{L}\rangle$ with $L = 2$, and m, n even or zero. This picture reduces to a spherical harmonic representation for molecules and phases with cylindrical symmetry.

1.5 Theoretical Phase Diagrams

Molecular field analyses of biaxial phase diagrams are presented in the articles by Virga, who discusses general aspects of molecular field theory in Chapter 3, and by Masters, whose discussion focusses on hard particles (Chapter 4). But it is worthwhile, even at this early stage, to give an outline of some key concepts and results. These have shaped expectations of what phase diagrams were likely to be observed, and what signatures to look for in a search for possible biaxial phases. One key question concerns how to parameterise the molecular biaxiality. Three different strategies seem to give qualitatively similar results.

Firstly, Shih and Alben [23] employ a Flory-type lattice model strategy (see ref. [13]), in which the molecules are larger than the individual lattice sites. The model can then allow molecules to take length L,

breadth B and width W, and forbids molecular overlap. The liquid crystalline behaviour is sterically induced, and the biaxiality results from the inequality of B and W.

A second approach was adopted by Straley [16], who used a model with with an orientationally-dependent intermolecular potential, which was solved in a molecular field approach. The interactions, also repulsive, were parameterised using an expansion in terms of basis functions whose mean values are the order parameters given by eqs (1.2, 1.4 –1.6); the solid angle Ω is now the relative orientation of the molecules. In order to give some physical feel for what would otherwise be a formal mathematical model, the ratios of the coefficients are motivated by an Onsager-like picture of the effective interaction energy due to volume exclusion between rectangular blocks. Once again explicit biaxiality involves the condition $B \neq W$. An interesting feature of the model is that, in general, there are two measures of the relative biaxiality.

A third approach was used by Boccara, Mejdani and de Seze [24], who solved what one might now consider as an infinite-range version of the standard liquid crystal lattice model of Lebwohl and Lasher [25]. On each lattice site α is a molecule associated with a tensor, which in its principal axis frame takes the form

$$q_{ij}^{\alpha} = q \begin{pmatrix} 1+\varepsilon & 0 & 0 \\ 0 & 1-\varepsilon & 0 \\ 0 & 0 & 2 \end{pmatrix}. \tag{1.12}$$

The Hamiltonian is then of the form

$$\mathcal{H} = -\frac{J}{2N} \sum_{\alpha\beta ij} q_{ij}^{\alpha} q_{ij}^{\beta}, \tag{1.13}$$

where the sum is taken over all sites $\alpha \neq \beta$, there are $N \to \infty$ sites, and the factor of $\frac{1}{N}$ in the sum is included to ensure that the energy is an extensive quantity.

In this approach there is an infinite range potential with a (reduced) interaction between all molecules in the system. In this case the usual molecular field result for the energy, given by eq. (1.13), is exact. But the infinite-range model may be regarded as a calculational convenience to avoid worrying about fluctuations at the phase transition while extracting the main features of the phase diagram. The energy is minimised if all local principal axis frames are aligned, and this corresponds just to a biaxial nematic state. The degree of molecular biaxiality evidently corresponds to the parameter ε, and we can identify

$$\epsilon = \frac{\epsilon_{xx} - \epsilon_{yy}}{\epsilon_{zz}} \tag{1.14}$$

where ϵ_{ii} are the principal axis components of the dielectric tensor $\boldsymbol{\epsilon}$ in the molecular frame. Subject to suitable rescalings, and restricting the sum to nearest neighbours, in the limit $\epsilon \to 0$ the model reduces to that of Lebwohl and Lasher [25], and the result to the classical molecular field theory of Maier and Saupe [11]. The phase diagram resulting from this calculation is shown in Figure 1.1, and leads to a maximum relative biaxiality at $\epsilon = 1$.

A number of common properties appear to emerge from these distinct studies. One is that in general Freiser's conjectures were more or less correct. In particular:

(i) As temperature is reduced, there is indeed in general a first-order phase transition from the isotropic to the uniaxial nematic phase, followed by a continuous transition from the uniaxial to the biaxial nematic.
(ii) As the degree of molecular biaxiality is increased, the first-order uniaxial nematic–isotropic phase transition becomes less pronounced [26, 27]. In particular, the entropy jump reduces, the nematic response at the phase transition to magnetic or electric field increases, and the implicit critical point T^* below the phase transition approaches the actual phase transition T_{NI} [27, 28].
(iii) The region over which the uniaxial nematic phase is stable reduces, with the uniaxial–biaxial phase transition temperature $T_{\mathrm{N_B N_U}}$ rapidly increasing as a function of molecular biaxiality.

(iv) If the biaxiality parameter is increased by a sufficiently large amount, it is as though two axes in the molecules have been exchanged. In the model of Boccara *et al*., this occurs at $\epsilon = 1$, and the molecular x and z axes are exchanged. The molecules are then again completely uniaxial, and the low temperature phase is uniquely uniaxial, but aligns the molecular x axes, rather than the molecular z axes.

(v) If the biaxiality parameter is not quite large enough to exchange the axes, there is some mirror symmetry in the model, in that the same succession of phases takes place as when there is low degree of molecular biaxiality. Some workers have regarded this as exchanging rods with discs (or prolate ellipsoids with oblate ellipsoids), although in our view sometimes this involves pushing the interpretation of the model rather further than is completely justified. In this regime $1 < \epsilon < 2$, the uniaxial phase aligns the molecular x axes, but for the biaxial phase (as in the $0 < \epsilon < 1$ case), all three molecular axes are aligned.

(vi) There is a single unique critical value of the biaxiality parameter at which the uniaxial phase disappears. At this point, known as a *Landau point* in statistical mechanics, there is a direct continuous transition to a biaxial phase. The Landau point and the biaxial phase separate completely the two different uniaxial phases from each other. In the Boccara *et al*. model, this occurs at $\epsilon = 1$.

More recent work, discussed in more detail by Virga in Chapter 3, will show that this picture is incomplete. The model of Luckhurst and Romano [29], for example, requires *two* biaxiality parameters. The specific calculations of Luckhurst and Romano gave rise to a phase diagram resembling that of Boccara *et al*. But other work, in particular by the Virga school (see e.g. [30]) gives a qualitatively different phase diagram, in which the Landau point is replaced by a line of first-order transitions between the isotropic and biaxial nematic phases.

