Biaxial nematics composed of flexible molecules: a molecular field theory

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Biaxial nematics composed of flexible molecules: a molecular field theory

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The key requirement for the formation of a biaxial nematic phase is clearly biaxiality in the shape or interactions of the constituent molecules. However, in addition to this feature mesogenic molecules are invariably flexible so that their anisotropy and biaxiality can change. The orientational order of the system is also coupled to the conformational distribution and this coupling may stabilise the biaxial nematic phase. Here a molecular field theory of nematics composed of flexible biaxial mesogenic molecules is assembled from its essential elements. Of special significance is the use of the variational approach employed by de Gennes to formulate a molecular field theory for uniaxial nematics. This has the distinct advantage that it avoids the use of a pair potential of unknown reliability. Instead it requires the identification of the dominant orientational order parameters for the phases involved. Invariants constructed from these and an interaction supertensor then give the free energy for the system. This powerful variational approach has been employed for the biaxial nematic phase composed of flexible molecules taking into account the relationship between the interaction supertensors for the numerous conformers. The way now seems to be open to explore the influence of molecular flexibility on the stability of the biaxial nematic phase for a molecularly realistic model.

Keywords: biaxial nematics; phase symmetry; flexible mesogenic molecules; molecular field theory; variational approach

1. Introduction

The possible existence of a thermotropic biaxial nematic phase was first appreciated by Freiser (*1*). He realised that mesogenic molecules do not possess the uniaxial symmetry normally assumed for them but that they were more board-like. As a result such compounds should form not only a uniaxial nematic phase but also a biaxial nematic in which the minor axes of the molecules as well as their major axes possess long-range orientational order. To quantify his ideas concerning the biaxial nematic phase Freiser developed a molecular field theory for rigid biaxial molecules which, implicitly, were taken to have D_{2h} point group symmetry. Very quickly the concept was taken further theoretically, again for rigid molecules (*2–4*). These theoretical ideas were tested successfully with the aid of computer simulations using model systems also for rigid molecules (*5*). They showed that a nematogen formed from biaxial molecules would exhibit a uniaxial nematic, N_U, followed by a biaxial nematic, N_B, with the N_U–I transition being first order while the N_B–N_U transition is second order. In addition, at a unique value of the molecular biaxiality there was a second-order transition directly from the isotropic to a biaxial nematic phase. In contrast to this burst of theoretical as well as simulation activity, experimental attempts to provide the ultimate test of Freiser's predictions were slow to appear in the literature. The first claim to have found a thermotropic biaxial nematic phase was not published until 16 years after its predicted existence (*6*). This was then followed by other claims at fairly regular intervals (*7, 8*) although it must be said that more detailed investigations, often using deuterium nuclear magnetic resonance (NMR) spectroscopy, did not always substantiate these initial claims (*9, 10*). More recently there have been further claims for V-shaped molecules (*11, 12*) and tetrapodes (*13*) which appear to be somewhat stronger. However, very recent work has cast doubt on the existence of a biaxial nematic previously claimed for one V-shaped molecule (*14*). A collage of the molecular structures for some of the mesogens thought to form thermotropic biaxial nematics is shown in Figure 1. It is immediately apparent that these molecules certainly deviate from cylindrical symmetry and so would be expected to form a biaxial nematic. However, it might well be that the formation of this elusive phase is blocked by the intervention of a transition to a smectic or to a crystal phase (*1, 18*).

The other significant feature of these molecular structures is that they are not rigid; indeed, this is a feature shared with almost all nematogens. Their non-rigidity often originates in the alkyl chains where the rotation about the carbon–carbon bonds is relatively unhindered. Such rotations do change the shape of the molecule and hence its ability to form particular liquid crystal phases. These changes are relatively small when
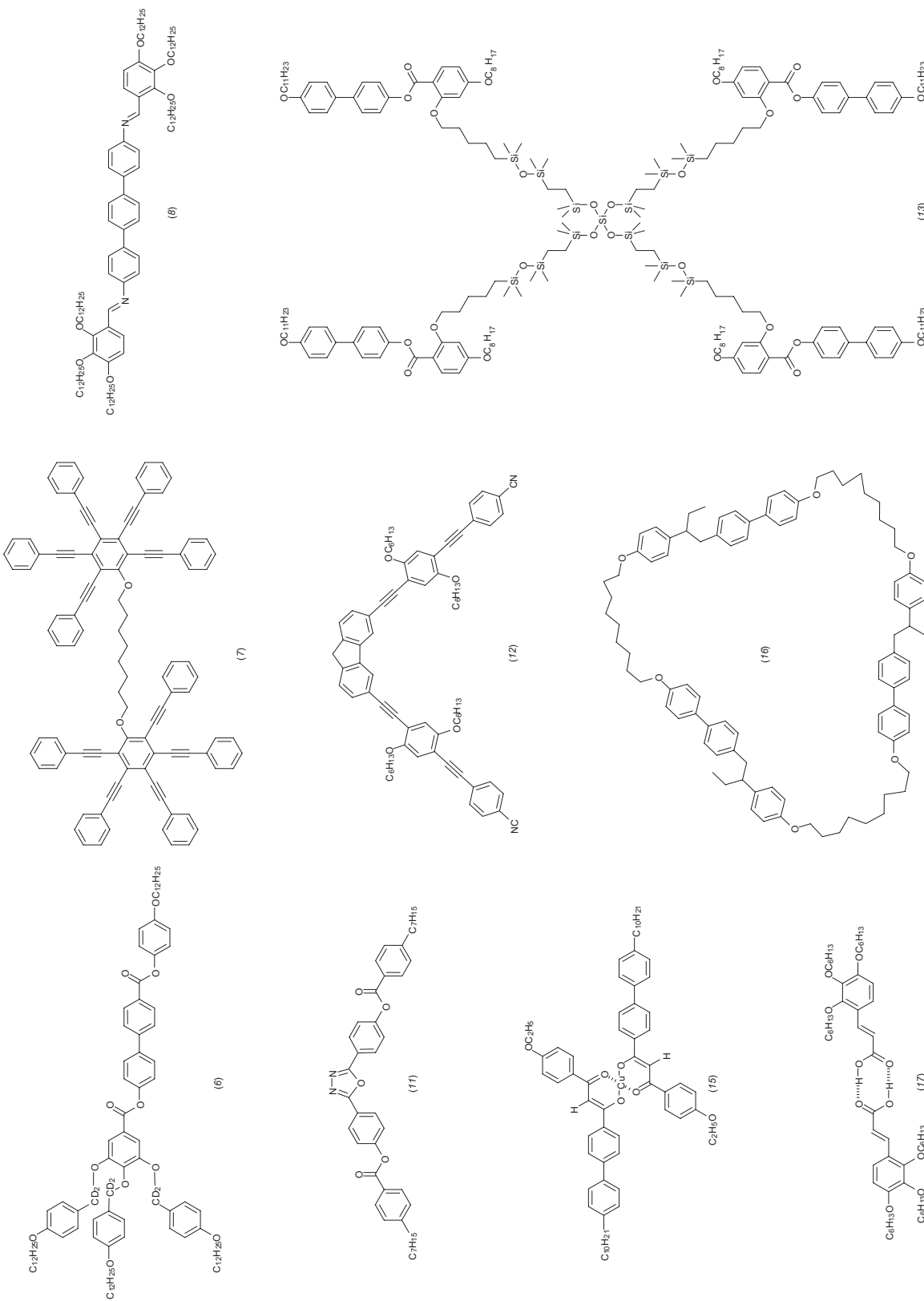
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Figure 1. The chemical structures of compounds claimed to form thermotropic biaxial nematic phases. The numbers associated with each structure are the references in which the claims appear.

the chains are attached to just a single mesogenic group. In contrast, when the chains link mesogenic groups as in liquid crystal dimers (*7, 19, 20*) and tetrapodes (*13*) then the change in shape and so in transitional properties are expected, and are found to be far more dramatic. This is certainly the case as far as the formation of uniaxial nematic phases are concerned, where the coupling between the orientational order and the conformational distribution is significant. It is to be expected that this coupling will also be important for the formation of the biaxial nematic phase, especially since the conformers are likely to differ in their biaxiality.

