

Molecular field theory for biaxial nematic liquid crystals composed of molecules with C_{2h} point group symmetry

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(Received 20 December 2010; published 8 July 2011)

The biaxial nematic phase is generally taken, either explicitly or implicitly, to have D_{2h} point group symmetry. However, it is possible for the biaxial phase to have a lower symmetry depending on that of its constituent molecules. Here we develop a molecular field theory for a nematogen composed of C_{2h} molecules in terms of the nine independent second rank orientational order parameters defining the C_{2h} biaxial nematic. In addition, there is a rank one order parameter constructed from two pseudovectors which is only nonzero in the C_{2h} phase. The theory is simplified by removing all but the three dominant order parameters. The predicted phase behavior is found to be rich with three possible biaxial nematic phases and with the transitions involving a biaxial nematic phase exhibiting tricritical points.

DOI: [10.1103/PhysRevE.84.011704](https://doi.org/10.1103/PhysRevE.84.011704)

PACS number(s): 61.30.Gd, 64.70.M–, 61.30.Cz

I. INTRODUCTION

Studies of thermotropic biaxial nematic liquid crystals continue to intrigue, frustrate, and excite. For example, it has long been appreciated that there should be more than one type of biaxial nematic each with a different point group symmetry. Recently, however, it has been shown how NMR spectroscopy might be used to distinguish between biaxial nematic phases with different point group symmetries; in particular those with D_{2h} and C_{2h} symmetries [1]. Here we refer to the symmetry of the singlet orientational distribution function and not to the translational pair distribution function [2]. The original prediction of the existence of biaxial nematic phases was based on a molecular field theory analysis which assumed implicitly that the molecules and hence the phase could have D_{2h} point group symmetry [3]. Subsequent theories have made this assumption explicit [4,5]. However, just three years after Freiser's seminal work Boccara [6] in 1973 noted that nematic liquid crystals could exist in a wide range of possible symmetries. These are C_n , C_{nv} , D_n , C_{nh} , D_{nh} , S_{2n} , and D_{nd} where n is an integer. In addition, the influence of the phase symmetry on the components of tensors representing its properties was also considered. Indeed this analysis mimicked, in part, that presented by Bhagavantam and Suryanarayana [7] for the relationship between the orientational symmetry of crystals and their tensorial properties.

The first molecular field theory of the biaxial nematic phase to make explicit use of the D_{2h} point group symmetry of the constituent molecules and the ground state phase was presented by Straley [4]. He also noted that nematic phases with lower symmetry would also be formed by molecules with the same low symmetry. However, he did not take this idea further. In their paper describing the symmetries of liquid crystal phases Goshen *et al.* [8] have returned to

the question of the symmetries allowed for biaxial nematic phases and added tetrahedral and octahedral to those given by Boccara [6]. The nature of topological defects in nematics depends on the phase symmetry and in considering these Mermin [9], in his review of the theory of defects, noted that there was no reason why only biaxial nematics with D_{2h} point group symmetry need to be considered. He pointed out that the defects in the other biaxial nematics would also be different but he did not pursue this interesting idea.

The influence of the symmetry of biaxial nematics on their hydrodynamic behavior, both static and dynamic, has been examined by Liu [10] who considered a range of other phase symmetries. In addition to the standard D_{2h} he also included triclinic C_1 and C_i as well as the less familiar biaxial phases with symmetries D_{6h} , C_{6v} , C_{6h} , C_6 , D_6 , D_{3h} , and C_{3h} . These phases are distinguished by the different numbers of independent elastic constants and viscosity coefficients that they possess. An analogous study of the hydrodynamic theory of biaxial nematics has been performed by Kini [11]; this includes the flexoelectric polarization resulting from deformations of the director field. Here the phase symmetries considered are monoclinic, C_2 , C_{2h} , and C_s , in addition to the triclinic, C_1 and C_i . The parameters, elastic, viscous, and flexoelectric, required for each of the biaxial phases were determined.

The work by Mettout *et al.* [12] is of more direct relevance because it is one of the first papers to describe a theory of biaxial nematic liquid crystals in which the molecular symmetry and hence that of the phase is lower than D_{2h} . This development was prompted by the experimental observation of a polar biaxial nematic phase formed by a semirigid thermotropic liquid crystal polymer of hydroxybenzoic acid and hydroxynaphthoic acid [13]. The theory is based on a Landau approach and for this the dominant orientational order parameters were identified as first rank; for the assumed C_s symmetry of the molecules there are six order parameters. Based on this the Landau theory predicts the formation of a polar uniaxial nematic, that is with $C_{\infty v}$ symmetry; and a polar biaxial nematic phase with C_s symmetry. Introduction of a

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second rank ordering tensor into the theory clearly increases the number of order parameter invariants, expansion coefficients, and hence the complexity. Indeed the theory predicts the existence of nematic phases with point group symmetries $D_{\infty h}$, $C_{\infty v}$, D_{2h} , C_{2v} , C_s , and, perhaps surprisingly, C_1 .

The discovery by Niori *et al.* of the banana phases [14] and the ensuing experimental studies prompted Lubensky and Radzihovsky [15] to propose a Landau theory of the phases and the transitions between them. When formulating the orientational order parameters the V-shaped or bent-core molecules were taken to have C_{2v} point group symmetry; the phase symmetry was taken from experiment. Thus for the uniaxial nematic with $D_{\infty h}$ symmetry just a single quadratic order parameter is needed. However, for this phase to undergo a transition to a uniaxial polar nematic with $C_{\infty v}$ symmetry a polar or vector order parameter is required together with a third rank tensor. This third rank tensor is introduced because it is essential for the description of the spontaneously ordered chiral phases with point group symmetries D_2 and C_2 . The set of three order parameters, first, second, and third rank, is able to describe a host of nematic phases which also includes those with point group symmetries D_{3h} , C_{3v} , D_{2d} , and C_{1h} . Also of relevance are the tensor order parameters which are needed to create these order parameters from phases with higher symmetry. Of particular interest for the bent-core mesogens is the transition from a biaxial nematic with D_{2h} symmetry to an achiral nematic with symmetry D_2 where the mesophase separates into domains of opposite handedness separated by domain walls. The extensive and detailed analysis presented by Lubensky and Radzihovsky [15] is aided by the use of pictorial representations to show the idealized organization in the different phases and their change at the phase transitions.