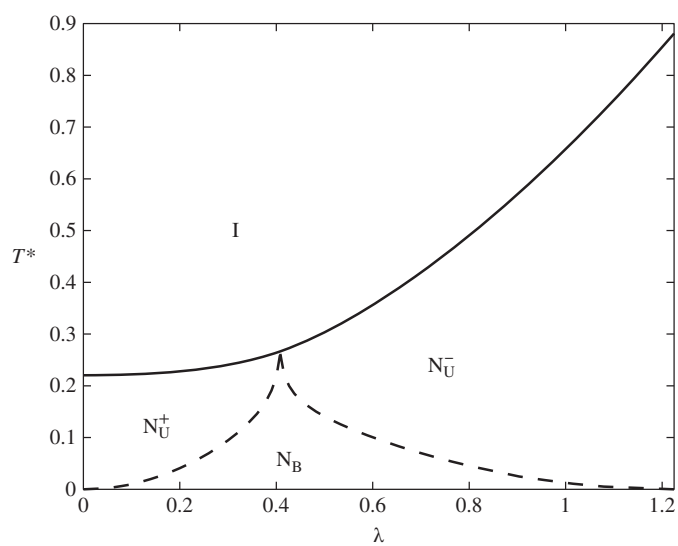

Figure 1.1 *Liquid crystal phase as a function of scaled temperature T^* and biaxiality, as calculated according to the scheme of ref. [24]. Legend: Continuous lines: first-order transitions. Broken lines: continuous transitions. λ: the relative biaxiality parameter. I: isotropic phase. N_U^+: uniaxial nematic phase formed from calamitic molecules. N_U^-: uniaxial nematic phase formed from discotic molecules. N_B: biaxial nematic phase. Note that T^* in this figure denotes scaled temperature, rather than, as more usually, the critical temperature below T_{NI} at which the isotropic phase becomes unstable with respect to orientational fluctuations (see eq. (1.15)) The parameter λ (see e.g. [83]) corresponds to $\frac{\epsilon}{\sqrt{6}}$.*

1.6 Landau–de Gennes Theory

There are some key common features of the liquid crystal phase diagrams outlined above. These include: (a) the biaxial nematic–uniaxial nematic–isotropic fluid phase succession, (b) the Landau point, and (c) the symmetry of the phase diagram around the Landau point. Although we now know that these properties are not as universal as seemed earlier, to begin with they seemed to be insensitive to the detailed theoretical strategy adopted. Under these circumstances it was tempting to seek some underlying unifying features which enable at least a sketch of the expected phase diagram (or diagrams!) to emerge from some much simpler considerations. The most common tool for such analyses in statistical mechanics is the Landau theory [31]. In Chapter 5, Longa addresses the use of this technique in the discussion of biaxial nematic phases.

Molecular field theory requires some detailed physical analysis of particular cases, and involves some model for particle intermolecular potentials. But Landau theory merely requires some simple assumptions about the symmetry group of the order parameter and the analytic behaviour of the free energy close to the phase transition under investigation. This method was first and most notably used in liquid crystals by de Gennes [14] in his analysis of the uniaxial nematic–isotropic phase transition. We briefly anticipate some of the issues here.

In practice, when considering the biaxial nematic phase the Landau strategy has turned out to be much harder than might have been anticipated. The standard Landau-de Gennes theory [14] for thermotropics is written in terms of the single tensor order parameter Q_{ij} from eq. (1.8). It takes the form

$$\mathcal{F} = a'(T - T^*)\mathrm{Tr}\,\boldsymbol{Q}^2 - c\mathrm{Tr}\,\boldsymbol{Q}^3 + b\left(\mathrm{Tr}\,\boldsymbol{Q}^2\right)^2, \tag{1.15}$$

where the parameters a', b, c are independent of temperature, T is temperature, and T^* is the hidden critical point just below the nematic–isotropic phase transition temperature T_{NI} at which the susceptibility to nematic probes, correlation lengths and response times all diverge.

The philosophy is that, in principle, this is an infinite series expansion in powers of invariants of $\boldsymbol{Q}$, but that truncating it at the fourth power is sufficient to extract analytically the important qualititative behaviour. The spirit of Landau theory merely requires that the anisotropic part of the free energy be analytic, and does not enquire about the origin of the terms. On the other hand, comparison with molecular field theory [32] naturally identifies different parts of this free energy. The higher order terms come from the entropy of ordering (a factor of T is suppressed because these terms are taken to change slowly with temperature). The quadratic term balances an entropy-driven temperature-dependent term with a temperature-independent intermolecular energy term; this latter yields the T^* term.

The result of the theory is well-known. As temperature is reduced, there is a phase transition from the isotropic phase to the nematic phase at a temperature T_{NI} slightly higher than T^*. Unless external fields are applied, the equilibrium nematic phase is *always* uniaxial, and takes the form given by eq. (1.8):

$$Q = S\begin{pmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{1.16}$$

where S can be identified with the analogous parameter in eq. (1.2).

With the theory of eq. (1.15), introducing a biaxial component to the tensor $\boldsymbol{Q}$ always costs free energy. What needs to be done to reverse this, and so allow it to sustain a biaxial phase? It turns out that if the truncation is taken at sixth order, following for instance Mukherjee [33], rather than at fourth order, then a biaxial nematic phase is possible. Some resemblance can be found to the molecular field phase diagrams, but the neat symmetries which come from exchanging the meaning of the internal axes are lost, and there is no apparent connection between a measure of molecular biaxiality parameter and the magnitude of the cofficient of the sixth order term in the Landau theory.

An alternative strategy is to build the Landau theory not from the single tensor order parameter Q_{ij}, but rather from a more complex object. In optical or dielectric experiments one can only measure one tensor, and we might argue for that reason, that a phenomenological description could thus only include a single tensor. On the other hand other experiments might be able to probe more features of the molecular orientation. If so, the elements of the supertensor Q_{ij}^{IJ}, or equivalently of the average of the rank 2 Wigner matrices $\langle D_{mn}^2 \rangle$ would be suitable elements out of which to build the Landau theory.