Our aim here is to construct a molecular field theory of biaxial nematics composed of flexible molecules which may then be used to explore the influence of flexibility on the stability of biaxial nematics. In fact, many of the elements of such a theory are already available in the literature so that the primary task is to assemble them in a consistent and coherent manner. The most important part of the theory is to determine the potential of mean torque experienced by a single molecule or conformer resulting from its interaction with the liquid crystal environment. This is usually achieved from the anisotropic pair potential expanded in a basis set of Legendre polynomials, modified spherical harmonics or Wigner functions, depending on the molecular symmetry (*21*). This pair potential is then averaged over the coordinates of one molecule to obtain the potential of mean torque experienced by the other. There is, unfortunately, a major problem with this approach which relates to the slowness of convergence of the series for the pair potential especially for molecules with the complexity of liquid crystal dimers and tetrapodes. However, de Gennes in the first edition of his classic book described an alternative approach (*22*) which he used rather effectively to provide an alternative derivation of the Maier–Saupe theory (*21*). In his variational approach the dominant order parameters are first identified and scalar invariants constructed from them to give the internal energy. Then the free energy is obtained using the singlet orientational distribution function whose optimum form is identified as that which minimises the free energy. This provides the basis of the molecular field theory. The variational approach given by de Gennes has the clear advantage that it is easy to see how quickly the order parameters converge and so avoids the difficulty with the uncertain convergence of the expansion of the pair potential as well as its functional complexity for flexible molecules.

This approach has been used to develop a molecular field theory for uniaxial nematics composed of flexible molecules (*23*). The form of the potential of mean torque was found to be in agreement with that developed by Marcelja (*24*) although without making some of the unsatisfactory assumptions in this theory.

Another essential element is clearly a theory for biaxial nematics composed of rigid molecules and this has been available since Freiser's seminal work (*1*). More recent derivations have been presented (*25*) one of which is based on the variational approach (*26*). As we shall see the combination of these two elements leads to a theory for biaxial nematics composed of flexible molecules whose solution is computationally formidable. This numerical problem has been resolved (*27*) for uniaxial nematics and at the same time this solution allows the rather large changes in the interaction coefficients with the conformation to be determined for a variety of models (*28–30*). The large changes in the coefficients, often between discrete values, are associated with the analogous variation in the angles between the mesogenic groups. Such large and discontinuous changes contrast with that of other models developed to study, either theoretically (*31*) or through simulation (*32, 33*), the influence of molecular flexibility on the molecular anisotropy and hence on the stability of the biaxial nematic phase. In one of these studies the conformational energy is taken to vary continuously with the angle between the rod-like and disc-like mesogenic groups in a dimer (*32*) while in a model for a V-shaped molecule the distribution of the intergroup angle and hence interactions is taken to be Gaussian (*31*).

The layout of this paper is as follows. In the next section we use rigid biaxial molecules to introduce a number of facets of the model. The first of these concerns the orientational order parameters needed to characterise the nematic phases. The way in which these can be used together with an interaction super-tensor to construct the thermodynamic internal energy is then discussed. Armed with this the orientational free energy is developed from the singlet orientational distribution which at this stage is unknown. Its optimal form is determined as that which minimises the free energy subject to certain constraints. The final part of this section deals with how the adjustable parameters in the theory, which are the components of the interaction supertensor, can be related to the molecular structure. This proves to be a challenging task which is only solvable, apparently, with the aid of what seems to be a dramatic approximation (*27*). The ideas encountered in Section 2 are extended in Section 3 to include molecular flexibility and the large number of conformers, often with significantly different anisotropies, that this entails. It also raises the problem of the conformational point group symmetry and its influence on that of the phase. This important issue is resolved by the dramatic approximation for the interaction supertensors introduced in Section 2. The other special aspect of the molecular field theory that emerges is how the

conformational distribution changes with the orientational order of the nematic phases and so with temperature. The uniaxial nematic–isotropic transition can be located from the free energy. This approach proves to be computationally difficult for the biaxial–uniaxial nematic transition but by taking advantage of the second-order character of this transition it is shown how it can be located via a bifurcation analysis. Our conclusions are in Section 4 together with some ideas for future developments in this significant area for thermotropic biaxial nematics.

2. Basic theory for rigid molecules

Here we describe the basic features of the variational approach, introduced by de Gennes to the molecular field theory for nematics (*22*), by considering a system of rigid molecules. The first step is to identify the dominant orientational order parameters that characterise the nematic phases formed by the system. For uniaxial nematics these dominant order parameters have been found to be the average of the second-rank Legendre polynomial, $<P_2>$, using techniques such as neutron scattering (*34*), electron spin resonance (ESR) spectroscopy (*35*) and Raman scattering (*36*). This result is also supported by computer simulation studies of the Gay–Berne generic model potential (*37*). It seems likely that the second-rank order parameters will also be dominant for biaxial molecules in a biaxial nematic phase. These second-rank order parameters can be described using averages of the second-rank Wigner functions, $D^2_{pm}(\Omega)$, where Ω denotes the Euler angles, $\alpha\beta\gamma$, linking the molecular and laboratory frames (*38*). Since p and m both take values from –2 to 2 there are, in principle, 25 independent order parameters, $\langle D^2_{pm} \rangle$. Here, the subscript p is associated with the laboratory frame defined by the directors and for a uniaxial phase only the order parameters $\langle D^2_{0m} \rangle$ are non-zero. The subscript m relates to the molecular frame and for a molecule with $D_{\infty h}$ point group symmetry only the order parameter $\langle D^2_{00} \rangle$ is non-zero in a uniaxial phase. By invoking the symmetry of the constituent molecules and the phase it is possible to reduce the number of the order parameters. By the symmetry of the phase we mean that of the singlet orientational distribution function $f(\Omega)$ (see (*39*)) and not the translational distribution.