The major challenge of working on a theory for bent-core molecules has also been addressed by Mettout [16] who used a single second rank ordering tensor. As a result he was not able to predict the rich polymorphism found by Lubensky and Radzihovsky [15]. However, they did miss the biaxial nematic phase having C_{2h} point group symmetry and this was noted by Mettout [16]. In his own paper he was primarily concerned with so-called conventional nematics, that is those with weakly biaxial molecules and unconventional nematics with molecules having a more pronounced biaxiality such as the bent-core mesogens. He points out that for unconventional mesogens there are two second rank tensorial order parameters. For the principal axes of these to coincide within the biaxial nematic phase then this requires the phase to possess D_{2h} symmetry. If, however, only one of the principal axes for the two tensors coincide then the biaxial nematic has C_{2h} point group symmetry and when none of the principal axes coincide the phase symmetry is C_i . The origin of the driving force for the change in symmetry from D_{2h} to C_{2h} and then C_i was not explained. Indeed the fact that the phase symmetry C_{2h} and C_i is lower than that of the constituent molecules is puzzling and was not commented on. Indeed it might have been expected that the molecular symmetry should be the same or lower than the liquid crystal phases that are formed.

Developing a molecular theory for biaxial nematic phases formed by real mesogenic molecules is an especially challenging task. This obtains because the molecules are invariably

nonrigid and the conformers are of low symmetry. This challenging task has been tackled by Mettout [17] albeit in the rigid-molecule limit. In his novel approach he introduces the concept of an effective molecular symmetry; this is defined by considering the effect of the true molecular symmetry on the elements of an orientational ordering tensor. This tensor is taken to be the average of a Wigner function $\langle D_{pm}^L \rangle$ of rank L , although the tensor is often taken to be second rank. As an example, when the molecular symmetry is D_{4h} then the nonzero order parameters would be $\langle D_{p0}^2 \rangle$. This would also occur if the molecules have the higher point group symmetry of $D_{\infty h}$ which would be identified as the effective molecular symmetry. With this effective symmetry it might be expected that such molecules would only exhibit a uniaxial nematic phase. However, Mettout [17] indicates that they should also form a biaxial nematic with D_{2h} point group symmetry. Clearly to establish the symmetry of the nematic phase some model theory is needed. This is appreciated by Mettout although he does not describe the use of such an approach to determine the symmetries of the stable nematic phases found for molecules with a particular effective symmetry. For a group of symmetry classes for the constituent molecules such as D_{2h} and still retaining a second rank ordering tensor to characterize the effective symmetry it is apparent that this is the same as the real molecular symmetry. It might have been anticipated that the phase symmetry of this system in its ground state would also be D_{2h} . Again Mettout suggests that the phase symmetry of the ground state could be lower, that is C_{2h} .

There would seem to be some doubt as to whether lowering the molecular symmetry from D_{2h} to C_{2h} point group symmetry is necessary for the creation of the C_{2h} biaxial nematic phase. However, it is certainly to be expected that the ground state nematic structure constituted of molecules with C_{2h} symmetry should also have the same symmetry. At a higher temperature the C_{2h} biaxial nematic could undergo a transition to a biaxial nematic with D_{2h} symmetry. A sketch showing the idealized organization of molecules with C_{2h} symmetry in these two biaxial nematic phases is shown in Fig. 1. The key feature in these sketches is the orientation of the constituent molecules and not their translational distribution. Following the ideas of Lubensky and Radzihovsky [15] it is of interest to consider an average structure for the molecules in the different phases. Thus in the D_{2h} biaxial nematic phase there are two types of molecule which are related by a 180° rotation about the molecular x axis, a so-called internal rotation [16]. The addition of these two gives a structure with D_{2h} point group symmetry having an H-shaped cross section in the xy plane [see Fig. 1(c)].

The ability to identify a biaxial nematic unambiguously has proved to be a major problem in the study of this intriguing phase [18,19]. In view of the subtleties in the differences between nonpolar biaxial nematics with C_{2h} and D_{2h} symmetries as well as C_i the identification of these new biaxial nematics promises to present even greater problems [1]. To help in this challenging task we have developed a molecular field theory for the phases, isotropic, uniaxial nematic, biaxial nematic both D_{2h} and C_{2h} formed by molecules with C_{2h} symmetry. In this way we hope to contribute to our understanding of thermotropic biaxial nematics and their investigation. The results of our theoretical studies are described in this paper.

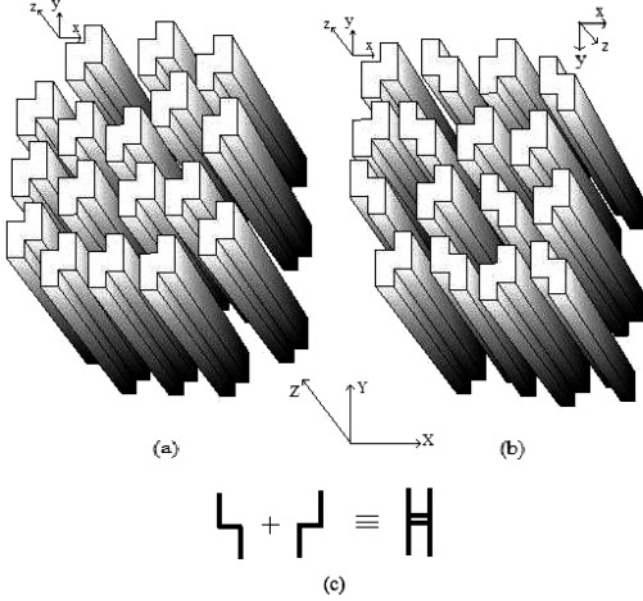


FIG. 1. A sketch of the idealized organization of elongated molecules with C_{2h} point group symmetry in a biaxial nematic phase with (a) C_{2h} symmetry and (b) D_{2h} symmetry. The coordinate systems are those for the phase (XYZ) and for the molecule (xyz). (c) The cross sections of the average molecular structure formed by combining two molecular orientations.

We note that we shall not consider the possible formation of a biaxial nematic phase with C_i symmetry here. As we shall see, the problem we have set ourselves is already a challenging task and so we defer its extension to include the triclinic biaxial nematic until later.