The complication in this case is constructing the correct invariants, which are now combinations (but not all combinations!) of Straley's [16] parameters (S, D, P, C) (these were (S, T, U, V) in Straley's original notation; for a comparison, see [18]). This programme was carried out by Lee, Allender and colleagues [17, 34]. However there are a large number of possible coefficients that one can vary as parameters in the theory, and these should be related to the degree of molecular biaxiality. Unfortunately, intuition is not helpful in identifying any relationship between the degrees of molecular and phase biaxiality. Once again the apparent neat symmetry of the molecular field theories, which related rod-like and disc-like uniaxial phases to the Landau point between them, seems very hard to extract from this theoretical paradigm, although the picture does predict both uniaxial and biaxial phases. A further theoretical subtlety, which does not seem to have entered the Allender–Lee–Hafiz picture, is the possibility that the molecular biaxiality permits some explicitly tensorial interactions, the effect of which is to enlarge the number of quadratic terms allowed in the Landau expansion [35a,b].

1.7 Computer Simulation

Computer simulation is by now an established technique which links macroscopic ideas to microscopic models in statistical mechanics. In the context of liquid crystals, it has been essential in establishing which molecular features play a role in the formation of liquid crystalline phases (for a recent review, see [36]). In Chapter 6, Berardi and Zannoni examine the problem of nematic biaxiality from this perspective.

There are two key questions which computer simulation of a system of interacting biaxial molecules can answer. The first question is whether the molecular field calculations are giving plausible answers. What intermolecular potential or molecular shape is most likely to promote a biaxial nematic phase? Is a biaxial nematic phase possible in principle, and if so, how good are the molecular field calculations in predicting a temperature-biaxiality phase map?

The second question is perhaps as interesting, and key when it comes to structure-property relations. Biaxial nematic phases may exist, but they seem to be rare, not the least because, unlike in the case of uniaxial nematics, the theoretical prediction of biaxial nematic phases predates their observation. Thus it seems at the very least that for the biaxial phase, deliberate manufacture of suitable molecules must be necessary. But what is the underlying chemistry? One may recall that even the uniaxial nematic phase is by no means universal even when the constituent molecules seem *prima facie* suitable candidates. But often the nematic phase does not so much not exist, as it is *pre-empted* by something else: solidification, perhaps, or a smectic phase, or even glassification. Maybe this is why the biaxial nematic phases seem so uncommonly rare. So now we can pose the additional question in a more precise way. What extra molecular features are required to *prevent* other phases from intervening to destabilise the biaxial nematic?

The first question is the easier to answer. Computer simulation has yielded enormous insight into the properties of the uniaxial nematic phase. In fact, if one wants to concentrate on the explicitly orientational properties, a sufficient strategy is to stick to a model in which the anisotropic particles are confined to a lattice. The liquid crystal paradigm is that of Lebwohl and Lasher [25]. This has the advantage that its molecular field solution coincides with the Maier–Saupe theory [11], and of course, it has been the subject of much simulation study.

The model of Boccara *et al*. [24] is an infinite range model, but a nearest neighbour version would serve as a starting point for biaxial simulations. The first biaxial lattice model, generalised version of this, was studied

in 1980 by Luckhurst and Romano [29], using Monte Carlo simulation. The basic conclusion was optimistic. The molecular field conclusions were at least qualitatively confirmed. A more extensive study by Zannoni and collaborators [37] confirmed the basic picture.

These lattice models did stimulate an important theoretical conjecture, which raised interesting cultural issues, pitting physical and chemical modes of explanation against each other. The molecular field version of the Luckhurst–Romano model [29] had already been studied in 1975 by Luckhurst with other coauthors [26], albeit only for the uniaxial phase. These authors were the first to observe the dramatic reduction in the first-order discontinuity at the uniaxial nematic–isotropic phase transition resulting from molecular biaxiality. They thus conjectured, very plausibly, that the reason that the observed first-order discontinuities at this phase transition were universally so weak was precisely this: real molecules are biaxial. It took the detailed computations on the (uniaxial) Lebwohl–Lasher model [38] to show that this was not the case. In this case the weakness of the first-order phase transition must be ascribed to (physical) critical fluctuations, rather than (chemical) molecular shape. However, the answer was not at all *a priori* obvious. We note also that it is the case that molecular biaxiality can drive the transition even weaker [39].

Attempts to answer our second fundamental question require the inclusion of translational degrees of freedom. Pioneering studies were made by Allen [40], by Sarman [41, 42] and by Berardi and Zannoni [43]. Allen carried out molecular dynamic (MD) studies of hard particles, while the Berardi–Zannoni study used the Monte Carlo (MC) method on a more realistic off-lattice molecular model of biaxial Gay–Berne particles. The Gay–Berne intermolecular potential has been widely used in computer simulations to model anisotropic molecules. Phases consisting of such molecules, with suitably tuned potential parameters, do indeed mimic other liquid crystal phases. Interestingly a biaxial smectic A phase was also found, in which the molecules align with a principal axis perpendicular to layers, but with secondary molecular axes aligned within the layers. The key conclusion already in the 1990s was that at least with suitable molecules, there were good reasons to suppose that it would be possible to construct biaxial phases. On the other hand, there is a strong dependence on molecular biaxiality, so it is easy for other phases to intervene, and the real computational challenge is to tune the intermolecular potential.

1.8 Other Theoretical Issues

Starting with Saupe [44], a number of authors [45–53] have constructed *continuum* theories for biaxial nematics. These theories use the Frank–Oseen elastic theory and the Leslie–Ericksen nematodynamics as paradigms. These theories work well experimentally for uniaxial nematics. In principle the analogies are relatively straightforward, but in practice there are problems concerned with the most appropriate formulation, the number of surface elastic terms, and the number of independent bulk elasticities and viscosities. In particular, the number of independent viscosities within the original Ericksen–Leslie formulation is reduced from that which might be expected on the basis of counting invariants, because of the so-called Parodi relation [54]. In Chapter 7, Stewart reviews the continuum theory of biaxal nematics.