Here, we shall take the molecules and the phase to have D_{2h} point group symmetry which constitutes the simplest but not the only biaxial nematic (*40*). For this system the symmetry reduces the number of independent second-rank orientational order parameters from 25 to just 4. These are

$$\begin{aligned}
&\langle D^2_{00} \rangle \\
&\langle D^2_{02} \rangle \left(\equiv \langle D^2_{0-2} \rangle \right) \\
&\langle D^2_{20} \rangle \left(\equiv \langle D^2_{-20} \rangle \right) \\
&\langle D^2_{22} \rangle \left(\equiv \langle D^2_{2-2} \rangle \equiv \langle D^2_{-22} \rangle \equiv \langle D^2_{-2-2} \rangle \right);
\end{aligned} \quad (1)$$

the remainder, with p or m equal to ± 1, vanish. The second-rank order parameters for a system with D_{2h} symmetry are real and related to averages over the Euler angles by

$$\begin{aligned}
\langle D^2_{00} \rangle &= \langle (3\cos^2\beta - 1)/2 \rangle, \\
\langle D^2_{02} \rangle &= \left\langle \sqrt{3/8} \sin^2\beta \cos 2\gamma \right\rangle, \\
\langle D^2_{20} \rangle &= \left\langle \sqrt{3/8} \sin^2\beta \cos 2\alpha \right\rangle, \\
\langle D^2_{22} \rangle &= \left\langle (1/4)(1 + \cos^2\beta)\cos 2\alpha \cos 2\gamma \right. \\
&\quad \left. - (1/2)\cos\beta \sin 2\alpha \sin 2\gamma \right\rangle.
\end{aligned} \quad (2)$$

The next step is to construct the thermodynamic internal energy, $\langle U \rangle$, from the dominant order parameters; the form of this has to yield a scalar which is also real. We are guided in this construction by the S-function expansion of the pair potential which is also real and a scalar (*41*). This expansion is given by

$$U(\Omega_1, \Omega_2, \omega_r, r) = \sum u^{mm'}_{LL'J}(r) S^{mm'}_{LL'J}(\Omega_1, \Omega_2, \omega_r), \quad (3)$$

where $u^{mm'}_{LL'J}(r)$ is a function of the intermolecular separation, r, and depends on the molecular symmetry and structure. The S-function is defined by

$$\begin{aligned}
S^{mm'}_{LL'J}(\Omega_1, \Omega_2, \omega_r) &= (i)^{L-L'-J} \\
&\times \sum \binom{LL'J}{pp'P} D^L_{pm}(\Omega_1) D^{L'}_{p'm'}(\Omega_2) C_{JP}(\omega_r),
\end{aligned} \quad (4)$$

where Ω_1 denotes the orientation of molecule 1 in the laboratory frame, $C_{JP}(\omega_r)$ is a modified spherical harmonic and ω_r is the orientation of the intermolecular vector, also in the laboratory frame. Since the intermolecular vector orientation or a function of it does not occur explicitly in the molecular field theory we project it out of the expression for the S-function which leads to the reduced form

$$S^{mm'}_{LL0}(\Omega_1, \Omega_2) = \sum \binom{LL0}{p-p0} D^L_{pm}(\Omega_1) D^L_{-pm'}(\Omega_2) \quad (5)$$

and gives the interaction energy as

$$U(\Omega_1, \Omega_2, r) = \sum u_{LL'0}^{mm'}(r) D_{pm}^L(\Omega_1) D_{-pm'}^L(\Omega_2). \quad (6)$$

Here, the value of the 3*j*-symbol, $\binom{LL0}{p-p0}$, of $(-)^{L-p}/(2L+1)^{1/2}$ is used to scale the intermolecular coefficient, $u_{LL'0}^{mm'}(r)$. This form for the pair potential, which is a function of the relative molecular orientation, suggests that a similar invariant can be constructed from the second-rank order parameters for the thermodynamic internal energy. We write this as

$$\langle U \rangle = -(N_A/2) \sum u_{2mn} \langle D_{pm}^2 \rangle \langle D_{-pn}^2 \rangle. \quad (7)$$

The tensorial coefficients, u_{2mn}, are clearly not now functions of the intermolecular separation, L has been set equal to two because of the second-rank nature of the dominant order parameters and the redundant variables have been removed. We have also introduced a minus sign so that the u_{2mn} that stabilise the ground state are positive. The factor of ½ is included so that the notation in the final result is consistent with that in other molecular field theories. Finally, since $\langle U \rangle$ is the molar internal energy, the Avogadro constant, N_A, is included.

Our aim is to determine the potential of mean torque, $U(\Omega)$, for a molecule in the nematic phase; this is related to the singlet orientational distribution function, $f(\Omega)$, which is as yet unknown, by

$$f(\Omega) = Q^{-1} \exp\{-U(\Omega)/k_B T\}, \quad (8)$$

where Q is the orientational partition function. The entropy is related to the many-body distribution function which in molecular field theory is a product of the singlet orientational distributions for all particles (*21*); the entropy can now be approximated by

$$S = -R \int f(\Omega) \ln f(\Omega) \, d\Omega. \quad (9)$$

The molar Helmholtz free energy is then given by

$$A = -(N_A/2) \sum u_{2mn} \langle D_{pm}^2 \rangle \langle D_{-pn}^2 \rangle$$
$$+ RT \int f(\Omega) \ln f(\Omega) d\Omega. \quad (10)$$

The optimum form for the singlet distribution is obtained by minimising the free energy with respect to $f(\Omega)$. This minimisation is subject to the constraints that the distribution function is normalised

$$\int f(\Omega) \, d\Omega = 1 \quad (11)$$

and that the orientational order parameters are related to $f(\Omega)$ by

$$\int D_{pm}^2(\Omega) f(\Omega) \, d\Omega = \langle D_{pm}^2 \rangle. \quad (12)$$

The variational process gives the potential of mean torque as (*26*)

$$U(\Omega) = -\sum u_{2mn} \langle D_{pm}^2 \rangle D_{-pn}^2(\Omega), \quad (13)$$

from which the equilibrium Helmholtz free energy can be obtained as

$$A = (N_A/2) \sum u_{2mn} \langle D_{pm}^2 \rangle \langle D_{-pn}^2 \rangle - RT \ln Q, \quad (14)$$

where the orientational partition function is related to the potential of mean torque by

$$Q = \int \exp\{-U(\Omega)/k_B T\} \, d\Omega. \quad (15)$$

The expression for the free energy from which the behaviour of the nematic phase is calculated is especially complicated because it is given in its most general form. Thus it depends on 25 order parameters and 15 independent components of the expansion supertensor, u_{2mn}. Both of these numbers can be reduced by invoking the symmetry of the molecules and of the phase. As we have seen, the D_{2h} point group symmetry of the molecules and of the phase reduces the number of independent order parameters from 25 to just 4 (see (*3,42*)). In addition, the molecular D_{2h} symmetry can be used to reduce the number of independent coefficients from 15 to just 3 (see (*41*)). These are

$$\begin{aligned} &u_{200} \\ &u_{220} (\equiv u_{202} \equiv u_{2-20} \equiv u_{20-2}) \\ &u_{222} (\equiv u_{22-2} \equiv u_{2-22} \equiv u_{2-2-2}); \end{aligned} \quad (16)$$

here the D_{2h} symmetry of the molecule also ensures that terms with *m* or *n* equal to ± 1 vanish. The molar Helmholtz free energy is then simplified to

$$A/u_{200} N_A = (\tfrac{1}{2})$$
$$\times \left[\begin{array}{l} \left(\langle R_{00} \rangle^2 + 2 \langle R_{20} \rangle^2 \right) + 4\gamma(\langle R_{00} \rangle \langle R_{02} \rangle + \langle R_{20} \rangle \langle R_{22} \rangle) \\ + 4\lambda^2 \left(\langle R_{02} \rangle^2 + 2 \langle R_{22} \rangle^2 \right) \end{array} \right]$$
$$- T^* \ln Q, \quad (17)$$