We begin in Sec. II with the orientational order parameters used to characterize the nematic phases formed by the biaxial molecules. In Sec. III these are then employed together with the intermolecular interaction coefficients allowed by the molecular symmetry [20] to construct the internal energy of the phases. A variational analysis analogous to that proposed by de Gennes [21] for uniaxial molecules in a uniaxial phase is then used to determine the potential of mean torque and the anisotropic Helmholtz free energy. The somewhat involved forms for these are subsequently simplified by reducing the number of order parameters and intermolecular interaction coefficients to just three for each which is sufficient to characterize the three nematic phases. These conventional second rank order parameters are found to be augmented by a new order parameter based on a rank one Wigner function but with a pseudovector character. We end with a description and discussion of the phases, as well as the transitions between them, predicted by the simplified or truncated model.

II. ORDER PARAMETERS

The orientational order parameters are defined as the averages of the Wigner functions $D_{pm}^2(\Omega)$, where Ω denotes the Euler angles α, β, γ , linking the molecular and laboratory frames [2]. The molecular axis z is defined as the twofold rotation axis and x and y are in the mirror plane orthogonal to z . It is convenient to take these axes to be those that evolve, without rotation, into the other twofold rotation axes when the

molecule is changed from C_{2h} to D_{2h} point group symmetry. In our model this would correspond to the two outer boards constituting the molecule overlapping exactly (see Fig. 1). In the biaxial nematic phase, also with C_{2h} symmetry, Z corresponds to the twofold rotation axis and X and Y are the axes in the mirror plane orthogonal to Z . At the transition to the D_{2h} biaxial nematic the X and Y axes would transform into the axes with twofold rotational symmetry. In these axis systems the order parameters $\langle D_{pm}^2 \rangle$ with $p, m = \pm 1$ vanish and the remaining independent order parameters are $\langle D_{00}^2 \rangle$, $\langle D_{02}^2 \rangle$, and $\langle D_{-2}^2 \rangle$. The first label refers to the phase and so these three order parameters appear when the uniaxial nematic phase is formed. They remain in the biaxial nematic phase and are joined by six more $\langle D_{20}^2 \rangle$, $\langle D_{-20}^2 \rangle$, $\langle D_{22}^2 \rangle$, $\langle D_{-22}^2 \rangle$, $\langle D_{-2-2}^2 \rangle$, and $\langle D_{2-2}^2 \rangle$, when this phase has C_{2h} symmetry. If, however, the biaxial nematic has D_{2h} symmetry then some order parameters become equal, namely

$$\langle D_{20}^2 \rangle = \langle D_{-20}^2 \rangle, \quad (1)$$

$$\langle D_{22}^2 \rangle = \langle D_{-22}^2 \rangle, \quad (2)$$

$$\langle D_{2-2}^2 \rangle = \langle D_{-2-2}^2 \rangle. \quad (3)$$

This set of order parameters based on the Wigner functions does not provide a completely convenient choice with which to distinguish between the two biaxial nematic phases and to do this we use the following combinations. The three order parameters

$$\langle I_{20} \rangle = ((D_{20}^2) - (D_{-20}^2)) / 2i, \quad (4)$$

$$\langle R_{22}^a \rangle = [((D_{22}^2) + (D_{-2-2}^2)) - ((D_{-22}^2) + (D_{2-2}^2))] / 2, \quad (5)$$

$$\langle I_{22}^a \rangle = [((D_{22}^2) - (D_{-2-2}^2)) - ((D_{-22}^2) - (D_{2-2}^2))] / 2i \quad (6)$$

vanish in the biaxial nematic with D_{2h} point group symmetry but are nonzero in that with C_{2h} symmetry. The remaining three

$$\langle R_{20} \rangle = ((D_{20}^2) + (D_{-20}^2)) / 2, \quad (7)$$

$$\langle R_{22}^s \rangle = [((D_{22}^2) + (D_{-2-2}^2)) + ((D_{-22}^2) + (D_{2-2}^2))] / 2, \quad (8)$$

$$\langle I_{22}^s \rangle = [((D_{22}^2) - (D_{-2-2}^2)) + ((D_{-22}^2) - (D_{2-2}^2))] / 2i \quad (9)$$

are nonzero in both biaxial nematics. In keeping with these definitions the nonzero order parameters for the uniaxial nematic are written as

$$\langle R_{00} \rangle = \langle D_{00}^2 \rangle, \quad (10)$$

$$\langle R_{02} \rangle = ((D_{02}^2) + (D_{0-2}^2)) / 2, \quad (11)$$

$$\langle I_{02} \rangle = ((D_{02}^2) - (D_{0-2}^2)) / 2i. \quad (12)$$

There is, in fact, an additional order parameter which vanishes in all but the biaxial nematic with C_{2h} symmetry.

As we show in Appendix A this order parameter is defined in terms of a first rank Wigner function $\tilde{D}_{00}^1(\Omega)$. Here the tilde indicates that the function is written in terms of pseudovectors and not polar vectors. As a consequence the order parameter $\langle \tilde{D}_{00}^1 \rangle$ does not change sign on inversion through the center of symmetry and so the order parameter does not vanish in the C_{2h} biaxial nematic. This contrasts with the polar order parameter $\langle D_{00}^1 \rangle$ defined in terms of polar vectors, which does vanish in the C_{2h} phase. We see, therefore, that the pseudovector based order parameter $\langle \tilde{D}_{00}^1 \rangle$ also provides a way to distinguish between the biaxial nematics with D_{2h} and C_{2h} point group symmetry. We note that in our current notation the rank of the Wigner functions has been suppressed and so for the two order parameters of rank 1 we shall retain $\langle \tilde{D}_{00}^1 \rangle$ and $\langle D_{00}^1 \rangle$.

In devising the notation for these nine combinations of second rank Wigner functions based order parameters we have decided against the use of simple letters, there are just too many. Instead we build on the notation suggested by Biscarini *et al.* [22] for the case when the molecules and phase have D_{2h} symmetry since this gives some information about the structure of the composite order parameter. Thus $\langle R_{02} \rangle$ denotes the real part of $\langle D_{02}^2 \rangle$ while $\langle I_{02} \rangle$ is its imaginary part. Extending this notation $\langle R_{22}^a \rangle$ denotes the antisymmetric combination of the real part of $\langle D_{22}^2 \rangle$ and that of $\langle D_{-22}^2 \rangle$. Similarly, $\langle I_{22}^s \rangle$ is the symmetric combination of the imaginary part of $\langle D_{22}^2 \rangle$ and that of $\langle D_{-22}^2 \rangle$.