In the biaxial theory it appears that there is now more than one Parodi relation. In the most recent version of the theory, there are 12 bulk elastic constants and 12 viscosities. The measurement of these parameters might present a considerable serious challenge to experimentalists.

The additional symmetries of the biaxial nematic would not only change the elastic theory and the hydrodynamics, but also the defect structure, as compared to the uniaxial nematic. As observed liquid crystal optical textures are in fact reflecting the defects sustained by the liquid crystal phase in question, we expect, therefore, some consequences on the observed liquid crystal optical textures. The most dramatic signature of the nematic phase, dating from the dawn of the liquid crystal era, is the Schlieren texture, in which disclination lines of index $\frac{1}{2}$ (with two brushes) and index 1 (with four brushes) can be observed between crossed polarisers. In fact

topological analysis of defect line structure in nematics [55] shows that all disclination lines of half-integer index can be deformed into each other. The interesting question of why four-brush defects are observed in conventional nematics seems to boil down to the fact that such defects avoid a singular structure by the so-called *escape into the third dimension* [56]. Because these structures are not singular, they have relatively low energy, and are not unstable to decay into two disclinations of half index. On the other hand, apparently it is not possible to unwind such singularities because of long-scale constraints.

By contrast, topological analysis of line defects in biaxial nematics [57, 58] indicates that escape into a third dimension for disclinations of integer index is no longer possible. Now integer-index defects are likely to be unstable with respect to dissociation into half-integer-index defects. In fact the situation is more complex, because there are three directors, but the basic result seems to be robust. These half-integer-index defects correspond to two-brush optical singularities under the polarising microscope; on entering the biaxial nematic phase, four-brush defects should disappear.

Finally we note also that, given the experimental challenges of synthesising suitable biaxial molecules, it has been suggested that a more fruitful strategy might be to *mix* rod-like and disc-like molecules. The major axes of the rod-like and the disc-like molecules would then be perpendicular to each other, and strongly coupled. Several authors [59–61] made molecular field calculations which indicated that this might indeed have the expected result. However, theoretical calculations by Palffy–Muhoray *et al*. [62, 63] that the energy penalty of such phases is such that a more likely scenario would be that the biaxial phase would be pre-empted by phase separation into rod-like and disc-like phases, results which were confirmed computationally by Hashim *et al*. [64].

The alignment of biaxial nematics is not only essential for any potential applications, but also important in a whole range of experimental contexts. In Chapter 8, Photinos addresses theoretical issues in this interesting area. The key extra feature of biaxial nematics, as opposed to the usual uniaxial case, lies in the extra possible degrees of alignment freedom, leading to new effects, whether in alignment by electric or magnetic fields, at surfaces, or by flow alignment. In all cases, the complexity of the formalism requires extra care.

1.9 Applications

The possibility of novel liquid crystal devices has been a motivating factor in driving research in biaxial nematics. The idea is that rotation of the minor director in a biaxial nematic might require a lower torque (and hence, by implication, lower alignment fields, and more rapid response times) than those required in conventional uniaxial nematics. In Chapter 9, Brimicombe discusses some of the questions involved. Surface alignment would be an issue, as now an easy surface frame of reference, rather than simply an easy direction, would be required, involving more careful surface preparation. In addition, Brimicombe discusses some ideas for devices which depend specifically on biaxial effects for their operation.

1.10 Characterisation

The standard classic method for detecting optical biaxiality, as articulated in many textbooks on optical crystallography and mineralogy [3, 4, 65] involves *optical conoscopy*. An aligned sample is viewed in converging light between crossed polarisers, with one of the principal axes of the sample normal to the planes of the polarisers. A uniaxial sample gives rise to the standard *Maltese Cross* pattern. But now if the dielectric constants in the two in-plane directions are different, the pattern depends on the relative orientation of the principal axis frame and the polariser/analyser axis frame. If these are aligned, the Maltese Cross remains. But if they are misaligned, a gap opens up at the centre of the cross, and the observed interference

lines (known as *isogyres*) widen into a hyperbolic curve. The separation of the two hyperbolic branches depends on the degree of axis frame misalignment, and also on the difference in the refractive indices of the two independent light beams passing at normal incidence.

However, even in a solid crystal, preparing an aligned sample is not always an easy task, and in a mesophase even more so. Also, as we have seen, phases can be optically biaxial (most notably the smectic C phase) when the biaxiality is a secondary rather than a primary property of the phase. Furthermore, biaxiality can be induced by a surface in a phase which far from the walls is uniaxial. In such a system, a well-aligned sample would exhibit the broken Maltese Cross property, and only very careful measurements would then demonstrate that the biaxiality was associated only with a broken surface symmetry and not with the bulk. So this method should be regarded as a technique which provides circumstantial rather than conclusive evidence of a biaxial liquid crystal phase.

An alternative technique involves examining the *optical liquid crystal texture* between crossed polarisers. Optical textures have until recent years been the standard method to identify different liquid crystal phases. The identifying feature of a nematic phase is the so-called Schlieren texture, with two-brush and four-brush defects whose positions are robust with respect to rotation of the sample in the polariser plane. As we have seen above, there is strong suspicion that whereas uniaxial nematics sustain both two-brush and four-brush defects, the biaxial phase will *only exhibit two-brush defects*. Thus the transition from the uniaxial to the biaxial phase might involve a break-up of four-brush defects into pairs of two-brush defects. However a drawback of this method is that there is no formal theorem (at least not yet!) to the effect that the four-brush defects will be absent in a biaxial nematic. So the texture evidence too would be circumstantial. In Chapter 10.13 Dierking addresses the question of determining biaxiality using evidence from textures.

A third optical method involves *explicit measurement of the three refractive indices*. Different techniques of measuring birefringence can use a modified Pockels cell [66], or alternatively the Fabry–Perot method [67]. But here again, one needs to prepare a uniform aligned sample, with principal axes in known directions. If this can be assured, then this method provides an unambiguous determination of phase biaxiality. However, as in the cases above, one needs other signals to assure oneself that the phase observed is nematic. In Chapter 10.2, Palangana reviews work on the explicit evaluation of refractive indices in biaxial nematics.