where the four functions, $R_{pm}(\Omega)$, are symmetry-adapted combinations of Wigner rotation matrices (*42*):

$$R_{00}(\Omega) = D_{00}^2(\Omega),$$
$$R_{02}(\Omega) = [D_{02}^2(\Omega) + D_{0-2}^2(\Omega)]/2$$
$$R_{20}(\Omega) = [D_{20}^2(\Omega) + D_{-20}^2(\Omega)]/2 \qquad (18)$$
$$R_{22}(\Omega) = [D_{22}^2(\Omega) + D_{-2-2}^2(\Omega)$$
$$\qquad\qquad + D_{2-2}^2(\Omega) + D_{-22}^2(\Omega)]/4;$$

their averages are identical to those given in Equation (2). The relative biaxialities, γ and λ, in the molecular interaction coefficients are defined by

$$\gamma = u_{220}/u_{200} \qquad (19)$$

$$\lambda^2 = u_{222}/u_{200} \qquad (20)$$

and T^* is the scaled temperature, $k_B T/u_{200}$. The potential of mean torque used to calculate the orientational partition function is

$$U(\Omega) = - u_{200}[(\langle R_{00}\rangle + 2\gamma\langle R_{02}\rangle)R_{00}(\Omega) + 2(\gamma\langle R_{00}\rangle$$
$$+ 2\lambda^2\langle R_{02}\rangle)R_{02}(\Omega) + 2(\langle R_{20}\rangle + 2\gamma\langle R_{22}\rangle)R_{20}(\Omega)$$
$$+ 4(\gamma\langle R_{20}\rangle + 2\lambda^2\langle R_{22}\rangle)R_{22}(\Omega)]. \qquad (21)$$

These results, both for A and $U(\Omega)$, have the same form as those obtained by Straley (*3*) and much later by Sonnet *et al.* (*25*). In these theories the starting point was taken to be the pair potential for biaxial molecules with D_{2h} symmetry but restricted to just second-rank terms. Such an expansion of the pair potential seems unlikely to converge, especially in the vicinity of the nematic–isotropic phase transition (*25–27*).

The other important aspect of the variational approach is the interpretation to be placed on the expansion coefficients and their relationship to the molecular structure. As we have seen constraints can be placed on the coefficients according to the molecular symmetry (*41*). However, their relationship to the molecular structure is essentially *ad hoc* but even such *ad hoc* connections are especially important when we deal with a system containing many thousands of conformations. In concluding this section on the theory for rigid molecules we introduce some of the ideas concerning the expansion supertensor which will be of considerable value when we consider systems of flexible molecules in the following section.

One of the early attempts to relate these tensorial coefficients, u_{2mn}, actually a tensor of tensors, to the molecular structure was made by Straley (*3*). He argued that the molecular anisotropy was related to the volume excluded for one molecule by the presence of another. The excluded volume depends on the relative orientations of the two molecules and this

orientational dependence was mapped onto the S-function expansion given in Equation (6) for parallelepipeds with dimensions L, B and W, along axes z, y and x, respectively. The tensorial coefficients were found to be proportional to the following functions of these dimensions

$$u_{200} \propto \{-2B(W^2 + L^2) - 2W(L^2 + B^2)$$
$$\qquad + L(W^2 + B^2) + 8WBL\}/3,$$
$$u_{220} \propto (L^2 - BW)(B - W)/\sqrt{6}, \qquad (22)$$
$$u_{222} \propto -L(W - B)^2/2.$$

Clearly when $B = W (< L)$ the molecule has D_{4h} symmetry and so the second-rank biaxiality parameters necessarily vanish. Equally when $L = W (> B)$ the molecule again has D_{4h} symmetry and is plate-like. However, without relabelling the molecular axes the biaxiality parameters are no longer zero but take values

$$u_{220} \propto -L(L - B)^2/\sqrt{6}$$
$$u_{222} \propto -L(L - B)^2/2. \qquad (23)$$

Although the use of the excluded volume is an interesting approach to the evaluation of the tensorial coefficients it is not one that is readily applicable to more realistic molecular shapes. However, it may be possible to calculate the excluded volume for collections of spheres (*43*) which would be a significant improvement.

Even with this development, evaluating the excluded volume for truly realistic molecular shapes is not yet possible, and so obtaining the tensorial coefficients appears to demand what seems to be a dramatic approximation which we now describe. The interaction coefficients, u_{2mn}, are tensorial properties of a pair of molecules and our aim is to write them in terms of tensorial properties of single molecules. This is a familiar problem in the theory of intermolecular forces; for example, the well depth, ε_{AB}, in the Lennard–Jones potential for a pair of unlike molecules is written as the geometric mean $(\varepsilon_{AA}\varepsilon_{BB})^{1/2}$ of the well-depths for the interactions between like molecules. This is known as the Berthelot combining rule (*44*) and is found to work reasonably well. In addition, the form of the pair potentials for specific intermolecular forces such as dispersion and electrostatic quadrupolar interactions (*41*) are also consistent with the Berthelot rule although this is of greater generality. This rule has been extended to the coefficients u_{2mn} (*45*) so that u_{220} is written as the geometric mean

$$u_{220} = (u_{200}u_{222})^{1/2}; \qquad (24)$$

we return to the benefits of this approximation shortly. For now we are more concerned with the relationship to the single molecule properties and to achieve this we note that the geometric mean combining rule is consistent with the separability approximation, namely

$$u_{2mn} = u_{2m}u_{2n}, \qquad (25)$$

where u_{2m} denotes a second-rank tensorial property of a single molecule. With this approximation we are able to define a molecular biaxiality rather than that in the interaction supertensor. Thus, for the system with D_{2h} symmetry there is a single measure of the relative biaxiality which is u_{22}/u_{20} and this is equal to λ where, within the separability approximation, λ^2 is given by Equation (20).

There have been many suggestions as to which property might best be used to determine the separate tensorial coefficients. Clearly, it must be second rank and should be related to the molecular shape and anisotropy. In addition, it should be readily calculated from a realistic and not just an idealised molecular structure. The moment of inertia tensor satisfies these requirements and has been used to explain the properties of uniaxial nematics (*46*) but not always successfully. This lead to the introduction of the surface interaction parameterisation based on the principle that in a nematic, calamitic molecules will want to align so that the director is parallel to as much of the molecular surface as possible. This leads to the expression for the surface interaction tensor (*30*)

$$T_{2m} \propto -\int_S C_{2m}(\omega)\, dS, \qquad (26)$$

where ω denotes the spherical polar coordinates of the normal to the molecular surface, S, in a molecular frame and $C_{2m}(\omega)$ is a second-rank modified spherical harmonic. The surface may be defined in a variety of ways including the exposed surface of van der Waals' spheres centred on the nuclear coordinates of the molecule or the Connolly surface (*47*) generated from this, which seems preferable (*48*). The form of the surface interaction tensor is readily determined for simple objects such as a parallelepiped for which (*30*)

$$\begin{aligned} T_{20} &\propto L(B + W) - 2BW, \\ T_{22} &= T_{2-2} \propto -\sqrt{3/2}L(B - W) \end{aligned} \qquad (27)$$