Although the Wigner function representation of the orientational order parameters is powerful when developing the molecular field theory it does not always provide a physically familiar description of the order. This can be achieved with the Cartesian description given by the supertensor S_{ab}^{AB} [21,23] defined as

$$S_{ab}^{AB} = \langle (3l_{aA}l_{bB} - \delta_{aA}\delta_{bB}) \rangle / 2, \quad (13)$$

where the superscripts denote laboratory axes and subscripts molecular axes; l_{aA} is the direction cosine between axes a and A . The components of the Cartesian supertensor are related to the averages of combinations of Wigner functions by (see Appendix A)

$$\langle R_{00} \rangle = S_{zz}^{ZZ}, \quad (14)$$

$$\langle R_{02} \rangle = \frac{1}{\sqrt{6}} (S_{xx}^{ZZ} - S_{yy}^{ZZ}), \quad (15)$$

$$\langle I_{02} \rangle = \sqrt{\frac{2}{3}} S_{xy}^{ZZ}, \quad (16)$$

which are nonzero in all of the nematic phases and related to the molecular symmetry. Thus $\langle R_{02} \rangle$ provides a measure of the biaxiality in the molecular ordering when the molecular symmetry is D_{2h} and $\langle I_{02} \rangle$, corresponding to an off-diagonal element in the Sauepe ordering matrix [23], indicates the effect on the ordering when the molecular symmetry is C_{2h} . Within the biaxial nematic phase with D_{2h} symmetry the three new order parameters are

$$\langle R_{20} \rangle = \frac{1}{\sqrt{6}} (S_{zz}^{XX} - S_{zz}^{YY}), \quad (17)$$

$$\langle R_{22}^s \rangle = \frac{1}{3} [(S_{xx}^{XX} - S_{xx}^{YY}) - (S_{yy}^{XX} - S_{yy}^{YY})], \quad (18)$$

$$\langle I_{22}^s \rangle = \frac{2}{3} (S_{xy}^{XX} - S_{xy}^{YY}), \quad (19)$$

where $\langle I_{22}^s \rangle$ clearly represents a new term reflecting the phase biaxiality and is related to the C_{2h} molecular symmetry. Finally, there are four new order parameters which distinguish between the C_{2h} and the D_{2h} biaxial nematic phase. At the second rank level there are three of these, namely

$$\langle I_{20} \rangle = -\sqrt{\frac{2}{3}} S_{zz}^{XY}, \quad (20)$$

$$\langle R_{22}^a \rangle = \frac{2}{3} (S_{xy}^{XY} + S_{xy}^{YX}), \quad (21)$$

$$\langle I_{22}^a \rangle = -\frac{2}{3} (S_{xx}^{XY} - S_{yy}^{XY}), \quad (22)$$

which result from the S_{ab}^{XY} off-diagonal elements of the supermatrix. The fourth order parameter of this set is the pseudovector based first rank Wigner function $\langle \tilde{D}_{00}^1 \rangle$. This is related to the antisymmetric combination of elements of the supermatrix by

$$\langle \tilde{D}_{00}^1 \rangle = \frac{2}{3} (S_{xy}^{XY} - S_{xy}^{YX}) \quad (23)$$

(see Appendix A).

III. MOLECULAR FIELD THEORY

To construct a molecular field theory based on these nine independent order parameters we use the variational approach described by de Gennes [21]. This starts with the construction of the thermodynamic internal energy from the dominant order parameters. As experiment and simulation demonstrate these are invariably second rank [24,25] which explains our prior concentration on the $\langle D_{pm}^2 \rangle$; they also allow us to distinguish between the phases. We now need to construct a scalar product of these order parameters bearing in mind that the intermolecular coefficients u_{2mn} are also tensorial [20]. This gives

$$\langle U \rangle = -1/2 \sum u_{2mn} \langle D_{pm}^2 \rangle \langle D_{-pn}^2 \rangle. \quad (24)$$

Since m and n both take values from -2 to 2 there are 25 intermolecular coefficients but this number can be reduced to just six independent terms by taking account of the system symmetry and the C_{2h} molecular symmetry [20]. They are u_{200} , $u_{202} \equiv u_{220}$, $u_{20-2} \equiv u_{2-20}$, u_{222} , u_{2-2-2} , and $u_{2-22} \equiv u_{22-2}$. The symmetry-based arguments leading to this result are given in Appendix B. As we shall see, to emphasise the symmetry of the problem we shall take combinations of these coefficients just as we did for the orientational order parameters. The Helmholtz free energy is given, in the molecular field theory, as

$$A = -(1/2) \sum u_{2mn} \langle D_{pm}^2 \rangle \langle D_{-pn}^2 \rangle + k_B T \int f(\Omega) \ln f(\Omega) d\Omega, \quad (25)$$

where, as yet, the singlet orientational distribution function $f(\Omega)$, is unknown. It is determined by a functional minimization of A with respect to $f(\Omega)$ subject to the constraints that

it is normalized and that the order parameters $\langle D_{pm}^2 \rangle$ are the averages of $D_{pm}^2(\Omega)$ with $f(\Omega)$. This minimization also leads to the potential of mean torque $U(\Omega)$; the resultant expression is somewhat formidable given its dependence on nine order parameters and six intermolecular coefficients. To simplify its appearance we have divided it into three parts, the first is responsible for the formation of the uniaxial nematic, the second drives the appearance of the biaxial nematic with D_{2h} symmetry, and the third part is responsible for the creation of the biaxial nematic with C_{2h} symmetry. The potential is then

$$U(\Omega) = U_U(\Omega) + U_{D_{2h}}(\Omega) + U_{C_{2h}}(\Omega), \quad (26)$$

where the individual terms responsible for driving the appearance of the three nematic phases N_U , $N_{D_{2h}}$, and $N_{C_{2h}}$ [26] are

$$\begin{aligned} U_U(\Omega) = & - [(\langle R_{00} \rangle + 2\gamma_s \langle R_{02} \rangle - 2\gamma_a \langle I_{02} \rangle) R_{00}(\Omega) \\ & + (2\gamma_s \langle R_{00} \rangle + 4\lambda_s \langle R_{02} \rangle - 2\lambda_0 \langle I_{02} \rangle) R_{02}(\Omega) \\ & + (-2\gamma_a \langle R_{00} \rangle - 2\lambda_0 \langle R_{02} \rangle - 4\lambda_a \langle I_{02} \rangle) I_{02}(\Omega)], \end{aligned} \quad (27)$$