Then in Chapter 10.3, Vij and Kocot give an exhaustive discussion of theory and experiment associated with the use of IR and Raman spectroscopies in the detection of biaxial phases. These methods employ the directional properties of molecular vibrational modes. The IR technique depends on the fact that absorption of polarized radiation in an oriented sample will differ from that in an isotropic phase. Raman spectroscopy, on the other hand, is the inelastic scattering of light from molecular rotational and vibrational modes, and gives information on both second- and fourth-rank order parameters.

A big drawback of many of the methods discussed so far is that they require aligned samples. Only the textures regard sample inhomogeneity as an opportunity rather than as a threat. In general if one observes an orientationally inhomogeneous sample using an optical method, one sees an essentially isotropic system, albeit one which scatters light so enthusiastically that it appears permanently turbid.

On the other hand, there are spectroscopic methods, such as NMR or ESR, which do not suffer from this disadvantage. Optical methods detect average optical properties. But NMR detects the sums of spectra associated with different regions in the sample, rather than their average. This signal can then be essentially distinguished from the signal of an isotropic medium, even if a detailed analysis of the data does require some sophisticated computational processing.

NMR has historically been a particularly useful measure of the magnitude of the scalar order parameter. Let us remind ourselves of the basic principles behind the NMR measurement of an order parameter in a unixial nematic liquid crystal. An imposed magnetic field splits the spin energy levels of any atomic nucleus with non-zero spin, leading to spectral emission or absorption lines corresponding to the energy difference between these levels. An interesting interaction for liquid crystal studies is the dipolar coupling which leads

to a splitting of the spectral lines. The magnitude of this depends on the angle between the vector linking the nuclei and the magnetic field, together with the separation between the two nuclei. In the isotropic phase the rotational motion of the molecules averages the dipolar splitting to zero. But in a liquid crystal phase, the anisotropic rotational motion does not average the splitting completely to zero, leaving the residual splitting $\Delta\nu$. It is this which allows the order paramater S associated with the internuclear vector to be determined. The link between the residual splitting and the order parameter is simply

$$\Delta\nu = cS, \tag{1.17}$$

where c is a constant, $S = \langle P_2 \rangle$, and $P_2(\cos\theta_i)) = \frac{1}{2}(3\cos^2\theta_i - 1)$ is the second Legendre polynomial.

The internuclear vector itself may be between identified atoms within the liquid crystal molecule. The identification can for example be effected by deuteriating only certain hydrogen atoms within a liquid crystal molecule. Or alternatively, the relevant internuclear direction can be within an impurity or "guest" molecule dissolved in the liquid crystal specifically for the purpose. In either case, the order parameter of the internuclear vector serves as a surrogate for the local ordering field, which in turn represents an order parameter for the whole system.

In an aligned sample, all that one needs to note is the angle between the field direction $\mathbf{B}$ and the director $\hat{\mathbf{n}}$. If $\mathbf{B} \parallel \hat{\mathbf{n}}$, then $\Delta\nu = cS$. But when $\mathbf{B} \perp \hat{\mathbf{n}}$, then $\Delta\nu = -\frac{1}{2}cS$; the minus sign is clearly unobservable if one is looking at splittings. Moreover, as the sample is rotated from a parallel to a perpendicular orientation with respect to the magnetic field, one starts with some splitting $\Delta\nu_0$. The splitting then reduces until at the *magic* angle $\cos^{-1}\left(\frac{1}{\sqrt{3}}\right)$ the splitting disappears altogether. Then the splitting increases until the two directions are perpendicular when the splitting reaches $\frac{1}{2}\nu_0$. Turning the sample halves the splitting.

On the other hand, if the sample is unaligned, then one sees a *lineshape*, or so-called powder pattern, which reflects the aggregate of line splittings coming from different parts of the sample. If one has some knowledge of the actual distribution of the directors (as is often the case), then some computations can deconvolute the lineshape to obtain the order parameter.

But this simplicity disappears in a biaxial sample. The calculation becomes more complicated, but a detailed calculation was carried out by Allender and Doane [68]. Its importance to the future of the subject is underlined by the fact that it was done as early as 1978. The key result is that the halving of the line splitting when the sample is rotated through $\pi/2$ with respect to the magnetic field no longer holds. So an NMR experiment serves as an *experimentum crucis* for the presence of a biaxial phase. In Chapter 10.4, Madsen shows that NMR has indeed played an absolutely central role in the analysis of candidate biaxial phases.

In our final section on characterisation, Davidson discusses static intermolecular correlations using X-ray and neutron diffraction techniques in Chapter 10.5. Unfortunately these methods also require aligned samples, which can be produced by a magnetic field. In a uniaxial system, the intermolecular correlations in the plane perpendicular to the principal axis possess $D_{\infty h}$ symmetry. But in the biaxial nematic the in-plane symmetry is broken orientationally, and this also affects the intermolecular correlations. We now expect D_{2h} symmetry. In terms of observed crystallographic patterns corresponding to nearest neighbour correlations, this turns the (uniaxial) ring into a (biaxial) set of four spots, symmetrically arranged into two pairs.

1.11 Lyotropic and Colloidal Systems

The search for thermotropic biaxial nematics has been long and difficult, and the results of the searches have provided much controversy. In contrast, therefore, it is more than noteworthy of remark, that lyotropic biaxial nematics were first observed already more than thirty years ago [69], and just ten years after Freiser's initial prediction [10]. In Chapter 11, Figueiredo Neto and Galerne review the current state of knowledge

about lyotropic biaxial nematics. The reasons for the dramatic difference in the biaxiality characteristics between lyotropic and thermotropic systems is not entirely understood. But one key important feature seems to be the micellar properties of these systems; the basic liquid-crystalline elements are not the elementary molecular units in the lyotropic solution, but rather some supramolecular anisotropic micellar aggregates of the amphiphilic molecules. This in turn may allow the elementary nematogenic objects, which are now micelles, themselves to adopt variable shapes. In particular it is conceivable that some thermodynamic conditions may favour biaxial objects of just such a shape to benefit, in an energetic sense, from phase biaxiality. In Chapter 11, we meet both molecular and field theoretical techniques for understanding the lyotropic biaxial nematic phases.