and the interaction coefficients are

$$\begin{aligned} u_{200} &\propto L^2(B + W)^2 - 4WBL(B + W) + 4B^2W^2, \\ u_{220} &\propto \sqrt{3/2}[L(B - W)(L(B + W) + 2BW)], \\ u_{222} &\propto \left(3/2\right)L^2(B - W)^2, \end{aligned} \qquad (28)$$

which resemble those found from the excluded volume. There is, however, the major difference that u_{220} determined from the excluded volume is not the geometric mean of u_{200} and u_{222} obtained from the same source. Another approach to the construction of molecular tensors used to predict the order parameters and transitional properties of mesogenic molecules is to deconstruct them into their basic constituents. For typical mesogenic molecules these basic units were taken, initially, to be the mesogenic groups and the C–C bonds in the alkyl chains (*23, 24, 28*). Subsequently, it was appreciated that the agreement with experiment could be improved by the inclusion of chords which link the mid-points of adjacent C–C bonds in the chains (*29, 49*). Thus, the molecular tensor is given by

$$u_{2m} = \sum_s u_{2m}^s, \qquad (29)$$

where s denotes a segment of the molecule and the tensor components are expressed in a common axis system set in the molecule. It is, however, more useful to give the segmental components in a local axis system fixed in the segment so that the molecular tensor is given by

$$u_{2m} = \sum u_{2n}^s D_{nm}^2(\Omega_s), \qquad (30)$$

where u_{2n}^s is the tensor in the segmental frame and Ω_s denotes the Euler angles relating the segmental to the common frame. The number of adjustable parameters, the u_{2n}^s, in this model can become large depending on the molecular complexity. To reduce this number the segmental tensors are often taken to have cylindrical symmetry so that the molecular tensor u_{2m} is given by

$$u_{2m} = \sum u_{20}^s C_{2m}(\omega_s); \qquad (31)$$

here ω_s denotes the spherical polar angles made by the segmental symmetry axis in the molecular frame. This approach also has the benefit of reducing the complexity of the molecular field equations and their numerical solution.

We now return to the geometric mean approximation and the simplifications this brings to the

molecular field theory. It follows from the definitions of the relative molecular biaxialities, γ and λ^2 (see Equations (19) and (20)), that γ equals λ in the geometric mean limit. This allows us to write the potential of mean torque in Equation (21) as

$$U(\Omega) = -u_{200}(\langle F_U \rangle F_U(\Omega) + 2\langle F_B \rangle F_B(\Omega)). \quad (32)$$

Now there are just two order parameters which are combinations of the symmetry-adapted order parameters (see Equation (18))

$$\langle F_U \rangle = \langle R_{00} \rangle + 2\lambda \langle R_{02} \rangle$$

and

$$\langle F_B \rangle = \langle R_{20} \rangle + 2\lambda \langle R_{22} \rangle. \quad (33)$$

In the uniaxial nematic $\langle F_U \rangle$ is non-zero while $\langle F_B \rangle$ vanishes; both order parameters are non-zero in the biaxial nematic. The angular functions associated with the order parameters are

$$F_U(\Omega) = R_{00}(\Omega) + 2\lambda R_{02}(\Omega)$$

and

$$F_B(\Omega) = R_{20}(\Omega) + 2\lambda R_{22}(\Omega). \quad (34)$$

The reduction in the number of order parameters from four to two clearly facilitates the numerical analysis. In addition, for this form of the theory the transition from the biaxial to uniaxial nematic is found to be second order (3, 4), which simplifies the location of the transition via a bifurcation analysis (42).

3. Theory for flexible molecules

Here we use the variational approach, employed by de Gennes for uniaxial nematics (22), to develop a molecular field theory for biaxial nematics composed of flexible molecules. The origin of the flexibility is general but to fix our ideas we associate the conformational changes with the alkyl chains in the molecule. The conformational states of the chains are adequately described by the Flory rotameric state theory (50), which means that there is a finite number of discrete states. It is conceptually convenient to develop the theory using such a discrete number of conformers although it could be extended to deal with a continuous set of states described by the torsional angles within the chain. In the discrete model there is now a set of second-rank orientational order parameters for each conformer j; in general these are $\left\langle D_{pm}^2 \right\rangle_j$. We can construct the molar thermodynamic internal energy

from these and this is taken to have a form analogous to that for a multicomponent mixture of nematogens (51). That is, there will be contributions from interactions between identical conformers as well as different conformers. Thus,

$$\langle U \rangle = -(N_A/2) \sum p_j p_k u_{2mn}^{jk} \left\langle D_{pm}^2 \right\rangle_j \left\langle D_{-pn}^2 \right\rangle_k, \quad (35)$$

where p_j is the relative amount of conformer j and u_{2mn}^{jk} is the tensorial interaction coefficient for conformers j and k. Although the internal energy in Equation (35) has the form expected for a multicomponent mixture there is one significant difference between this system and a collection of conformers. Since the conformers are interconverting the system cannot undergo phase separation (52) unlike the multicomponent mixture which, since the transition is first order, can separate into coexisting nematic and isotropic phases (53).

There is an additional contribution to the internal energy which comes, in large part, from the conformational energy. This takes the form

$$\langle U_{\text{conf}} \rangle = N_A \sum p_j u_{\text{conf}}^j \quad (36)$$

and controls, to a certain extent, the conformational distribution, p_j. There is, however, an additional contribution from the scalar interaction, u_0^{jk}, between the conformers. For mixtures of rigid molecules this term is not important because the concentrations of the components in the isotropic and nematic phases are the same. Of course, if the mixture undergoes a transition into coexisting nematic and isotropic phases, necessarily with different compositions, then the scalar interactions between the components will be of significance for the coexisting phases. In general, however, when the mixture exists in a single phase the composition does not change. Significantly, this is not the case for systems with flexible molecules, as the conformational distribution can change with the orientational order of the nematic phases, which will favour the more anisometric conformers (54). It does not prove to be possible to allow exactly for the scalar interaction energy, but, to a reasonable approximation, it can be included by using a dressed conformational energy, $\tilde{u}_{\text{conf}}^j$ (23). This is defined by

$$\tilde{u}_{\text{conf}}^j = u_{\text{conf}}^j + u_0^{jj}, \quad (37)$$

based on approximating the mixed scalar interaction, u_0^{jk}, by $(u_0^{jj} + u_0^{kk})/2$. The total molar internal energy that we need to construct the molar Helmholtz free energy is then

$$\langle U_{anis}\rangle + \langle U_{\text{conf}}\rangle = -(N_A/2)\sum p_j p_k u_{2mn}^{jk}\langle D_{pm}^2\rangle_j$$
$$\times \langle D_{-pn}^2\rangle_k + N_A \sum p_j \tilde{u}_{\text{conf}}^j. \quad (38)$$

The entropy is also made of two contributions; one comes from the singlet orientational distribution functions for each of the conformers, $f_j(\Omega)$, and the other from the conformational distribution function, p_j. The total molar entropy is

$$S = -R\sum\left\{p_j\int f_j(\Omega)\ln f_j(\Omega)\,d\Omega + p_j\ln p_j\right\}; \quad (39)$$

the conformational entropy or entropy of mixing results because the p_j change with the orientational order of the nematics.