$$\begin{aligned} U_{D_{2h}}(\Omega) = & -2 \{ (\langle R_{20} \rangle + \gamma_s \langle R_{22}^s \rangle - \gamma_a \langle I_{22}^s \rangle) R_{20}(\Omega) \\ & + [\gamma_s \langle R_{20} \rangle + \lambda_s \langle R_{22}^s \rangle - (1/2)\lambda_0 \langle I_{22}^s \rangle] R_{22}^s(\Omega) \\ & + [-\gamma_a \langle R_{20} \rangle - (1/2)\lambda_0 \langle R_{22}^s \rangle - \lambda_a \langle I_{22}^s \rangle] I_{22}^s(\Omega) \}, \end{aligned} \quad (28)$$

$$\begin{aligned} U_{C_{2h}}(\Omega) = & -2 \{ (\langle I_{20} \rangle + \gamma_s \langle I_{22}^a \rangle + \gamma_a \langle R_{22}^a \rangle) I_{20}(\Omega) \\ & + [\gamma_a \langle I_{20} \rangle + (1/2)\lambda_0 \langle I_{22}^a \rangle - \lambda_a \langle R_{22}^a \rangle] R_{22}^a(\Omega) \\ & + [\gamma_s \langle I_{20} \rangle + \lambda_s \langle I_{22}^a \rangle + (1/2)\lambda_0 \langle R_{22}^a \rangle] I_{22}^a(\Omega) \}. \end{aligned} \quad (29)$$

In these expressions for $U(\Omega)$ we have scaled the potential of mean torque with the intermolecular coefficient u_{200} . More importantly, the particular combinations of order parameters appropriate for the three nematic phases have lead us to introduce related combinations of intermolecular coefficients. These real, scaled combinations are

$$\begin{aligned} \gamma_s &= (u_{220} + u_{2-20})/2u_{200}, \\ \gamma_a &= (u_{220} - u_{2-20})/2iu_{200}, \\ \lambda_s &= (\text{Re}u_{222} + u_{2-22})/2u_{200}, \\ \lambda_a &= (\text{Re}u_{222} - u_{2-22})/2u_{200}, \\ \lambda_0 &= (u_{222} - u_{2-2-2})/2iu_{200}, \end{aligned} \quad (30)$$

where the labels s and a denote symmetric and antisymmetric combinations of particular intermolecular coefficients. This choice is especially convenient because when the mesogenic molecule has D_{2h} symmetry the antisymmetric combinations vanish as does λ_0 since then u_{222} is real and equal to u_{2-2-2} . This leaves the expected three independent coefficients as u_{200} , u_{220} , and u_{222} . When, however, the molecule has C_{2h} symmetry the three coefficients γ_s , λ_a , and λ_0 are no longer zero and provide a measure of the extent to which it deviates from D_{2h} symmetry. These coefficients enter all three contributions to the potential of mean torque since the

molecular symmetry influences the orientational ordering in all three nematic phases. In contrast, the key order parameters for the contributions to the potential for the three nematic phases only appear in the potential of mean torque associated with that phase.

Given the potential of mean torque we can construct the orientational Helmholtz free energy. This can then be minimized with respect to the order parameters to determine their temperature dependence from which the transition temperatures and phase map are estimated [27]. However, since there are nine order parameters and six intermolecular coefficients for this nematogen it is a formidable task. We have, therefore, sought to simplify the problem while retaining its essential physics. One possible strategy with which to achieve this is suggested by the four independent order parameters when both the molecules and the biaxial nematic phase have D_{2h} symmetry. These order parameters $\langle R_{00} \rangle$, $\langle R_{02} \rangle$, $\langle R_{20} \rangle$, and $\langle R_{22}^s \rangle$ are of particular interest since, in the limit of high order, as $\langle R_{00} \rangle$ tends to unity, the order parameters $\langle R_{02} \rangle$ and $\langle R_{20} \rangle$ tend to zero while $\langle R_{22}^s \rangle$ also tends to unity [see Eqs. (14), (15), (17), and (18)]. At higher temperatures $\langle R_{00} \rangle$ and $\langle R_{22}^s \rangle$ remain dominant and a molecular field theory based, in essence, on just these two order parameters with u_{220} set equal to zero to ensure the order parameters remain zero also captures much of the essential behavior [28]. For biaxial nematogenic molecules with C_{2h} symmetry in a biaxial phase also with C_{2h} symmetry we see that in the high order limit $\langle R_{00} \rangle$, $\langle R_{22}^s \rangle$, and $\langle R_{22}^a \rangle$ are expected to be large, whereas the remaining six order parameters should be small. If we set them to zero in the potential of mean torque together with γ_s , γ_a , and λ_0 then we obtain the truncated potential

$$\begin{aligned} U_{\text{trun}}(\Omega)/u_{200} = & - [\langle R_{00} \rangle R_{00}(\Omega) + 2\lambda_s \langle R_{22}^s \rangle R_{22}^s(\Omega) \\ & + 2\lambda_a \langle R_{22}^a \rangle R_{22}^a(\Omega)]. \end{aligned} \quad (31)$$

The Helmholtz free energy associated with this takes the form

$$\begin{aligned} A/u_{200} = & (1/2)(\langle R_{00} \rangle^2 + 2\lambda_s \langle R_{22}^s \rangle^2 + 2\lambda_a \langle R_{22}^a \rangle^2) \\ & - T^* \ln Q, \end{aligned} \quad (32)$$

where the partition function is given by

$$Q = \int \exp[-U_{\text{trun}}^*(\Omega)/T^*] d\Omega, \quad (33)$$

$U_{\text{trun}}^*(\Omega)$ is the scaled potential of mean torque $U_{\text{trun}}(\Omega)/u_{200}$ and T^* is the scaled temperature $k_B T/u_{200}$.