The distinction between lyotropic liquid crystals and anisotropic colloidal systems is not clear-cut. Colloidal systems are usually thought of as dispersions of large particles in a matrix or solvent of smaller molecules. Often, as for lyotropics, the solvent is water. In isotropic colloids, the larger particles can be e.g. oil droplets (in milk) or TiO_2 particles (white paint). If either the solvent or the colloidal particles (or both) are anisotropic, the resulting suspension may be liquid crystalline, and specifically nematic. One example of such colloidal particles in this context is viruses, for which the classic example is tobacco mosaic virus (TMV) [70], while Langmuir [71] in the 1930s studied a whole set of other types of colloidal dispersion. These works inspired Onsager in his model [12] of athermal rod-like molecules in an inert background, often thought of as the standard theoretical work in the theory of lyotropic liquid crystals. However, systems such as poly(γ-benzyl-L-glutamate) dispersed in dimethylformamide, sometimes thought of as lyotropic liquid crystals, are more correctly thought of as thermotropic liquid crystals diluted by an isotropic solvent [72]. Complicating factors in such systems include shape and size polydispersity, for now the "molecules" of the system are supramolecular, and necessarily non-uniform – how non-uniform depends in detail on the nature of the preparation process–as well as the existence of double layers in the solvent, induced by a very low impurity ionic concentration. Phase biaxiality can then be the consequence either of intrinsic biaxiality in the colloidal particle shape, or possibly because the suspension is a mixture of rod-like and disc-like particles whose orientation is coupled. The subject of colloidal biaxial nematics is addressed by Vroege in Chapter 12.

1.12 Molecular Design

Finally we turn to the vexed question of how to create a material which might exhibit biaxial nematic properties. In Chapter 13, Hoffmann, Brömmel, and Finkelmann discuss this question for liquid-crystalline polymers. Here a key distinction needs to be made between side-chain and main-chain polymers. In the latter, indeed, a copolyester has been observed which curiously forms a nematic phase with both biaxiality and polarity [73]. A possible advantage in using polymers in this context is the suppression of crystallinity in polymeric systems. However, the alternative to crystallinity is the glass state, and glasses present other theoretical problems.

Then in Chapter 14, Lehmann discusses molecular design strategies for low molar mass thermotropic biaxial nematics. The seminal paper by Freiser [10] predicting the existence of the thermotropic biaxial nematic phase made it apparent that the calamitic molecule need only deviate from cylindrical symmetry for the mesogen to form a biaxial nematic. But it is difficult, if not impossible, to synthesise a mesogenic molecule which does *not* deviate from cylindrical symmetry. From this point view it is extremely surprising that the biaxial phase is not easier to find than it is proving to be. One reason for the difficulty might simply be that the molecular biaxiality is not sufficiently large. The early attempts to synthesise compounds capable of forming a biaxial nematic therefore focussed on the molecular shape, and its optimisation to yield high molecular biaxiality.

The first structure to be designed and synthesised was, it might be speculated, stimulated by the behaviour of the lyotropic biaxial nematic discovered by Yu and Saupe [69]. Here it was found that the biaxial nematic

was bordered by two uniaxial nematic phases, one composed of rod-like micelles, the other from disc-like micelles. As one proceeds along the path from one uniaxial phase to the other through the biaxial nematic phase, it is reasonable to suppose, by analogy, that the rod-like micelles transform first into biaxial micelles, acquire maximum biaxiality which then again decreases, and finally transform into disc-like micelles. It is not surprising, therefore, that Chandrasekhar [74] speculated that one route to the thermotropic biaxial nematic was through molecules possessng both rod-like and disc-like characteristics. It was not until three years later that he put this notion to the test [75], based on a copper complex. In Figure 1.2 we show a collage showing a wide-ranging set of molecular structures, including that of Chandrasekhar, which have been created in the hunt for the biaxial nematic phase.

As it turned out, Malthête and colleagues [76, 77] had created a molecule combining rod-like and disc-like structural features some years earlier. The structure, which is clearly biaxial, consists of a rod attached to a semi-disc, both of which are decorated by chains (see again Figure 1.2). Despite numerous studies of this compound, some of which appeared positive, it was eventually found that the nematic phase was not biaxial, but rather uniaxial [78]. It would appear that the shape is not quite correct, or that the molecular biaxiality is too small.

The question of which deviations from uniaxial calamitics might be apposite for the creation of a biaxial nematic phase was considered by Praefcke and coworkers [79]. A cartoon showing the structures demonstrated in this paper is shown in Figure 1.3. The spoon in this figure clearly resembles the molecule designed by Malthête and colleagues [76, 77]. The bone, by design a biaxial shape, is similar to the molecular structure of the compound prepared by Praefcke's group. However, this compound was also found not to exhibit a biaxial nematic phase [80]. A more bone-like structure, in which two two disc-like mesogenic groups are linked by a flexible rod-like spacer was also prepared by the Praefcke group [81]. This clearly has a shape deviating from uniaxiality, and is also shown in Figure 1.2. But measurements of the optical refractive indices showed that this too only yielded a uniaxial nematic phase [67].

The failure to observe a biaxial nematic phase for these compounds, in which the molecular shape possesses clear biaxiality, is both surprising and disappointing. However, although it is clear that the molecules possess some degree of biaxiality, how the magnitude of the relative biaxiality influences the phase behaviour is less clear. Some indication of this property can be gleaned from the molecular field theory predictions in the phase map shown in Figure 1.1. Here we see that as the relative biaxiality parameter λ is increased from zero, so a biaxial nematic is injected into the phase map. In addition, the stability of the biaxial nematic with respect to the uniaxial nematic increases until $\lambda = \lambda_c = 1/\sqrt{6}$, at which value the isotropic phase undergoes a direct transition to the biaxial nematic.