The molar Helmholtz free energy is given by

$$A = -(N_A/2)\sum p_j p_k u_{2mn}^{jk}\langle D_{pm}^2\rangle_j\langle D_{-pn}^2\rangle_k$$
$$+ N_A\sum p_j\tilde{u}_{\text{conf}}^j$$
$$+ RT\sum\left\{p_j\int f_j(\Omega)\ln f_j(\Omega)d\Omega + p_j\ln p_j\right\}. \quad (40)$$

The orientational distribution functions, $f_j(\Omega)$, and the conformational distribution functions, p_j, are all unknown. However, their optimum forms can be determined by minimising the free energy with respect to both $f_j(\Omega)$ and p_j. This functional minimisation must be performed subject to the constraints that the distribution functions are normalised and that the orientational order parameters are related to the distribution functions; that is,

$$\int f_j(\Omega)\,d\Omega = 1,$$

$$\sum p_j = 1,$$

$$\int D_{pm}^2(\Omega)f_j(\Omega)\,d\Omega = \langle D_{pm}^2\rangle_j. \quad (41)$$

The singlet distribution functions, both orientational and conformational, obtained in this way are

$$f_k(\Omega) = Q_k^{-1}\exp\left\{(1/k_BT)\sum p_j u_{2mn}^{jk}\langle D_{pm}^2\rangle_j D_{-pn}^2(\Omega)\right\}, \quad (42)$$

where the orientational partition function for conformer, k, is

$$Q_k = \int\exp\left\{(1/k_BT)\sum p_j u_{2mn}^{jk}\langle D_{pm}^2\rangle_j D_{-pn}^2(\Omega)\right\}d\Omega. \quad (43)$$

The conformational distribution is found to be

$$p_k = Z^{-1}\exp\left(-\tilde{u}_{\text{conf}}^k/k_BT\right)Q_k, \quad (44)$$

where the conformational–orientational partition function is

$$Z = \sum\exp\left(-\tilde{u}_{\text{conf}}^k/k_BT\right)Q_k. \quad (45)$$

In the isotropic phase the orientational partition functions are all equal and so the conformational distribution is determined solely by the dressed conformational energy, $\tilde{u}_{\text{conf}}^k$. In the nematic phase the orientational partition functions, Q_k, will differ and the difference will increase with increasing orientational order; consequently the conformational probabilities will vary, often significantly, with decreasing temperature. The precise magnitude of this variation will depend on the major tensor component for the conformer, u_{20}^k, as well as its relative biaxiality, λ_k, but it is expected that the more anisometric conformers will be favoured (*54*). It remains to be seen to what extent the molecular biaxiality will couple to the biaxial order of the phase and so enhance the fraction of biaxial conformers and stabilise the phase. The orientational ordering tensors for the conformers are found from the singlet orientational distribution function to be

$$\langle D_{pn}^2\rangle_k = Q_k^{-1}\int D_{pn}^2(\Omega)$$
$$\times\exp\left[(1/k_BT)\sum p_j u_{2mn}^{jk}\langle D_{pm}^2\rangle_j D_{-pn}^2(\Omega)\right]d\Omega, \quad (46)$$

which is a consistency equation for the components of the ordering tensor. The Helmholtz free energy is obtained from Equation (40) by substituting for the distribution functions given in Equations (42) and (44). Armed with these key equations it is possible, in principle, to determine the orientational order parameters (see Equation (46)) and conformational distribution (see Equation (44)) as a function of temperature, to locate the phase transitions and determine their order (see Equations (40), (42) and (44)). The equations are, however, tightly coupled and their numerical solution for a significant number of conformers is computationally demanding.

The problem is compounded by the fact that for real mesogenic systems many, if not all, of the conformers will have low symmetry. This implies that a range of

biaxial phases will be formed (*40*) and that the most stable of these will also have low symmetry. This view is based on the reasonable conjecture that for such systems the molecular symmetry will determine that of the most stable nematic phase; above this phase, nematics with higher symmetry may appear. In the most intriguing or worst possible case this would mean that 25 components of the ordering tensor, $\langle D^2_{pm}\rangle$, would be needed to define the orientational order, even at the second-rank level. In addition, for interactions between different conformers with C_1 symmetry there are 25 independent expansion coefficients, u^{jk}_{2mn}. When the conformers are identical but still have C_1 point group symmetry there are fifteen independent coefficients (*41*). With such a large number of independent order parameters and expansion coefficients the problem is certainly intriguing but numerically formidable. However, these problems can be removed if we use the separability approximation for the coefficients, u_{2mn}.

By invoking separability we can write

$$u_{2mn} = u_{2m}u_{2n}, \qquad (47)$$

but because the u_{2m} are second-rank tensors, their Cartesian form can always be diagonalised since they are both real and symmetric. In addition, because this Cartesian tensor is traceless there are just two independent elements which in irreducible tensor form are u_{20} and $u_{22}(\equiv u_{2-2})$. The molecular tensor, in its principal axis system, has the same form as if the conformer had possessed D_{2h} point group symmetry. Accordingly, it is also to be expected that the conformers will behave, as far as their molecular field interactions are concerned, as if they had D_{2h} symmetry (*55*). Then, for identical conformers, there will be just three independent coefficients u^{jj}_{200}, $u^{jj}_{220}(\equiv u^{jj}_{2-20}\equiv u^{jj}_{202}\equiv u^{jj}_{20-2})$ and $u^{jj}_{222}(\equiv u^{jj}_{2-22}\equiv u^{jj}_{22-2}\equiv u^{jj}_{2-2-2})$. When the *j*th and *k*th conformers differ there are four independent coefficients; these are u^{jk}_{200}, $u^{jk}_{220}(\equiv u^{jk}_{2-20})$, $u^{jk}_{202}(\equiv u^{jk}_{20-2})$, $u^{jk}_{222}(\equiv u^{jk}_{2-2-2}\equiv u^{jk}_{22-2}\equiv u^{jk}_{22-2})$. The D_{2h} point group symmetry, associated with the anisotropic molecular interactions, will mean that there will be just a single biaxial nematic phase which will also have D_{2h} symmetry. Accordingly there will be just four independent components for the ordering tensor of each conformer, as listed in Equation (2). Armed with these considerable simplifications resulting from the separability approximation we now return to the potential of mean torque implicit in Equation (42). This can be written for the uniaxial phase in the simpler form

$$U_k(\Omega) = -\sum \langle F_U\rangle_{\text{mixt}} u^k_{2n} D^2_{0n}(\Omega), \qquad (48)$$

where the strength of the molecular field responsible for the orientational order of the *k*th conformer is

$$\langle F_U\rangle_{\text{mixt}} = \sum p_j u^j_{2m}\langle D^2_{0m}\rangle_j. \qquad (49)$$

In view of the constraints on the ordering tensor $\langle D^2_{om}\rangle$, this composite order parameter may be written as

$$\langle F_U\rangle_{\text{mixt}} = \sum p_j\left(u^j_{20}\langle R_{00}\rangle_j + 2u^j_{22}\langle R_{02}\rangle_j\right) \qquad (50)$$

and the potential of mean torque becomes

$$U_k(\Omega) = -\left[\langle F_U\rangle_{\text{mixt}}\{u^k_{20}R_{00}(\Omega) + 2u^k_{22}R_{02}(\Omega)\}\right]. \qquad (51)$$