We have not included terms involving the pseudovector based order parameter $\langle \tilde{D}_{00}^1 \rangle$ in the molecular field theory. Our reason for the omission is not that the order parameter is small; it is not, as we shall show in Sec. IV. Our argument for ignoring this contribution is the following. The new term in the internal energy would take the form

$$\langle U \rangle = -(1/2)\tilde{u}_{100} \langle \tilde{D}_{00}^1 \rangle^2. \quad (34)$$

Since the order parameter is invariant under inversion through the center of symmetry for the constituent molecules then for the contribution to the internal energy not to vanish the intermolecular coefficient \tilde{u}_{100} should also be invariant under inversion. For molecules with C_{2h} point group symmetry the supertensor intermolecular coefficients u_{Lmn} will vanish if L is odd [20]. However, this would not be the case for \tilde{u}_{100}

if it is a component of a pseudosupertensor; this would be consistent with \tilde{u}_{100} being constructed from an antisymmetric molecular interaction second rank tensor. We are not aware of molecular interactions which involve nonsymmetric tensors [7] so that the antisymmetric components can be assumed to be insignificant. However, relating the supertensor components to the excluded volume between two molecules [4] may change this perception. We shall consider this possibility in the following section.

It seems appropriate to finish this section by commenting on the likely reliability of the predictions of our theory for molecules with C_{2h} point group symmetry. Molecular field theories clearly have the advantage of simplicity which results from the major approximation of decoupling the direct orientational correlations between molecules. The effect of this approximation has been explored for nematics by comparing the predictions with the results of computer simulations. In these the pair potential is usually chosen to be consistent with the Helmholtz free energy which forms the basis of the molecular field theory. Using this approach there have been numerous tests of the predictions of the Maier-Saupe theory for uniaxial nematics [24,29,30]. These have shown that the predictions are surprisingly reliable. As the system becomes more complicated, for example, the molecules and phase are biaxial with D_{2h} point group symmetry, it is important to see if the molecular field predictions are any less reliable. Again simulation results are available for this symmetry and it appears that the predictions are still good [22,31,32]. Of particular importance is the phase map showing how the nematic phases formed vary with the molecular biaxiality parameters. The agreement between theory and simulation appears to be reliable at both a qualitative and even semiquantitative level. This agreement extends to the temperature variation of the order parameters characterizing the different phases. It seems likely, therefore, that the predictions of our molecular field theory will be just as reliable; indeed this expectation is consistent with preliminary results of computer simulations.

IV. CALCULATIONS, PARAMETERIZATION, AND RESULTS

In order to determine the phase stability at a given temperature, the scaled free energy is minimized with respect to the three order parameters $\langle R_{00} \rangle$, $\langle R_{22}^s \rangle$, and $\langle R_{22}^a \rangle$ using the MATLAB minimization function *fmincon*. It is a function to find the minima of a nonlinear smooth function with nonlinear smooth constraints. In the computer program we specifically chose the method of Active Set Sequential Quadratic Programming. The algorithm is an application of Newton's method to the first order optimality conditions for the minimization of a function. It generates a quadratic program at each step and can be solved to obtain the search direction and so find the next iterate. In *fmincon* at each step a quasi-Newtonian approximation of the Hessian matrix is employed instead of a direct calculation. In addition, the Active Set method is used to deal with constraints. A description of these methods can be found in the book by Nocedal and Wright [33]. Since this method only finds local minima of the free energy corresponding to different nematic phases, we often need to make comparison between the values of the free energy at the local minima to obtain the global

minimum at a given temperature. Moreover, the integration of the partition function over the Euler angles is performed by a method suggested by Bisi, Romano, and Virga [34].

The first step in the application of our molecular field theory is to select the scaled parameters λ_s and λ_a . It would be desirable to relate these parameters to the molecular geometry even for that as idealized as the structure in Fig. 1. However, to achieve this the only quantity to our knowledge that might be related to the intermolecular supertensor is the excluded volume [4]. In this approach the excluded volume is expanded in a basis of Wigner functions and the expansion coefficients a_{Lmn} are taken to be related to the supertensor u_{Lmn} . The use of the excluded volume is especially relevant because it is associated with the repulsive forces thought to be important in determining liquid structure. For block-shaped molecules with D_{2h} point group symmetry Straley has obtained analytic expressions for the three independent supertensor components u_{200} , u_{220} , and u_{222} based on a particular and limited choice of the relative molecular orientations. For molecules with C_{2h} point group symmetry it is not possible to obtain analytic expressions even in this approximate way. Numerical values for the components of the interaction supertensor can be determined but this tends to obscure the physics of the problem [35]. However, general symmetry based arguments show that the expansion coefficient a_{100} is not zero [36]. Although this coefficient does not vanish we require a specific model for the molecular shape, with C_{2h} point group symmetry, to determine how large it might be in comparison with the second rank coefficients a_{2mn} . Preliminary calculations for some trial structures having C_{2h} point group symmetry indicate that a_{100}/a_{200} is negligibly small [37]. This suggests that the contribution of the pseudovector order parameters to the molecular field theory may be ignored. However, more detailed calculations of the excluded volume expansion coefficients for different C_{2h} models need to be undertaken to confirm this.

In view of this difficulty we were guided in our choice of the scaled coefficient λ_s by results which Sonnet, Virga, and Durand obtained [38] in their calculations for what is, in essence, the two order parameter model. Thus for $\lambda_s = 0.2$ they find the phase sequence $ND_{2h}-N_U-I$. We have used this value together with a range of values for λ_a and from the temperature dependence of the order parameters we have determined the variation of the transition temperatures as a function of the relative biaxiality λ_a . The results for the phase maps are shown in Fig. 2(a). For λ_a of zero we find the transitions N_U-I and $ND_{2h}-N_U$ in agreement with those reported by Sonnet *et al.* [38]. We see that the N_U-I and $ND_{2h}-N_U$ transition temperatures do not change with λ_a , as required, because it does not contribute to the orientational order of the phases involved. However, as soon as λ_a does deviate from zero we find that the biaxial nematic phase with C_{2h} symmetry and identified by the nonzero value of $\langle R_{22}^a \rangle$ as well as the order parameters $\langle R_{00} \rangle$ and $\langle R_{22}^s \rangle$ appears in the phase map. For small values of λ_a the transition $NC_{2h}-ND_{2h}$ is observed to be second order. The stability of the NC_{2h} phase grows with increasing λ_a , as is to be expected. What was not anticipated was the appearance of another biaxial nematic phase at the point at which the $ND_{2h}-N_U$ transition line meets the $NC_{2h}-ND_{2h}$ phase boundary. This new phase was identified by the fact that the biaxial order parameter