The observation of the biaxial nematic phase depends not only on its stability with respect to the uniaxial nematic, but also on its stability with respect to smectic or crystalline phases. Experience suggests that nematic phases freeze at absolute temperatures usually higher than a factor of 0.9, and always above a factor of 0.8 times the isotropic–nematic transition temperature. For a nematogen with $T_{\mathrm{NI}} = 400$ K, this would correspond to nematic range of some 80 K, which is quite considerable.

In order to focus on the consequences of this observation, we have in Figure 1.4 plotted the phase map for λ over the range $0 < \lambda < \lambda_c$, where the maximal biaxiality is achieved at λ_c. In this figure, the reasonable anticipated variation of the freezing point of the nematic phase is shown as a dashed line. It is immediately apparent that even when the nematic range is relatively large, the values of λ for which the biaxial nematic should be stable should be extremely small. Indeed Figure 1.4 suggests that only for $0.39 \lesssim \lambda \lesssim \lambda_c \approx 0.41$ will there be a realistic chance of finding a biaxial nematic phase. We note not only the proximity of the required molecular biaxiality λ to its optimal value λ_c, but also the difficulty of preparing molecules with specific values of λ. As a consequence, the accidental (or even the deliberate) synthesis of materials with parameters suitable for the formation of a biaxial nematic seems most unlikely.

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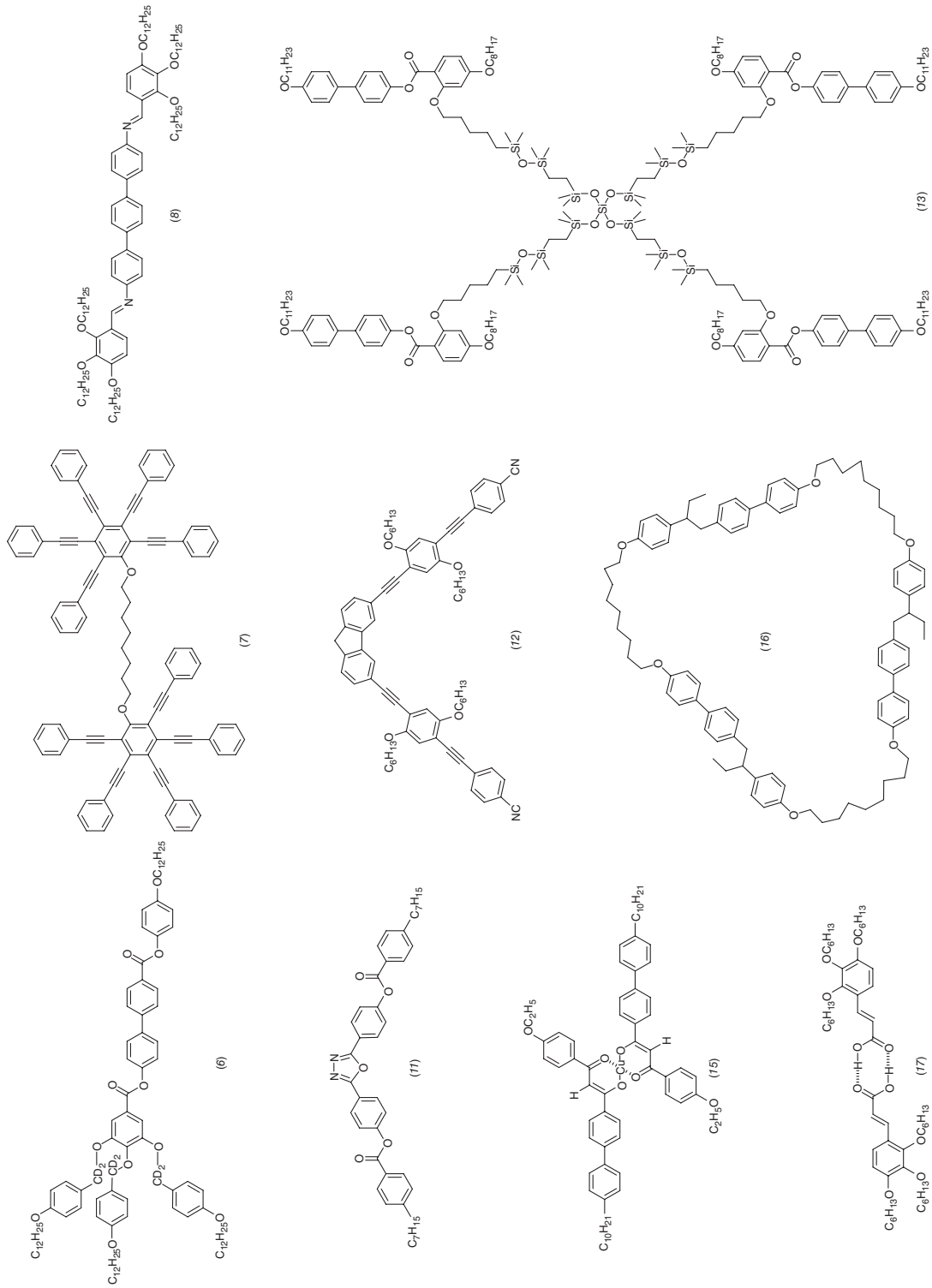

Figure 1.2 *Chemical structures for candidate biaxial nematic mesogenic molecules. Reproduced with permission from Luckhurst, C.R., Biaxial nematics composed of flexible molecules: a molecular field theory,* Liq. Cryst. ***36****, 1295–1308 (2009).*

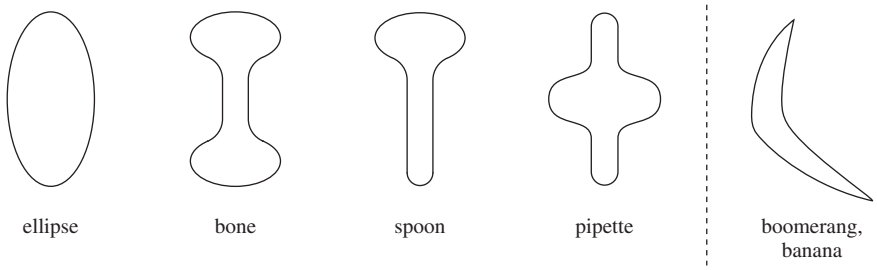

Figure 1.3 *Cartoons of candidate biaxial nematic molecular shapes ([79], reprinted by permission of the publisher (Taylor & Francis Ltd, http://www.tandf.co.uk/journals). The banana shape was only added to the collection later (reproduced from [82]).*