The two contributing order parameters for the *k*th conformer in the uniaxial nematic are

$$\langle R_{00}\rangle_k = Q_k^{-1}\int R_{00}(\Omega)\exp\Big[(\langle F_U\rangle_{\text{mixt}}/k_BT) \times \{u^k_{20}R_{00}(\Omega)+2u^k_{22}R_{02}(\Omega)\}\Big]d\Omega$$

and

$$\langle R_{02}\rangle_k = Q_k^{-1}\int R_{02}(\Omega)\exp\Big[(\langle F_U\rangle_{\text{mixt}}/k_BT) \times \{u^k_{20}R_{00}(\Omega) + 2u^k_{22}R_{02}(\Omega)\}\Big]d\Omega. \qquad (52)$$

In the numerical analysis based on these equations, the ratio $\langle F_U\rangle_{\text{mixt}}/k_BT$ is assigned a given value and the order parameters for the *k*th conformer in the uniaxial phase are calculated from Equation (52). To do this, the principal components of the molecular tensor, u^k_{20} and u^k_{22}, are calculated from the geometry of the conformer. In evaluating the order parameters the orientational partition function, Q_k, is obtained; this is then used together with the dressed conformational energy, $\tilde{u}^k_{\text{conf}}$, to determine the conformational probability, p_k (see Equation (44)). Armed with these results for all of the conformers, the composite order parameter for the system, $\langle F_U\rangle_{\text{mixt}}$, can be calculated via Equation (50). This together with the value for $\langle F_U\rangle_{\text{mixt}}/k_BT$ can be employed to give the scaled temperature, k_BT/u^{jj}_{200}, for which the order parameters and the conformational probabilities have been calculated; the scaling coefficient, u^{jj}_{200}, is conveniently chosen to be the largest, that is, for the most anisometric conformer. The nematic–isotropic transition temperature is then determined from the molar Helmholtz free energy which is obtained from Equations (40), (42)–(45) as

$$A = (N_A/2)\langle F_U\rangle^2_{\text{mixt}} - RT\ln Z. \qquad (53)$$

The composite order parameter, $\langle F_U\rangle_{\text{mixt}}$, for the uniaxial nematic is defined by Equation (50) and Z is the orientational–conformational partition function given

by Equation (45). The individual orientational partition functions occurring in Z are defined by

$$Q_k = \int \exp\left[(\langle F_U \rangle_{\text{mixt}}/k_B T)\{u_{20}^k R_{00}(\Omega) \right.$$
$$\left. + 2u_{22}^k R_{02}(\Omega)\}\right] d\Omega. \tag{54}$$

We now turn to the location of the transition to the biaxial nematic phase. On entry to the biaxial nematic phase with D_{2h} symmetry, two new order parameters are introduced for each conformer; these are $\langle R_{20}^2 \rangle_k$ and $\langle R_{22}^2 \rangle_k$, defined implicitly in Equation (18). Here we have introduced a superscript 2 to emphasise that they are combinations of second-rank Wigner functions, since we shall encounter their fourth-rank counterparts shortly. The potential of mean torque given in Equation (51) for the kth conformer in the uniaxial nematic was obtained from the more general potential in Equation (42) by using the powerful separability approximation. The same approach can be used to determine the additional terms that appear in the biaxial nematic. Now the total potential of mean torque is

$$U_k(\Omega) = -\left[\langle F_U \rangle_{\text{mixt}}\{u_{20}^k R_{00}^2(\Omega) + 2u_{22}^k R_{02}^2(\Omega)\}\right]$$
$$- \left[2\langle F_B \rangle_{\text{mixt}}\{u_{20}^k R_{20}^2(\Omega) + 2u_{22}^k R_{22}^2(\Omega)\}\right], \tag{55}$$

where $\langle F_B \rangle_{\text{mixt}}$ is the contribution to the strength of the molecular field resulting from the phase biaxiality; this strength parameter is defined by

$$\langle F_B \rangle_{\text{mixt}} = \sum p_j \left(u_{20}^j \langle R_{20}^2 \rangle_j + 2u_{22}^j \langle R_{22}^2 \rangle\right). \tag{56}$$

The strategy employed previously to determine the order parameters, conformational probabilities and phase transition for the uniaxial nematic is not possible for the biaxial nematic. This is because the strengths, $\langle F_U \rangle_{\text{mixt}}$ and $\langle F_B \rangle_{\text{mixt}}$, of the two contributions to the molecular field in the biaxial phase depend on different combinations of order parameters (see Equations (50) and (56)) and so will vary differently with temperature. In principle, it might be possible to determine the values of the order parameters that minimise the molar Helmholtz free energy which is

$$A = (N_A/2)(\langle F_U \rangle_{\text{mixt}}^2 + 2\langle F_B \rangle_{\text{mixt}}^2) - RT\ln Z, \tag{57}$$

where the partition functions in Z now depend on the biaxial as well as the uniaxial order. While this determination is certainly possible when the number of conformers is relatively small, it is numerically challenging for the large number of conformers expected for many of the mesogenic molecules of interest. We have, therefore, adopted an alternative strategy which takes advantage of the observation that for systems in which the interaction coefficients are separable the transitions to the biaxial nematic are second order (4). The transition to the biaxial nematic can be identified, therefore, as the point at which the biaxial order emerges continuously from zero; this temperature is evaluated readily in the following manner from molecular field theory. To determine the biaxial order parameter or molecular field strength, $\langle F_B \rangle_{\text{mixt}}$, for the mixture, we need the biaxial order parameters for the various conformers. These are given within the molecular field theory by

$$\langle R_{20}^2 \rangle_k = Q_k^{-1} \int R_{20}^2(\Omega) \exp\left[\left(\langle F_U \rangle_{\text{mixt}}/k_B T\right) \right.$$
$$\times \{u_{20}^k R_{00}^2(\Omega) + 2u_{22}^k R_{02}^2(\Omega)\}$$
$$\times \left(2\langle F_B \rangle_{\text{mixt}}/k_B T\right)$$
$$\left. \times \{u_{20}^k R_{20}^2(\Omega) + 2u_{22}^k R_{22}^2(\Omega)\}\right] d\Omega, \tag{58}$$

with an analogous expression for $\langle R_{22} \rangle_k$. Since the biaxial order is small in the vicinity of the transition from the biaxial to the uniaxial nematic the part of the Boltzmann factor involving $\langle F_B \rangle_{\text{mixt}}$ can be expanded and truncated at the second term. This gives

$$\langle R_{20}^2 \rangle_k = \left(2\langle F_B \rangle_{\text{mixt}}/k_B T\right) Q_k^{-1}$$
$$\times \int \{u_{20}^k R_{20}^2(\Omega) R_{20}^2(\Omega)$$
$$+ 2u_{22}^k R_{20}^2(\Omega) R_{22}^2(\Omega)\}$$
$$\times \exp\left[\left(\langle F_U \rangle_{\text{mixt}}/k_B T\right) \right.$$
$$\left. \times \{u_{20}^k R_{00}^2(\Omega) + 2u_{22}^k R_{02}^2(\Omega)\}\right] d\Omega. \tag{59}$$