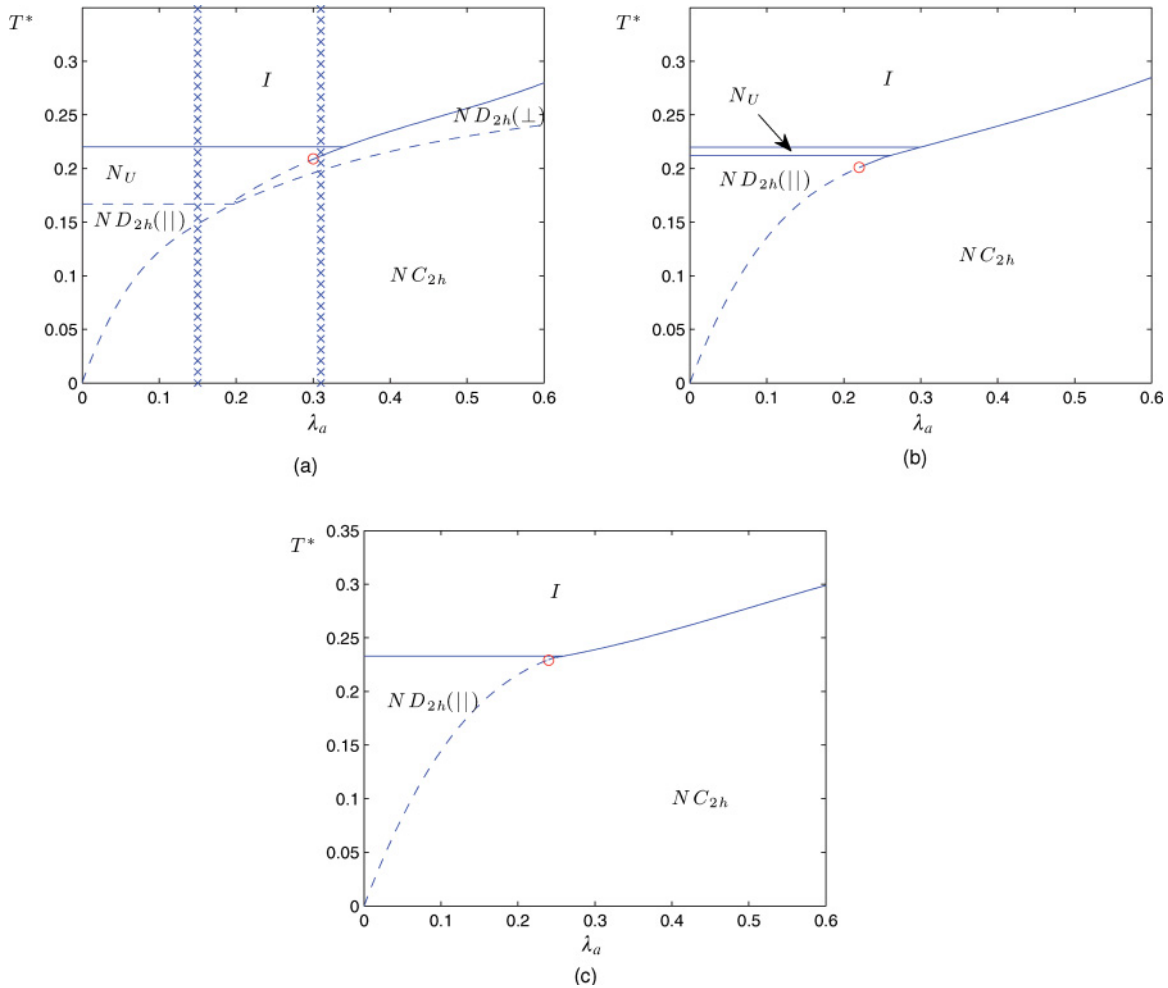


FIG. 2. (Color online) The phase map predicted by the truncated model potential [see Eq. (31)] for a nematogen composed of biaxial molecules with C_{2h} symmetry; the phase behavior is shown as a function of the relative biaxiality coefficient λ_a , with λ_s of (a) 0.2, (b) 0.3, and (c) 0.4. The phase previously labeled as N_{B-} is here indicated by $ND_{2h}(\perp)$ given its subsequent identification. The dashed line indicates second order phase transitions and solid lines denotes first order phase transitions; a circle shows a tricritical point. The vertical crosses indicate the temperature range over which the order parameters shown in Fig. 3 were calculated.

$\langle R_{22}^s \rangle$ is zero, while $\langle R_{00} \rangle$ and $\langle R_{22}^a \rangle$ are not; since one order parameter is absent we denote this phase, for the moment, as N_{B-} . This phase separates the biaxial nematic NC_{2h} first from the uniaxial nematic and then from the isotropic phase. Its existence had not been expected because in the biaxial nematic phase NC_{2h} it was thought that all three major order parameters would occur together and that the order parameter $\langle R_{22}^a \rangle$ would vanish before $\langle R_{22}^s \rangle$. The fact that the reverse can occur may be attributed to the absence of coupling between the order parameters and the angular function associated with a different order parameter in Eq. (31). The transition between the new biaxial nematic N_{B-} and the NC_{2h} phase is found to be second order while that to the isotropic phase is first order. We shall return to the identification of this biaxial nematic phase at the end of the section.

The occurrence in a nematic phase of the biaxial orientational order reflected by $\langle R_{22}^s \rangle$ is controlled in the truncated molecular field model by the scaled biaxiality coefficient λ_s . We have, therefore, repeated our calculations with the larger value for λ_s of 0.3 to explore its influence on the appearance

of the new phase N_{B-} in the phase map. When λ_a is zero the system exhibits the phase sequence $ND_{2h}-N_U-I$ but now the extent of the uniaxial nematic is considerably reduced as is apparent from the results in Fig. 2(b). What will not be clear is that the $ND_{2h}-N_U$ transition is first order showing that this transition exhibits tricritical behavior [38]. As soon as λ_a departs from zero the NC_{2h} phase appears and the $NC_{2h}-ND_{2h}$ transition temperature grows with λ_a as we had observed for the smaller value of λ_s . At the triple point we do not detect a transition to the N_{B-} phase and nor did this phase appear at the boundary between the NC_{2h} and I phases as we had found when λ_s was 0.2, in keeping with our expectations.