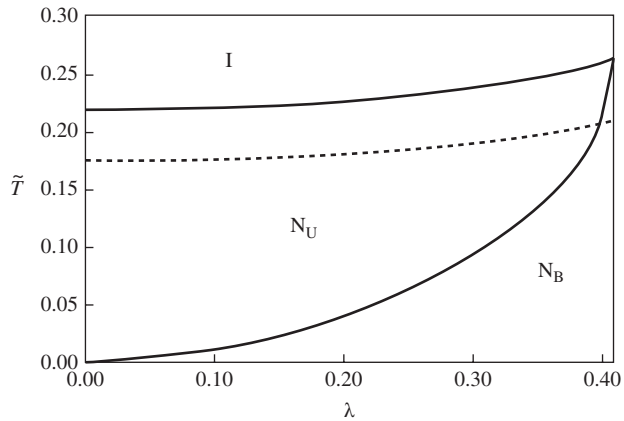

Figure 1.4 *Phase map showing uniaxial* N_U *and biaxial* N_B *phases as a function of the relative molecular biaxiality* λ *and scaled temperature* $\tilde{T}$*, in the range* $0 < \lambda < \lambda_c = 1/\sqrt{6}$*. Nematic phase boundaries calculated with molecular field theory. The dotted line represents an estimate of a nematic–crystal (or nematic–smectic) phase transition temperature. The biaxial nematic phase is only expected to be observable in a very small region at the top right-hand corner of the map. See text for further explanation. Reproduced with permission from [83]. Copyright © 1995, The Royal Society of Chemistry.*

In this regard, it may be noted that a related and apparently analogous phenomenon occurs with respect to the formation of lyotropic biaxial nematics. The lyotropic phase diagram is similarly and remarkably sensitive. But in this case the relevant parameter is amphiphile concentration rather than molecular shape. In the lyotropic case, unless the amphiphile concentration is extremely close to an optimum concentration – within some 1%, in fact – no biaxial phase is ever observed [69]. In other words, therefore, the challenge of locating a lyotropic biaxial nematic is in some sense as great as that of locating a thermotropic biaxial nematic. There is an essential difference, but it does not lie in the molecular physics of the systems. Rather, it is the fact that the amphiphilic concentration can be varied continuously, whereas the structural variables cannot.

In more recent times, attention has turned to the use of compounds composed of V-shaped molecules as better candidates for thermotropic biaxial nematics [84–86]. Some of the compounds that have been synthesised are shown in Figure 1.2. Again it is apparent that these structures are biaxial. The magnitude of the molecular biaxiality depends on the angle between the two arms of the V. This dependence could be explored

experimentally by synthesising a range of V-shaped molecules. But here it proves to be much easier to predict this dependence.

There are two apparently unrelated theoretical models, one based on repulsive forces [87], and one on molecular field theory [88]. Interestingly, despite the significant differences between the two models, their predictions are very close. For the molecular field theory, the maximum biaxiality occurs for an interarm angle equal to the tetrahedral angle 109.47°. As in the other case above, we require the transition from the uniaxial to the biaxial nematic phase to occur above the hypothetical freezing point at a reduced temperature of 0.8. If this is to hold, then the interarm angle should not depart by more than (the extremely small value of) 1° from the tetrahedral value. Once again we predict that the existence of a biaxial phase will exhibit great sensitivity to molecular design. Once again, it seems that the likelihood of synthesising a molecular structure with just the right properties seems intrinsically unlikely, particularly in view of the flexibility of mesogenic molecules.

It is of some concern, therefore, that the interarm angle in the V-shaped molecule shown in Figure 1.2 is about 140°, and yet there is some evidence [89] that it does display a biaxial nematic phase. It may be that the theory is inaccurate, or the underlying model incomplete. One factor known to be missing from the theory has been the polarity of the structure, by which we mean the large electric dipole moment in a direction bisecting the V. This has recently been included in the molecular theory and Monte Carlo simulations [90]. The calculations do suggest that there will now be a significantly larger range of bend angles capable of yielding a biaxial nematic phase above the likely freezing point.

An alternative and possibly valuable approach to the creation of the elusive biaxial nematic phase is to rely on serendipity. One case in point is the tetrapode, constructed by Merkel and co-workers [91] and also shown in Figure 1.2. This compound possesses four mesogenic groups attached laterally to a central silicon atom. The molecule deviates from uniaxial symmetry, but might not have been the first choice for a biaxial nematic. Nevertheless, it does form a nematic phase, and moreover, some of the properties of this nematic hint at the existence of a macroscopic biaxial phase [92].

As an illustration of this point, using surface forces, the authors of ref. [91] succeeded in producing a monodomain sample of the tetrapode. Using FTIR (Fourier-Transform Infra-Red) spectroscopy [93], their study revealed that the symmetry of the spectral intensities was consistent with that of a biaxial nematic phase. Furthermore, by supposing that the phase and its consituent molecules possessed D_{2h} symmetry, it was possible to use these measurements to determine the four orientational order parameters associated with the biaxial nematic phase. However, the experimental values for the order parameters in the phase thought to be biaxial have been found to be in poor agreement with the predictions of molecular field theory [94]. This disagreement is significant because these predictions do account for the order parameters determined via Monte Carlo simulations for a biaxial Gay-Berne mesogen [43]. Nonetheless, the results are encouraging. It is to be hoped that one can build on these results by synthesising analogous molecular structures. In this way, it may be possible to tease out the factors which stabilise the biaxial nematic phase.

* * *

In this introductory chapter we have merely skimmed the surface of what we see as important issues in the physics and chemistry of the biaxial nematic phase at the time of writing. We now invite the reader to explore the subject in more detail through the expert expositions of the authors of the different chapters in this book.

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