The Boltzmann factor is now just that for the uniaxial nematic and in this limit of low biaxial order the orientational partition function, Q_k^{-1}, may also be approximated by that for the uniaxial phase. The products of the $R_{mn}^2(\Omega)$ functions can be written as single R functions by using the product rule for Wigner functions (39)

$$D^2_{pm}(\Omega)D^2_{qn}(\Omega) = \Sigma C(22L; pq)C(22L; mn)D^L_{p+q,m+n}(\Omega) \tag{60}$$

to give a sum of single Wigner functions. Here $C(22L; pq)$ is a Clebsch–Gordan coefficient and L takes values from zero to four. It is apparent that the averages in Equation (59) taken over the uniaxial nematic will yield order parameters of rank zero, two and four; the odd rank averages will vanish because the phase is non-polar. Combining the Wigner functions we obtain

$$\langle R^2_{20}\rangle_k = (\langle F_B\rangle_{mixt}/k_BT)\{u^k_{20}((1/5) \\ -(2/7)\langle R^2_{00}\rangle_k + (3/35)\langle R^4_{00}\rangle_k) \\ +u^k_{22}((4/7)\langle R^2_{02}\rangle_k + (1/7)\sqrt{3/5}\langle R^4_{02}\rangle_k)\} \tag{61}$$

where the functions $R^2_{00}(\Omega)$ and $R^2_{02}(\Omega)$ are defined in Equation (18). The fourth-rank functions are given by

$$R^4_{00}(\Omega) = D^4_{00}(\Omega) = (35\cos^4\beta - 30\cos^2\beta + 3)/8,$$
$$R^4_{02}(\Omega) = [D^4_{02}(\Omega) + D^4_{0-2}(\Omega)]/2 \\ = (\sqrt{10}/8)(-7\cos^4\beta + 8\cos^2\beta - 1)\cos 2\gamma,$$
$$R^4_{04}(\Omega) = [D^4_{04}(\Omega) + D^4_{0-4}(\Omega)]/2 \\ = (\sqrt{70}/16)(\cos^4\beta - 2\cos^2\beta - 1)\cos 4\gamma. \tag{62}$$

Similarly the other biaxial order parameter obtained in the limit of low biaxial order is

$$\langle R^2_{22}\rangle_k = (\langle F_B\rangle_{mixt}/k_BT)\{2u^k_{20}((2/7)\langle R^2_{02}\rangle_k \\ + (1/14)\sqrt{3/5}\langle R^4_{02}\rangle_k) + u^k_{22}((1/10) \\ + (1/70)\langle R^4_{00}\rangle_k + \sqrt{1/70}\langle R^4_{04}\rangle_k)\} \tag{63}$$

From such order parameters we can construct the strength of the biaxial molecular field as

$$\langle F_B\rangle_{mixt} = (\langle F_B\rangle_{mixt}/k_BT)\Sigma p_k u^{kk}_{200}\left\{\frac{1 + 2\lambda_k^2}{5} \\ + \left(\frac{-2 + 4\lambda_k^2}{7}\right)\langle R^2_{00}\rangle_k + \frac{8}{7}\lambda_k\langle R^2_{02}\rangle_k \\ + \left(\frac{3 + \lambda_k^2}{35}\right)\langle R^4_{00}\rangle_k + \frac{2}{7}\sqrt{\frac{3}{5}}\lambda_k\langle R^4_{02}\rangle_k \\ + \sqrt{\frac{2}{35}}\lambda_k^2\langle R^4_{04}\rangle_k\right\}. \tag{64}$$

The molecular field parameter $\langle F_B\rangle_{mixt}$ can be cancelled and we can remove one of the major uniaxial interaction coefficients, u^{jj}_{200}, to scale the temperature as we did for the uniaxial nematic. This gives

$$k_BT\Big/u^{jj}_{200} = \Sigma p_k\varepsilon_{jk}^2\left\{\frac{1 + 2\lambda_k^2}{5} \\ + \left(\frac{-2 + 4\lambda_k^2}{7}\right)\langle R^2_{00}\rangle_k \\ + \frac{8}{7}\lambda_k\langle R^2_{02}\rangle_k + \left(\frac{3 + \lambda_k^2}{35}\right)\langle R^4_{00}\rangle_k \\ + \frac{2}{7}\sqrt{\frac{3}{5}}\lambda_k\langle R^4_{02}\rangle_k \\ + \sqrt{\frac{2}{35}}\lambda_k^2\langle R^4_{04}\rangle_k\right\}, \tag{65}$$

where ε_{jk} is the ratio, u^k_{20}/u^j_{20}, of the uniaxial components of the molecular tensor for conformers k and j. The biaxial–uniaxial nematic transition occurs when the scaled temperature is equal to the weighted sum of the second- and fourth-rank order parameters evaluated in the uniaxial nematic phase.

4. Conclusions

We have developed a molecular field theory for biaxial nematics composed of flexible molecules, made more convincing by the use of the de Gennes variational approach (*22*). The theory is not specific to any particular origin of the flexibility but the most likely cause would be conformational changes resulting from rotations about the carbon–carbon bonds in the constituent alkyl chains. These rotations will produce especially large changes in the molecular anisotropy when the chains link different mesogenic groups. The general version of the theory is particularly complicated because the conformers are of low symmetry, there is a large number of them and biaxial nematic phases with D_{2h}, C_{2h} and C_1 point group symmetry may be formed (*40*).

These non-trivial problems have been removed by assuming that the interaction supertensors can be written as products of single molecule property tensors. Since these are second rank they can be cast in diagonal form and so, as far as the anisotropic interactions are concerned, the conformers behave as if they have D_{2h} point group symmetry. A variety of properties can be chosen to construct the supertensor using the separability approximation, but one that is readily evaluated for realistic conformations is the surface interaction tensor (*30*). This then allows the interactions between the numerous conformers to be calculated and employed in the determination of the phase diagram. Whereas the N_U–I transition temperature may be calculated directly from the free energy, that for the N_B–N_U transition is obtained via a bifurcation analysis. This is non-trivial and requires that the transition is second order. The use of the

separability approximation will ensure that this is the case provided that the conformational distribution function does not undergo a discontinuous change as it does for a highly specialised model uniaxial nematic in which only two conformers are allowed, namely linear and bent (*52*). The way now seems to be open to use this simplified version of the general molecular field theory to explore the formation of the biaxial nematic phase by mesogenic molecules with significant flexibility, such as dendrimers (*13*), dimers (*17, 19, 20*) and a cyclic system (*16*).

The theory that we have presented can be extended in a variety of ways. The most important of these is to remove the separability approximation; for example, by relating the tensorial interaction coefficients to the excluded volumes of pairs of conformers. This will introduce a range of challenges, not least of which will be the determination of the orientational order parameters for all conformers from the molecular field free energy or from the consistency equations. An alternative variation to the theory would be to simplify it by setting the minor orientational order parameters, $\langle R_{20}^2 \rangle_k$ and $\langle R_{02}^2 \rangle_k$, for the conformers equal to zero. This is equivalent to neglecting the interaction coefficients, u_{2mn}^{jj} and u_{2mn}^{jk} which have either m or n equal to zero; this would, in effect, extend the Sonnet–Virga–Durand model (*25*) to flexible systems. Paradoxically, this simplification of the theory for flexible mesogens would be expected to result in richer phase behaviour with the possibility of tricritical behaviour at the N_B–N_U transition and direct transitions from the isotropic to the biaxial nematic phase, as found for a single-component rigid system (*25*).

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