We have also explored another region of the phase map by setting λ_s equal to the higher value of 0.4. According to the calculation of Sonnet *et al.* [38] with λ_a equal to zero the system exhibits a first order transition directly from the isotropic phase to the ND_{2h} phase. Then as λ_a increases from zero the $ND_{2h}-I$ transition temperature does not change, as expected and shown in Fig. 2(c). More interestingly, first the $NC_{2h}-ND_{2h}$ transition temperature and then that for the

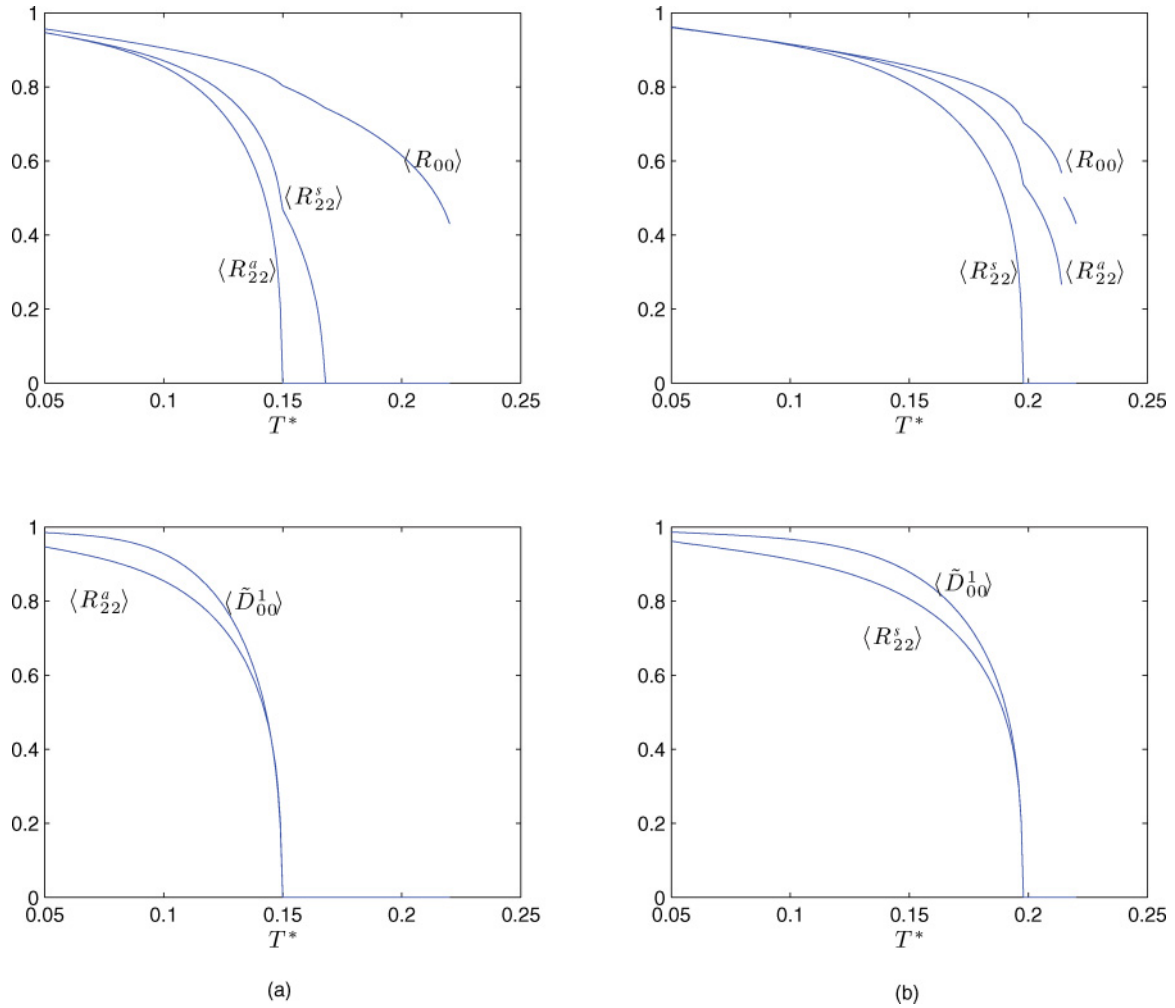


FIG. 3. (Color online) The dependence of the three order parameters $\langle R_{00} \rangle$, $\langle R_{22}^s \rangle$, and $\langle R_{22}^a \rangle$ calculated with $\lambda_s = 0.2$ and (a) $\lambda_a = 0.15$ and (b) $\lambda_a = 0.31$ on the scaled temperature T^* . In addition, the temperature variation of the pseudovector based order parameter $\langle \tilde{D}_{00}^1 \rangle$ is shown in comparison with (a) $\langle R_{22}^a \rangle$ and (b) $\langle R_{22}^s \rangle$.

NC_{2h} - I transition grow with λ_a . As for the calculations with λ_s of 0.3, the system exhibits only the NC_{2h} and ND_{2h} biaxial nematic phase but not the N_{B-} phase. This is in keeping with the larger value for λ_s driving the appearance of the order parameter $\langle R_{22}^s \rangle$ and so inhibiting the formation of the N_{B-} phase.

The phase maps shown in Fig. 2 were constructed from the temperature dependence of the three order parameters $\langle R_{00} \rangle$, $\langle R_{22}^s \rangle$, and $\langle R_{22}^a \rangle$. However, this dependence is of interest in its own right and so we have shown in Fig. 3 the variation of these dominant order parameters with the scaled temperature calculated with λ_s of 0.20 and λ_a of 0.15 and 0.31. The results for λ_a of 0.15 are shown in Fig 3(a); here we see that $\langle R_{00} \rangle$ is the first order parameter to appear on lowering the scaled temperature T^* , corresponding to the formation of the uniaxial nematic phase from the isotropic at T^* of 0.2202. The order parameter changes discontinuously in keeping with the expected first order nature of the transition [23]. To obtain the order of the phase transition from the calculations we have determined the order parameters and the scaled temperature both to four decimal places. The phase transition is taken as second order if the order parameters

corresponding to the lower symmetry phase changes continuously at the phase transition. In other words, the minimum of the free energy corresponding to the lower symmetry phase is always the global minimum. On the other hand, the order parameters corresponding to the lower symmetry phase change discontinuously at the first order phase transition. In our methodology it means that just slightly above the transition temperature we would find a region where there are two minima of the free energy. One minimum corresponding to the lower symmetry phase is the local minimum, whereas the other free energy minimum corresponding to the higher symmetry phase is the global minimum. As the temperature is lowered further the next order parameter to appear is $\langle R_{22}^s \rangle$ at T^* of 0.1674 corresponding to the formation of the biaxial nematic with D_{2h} symmetry. The order parameter $\langle R_{22}^s \rangle$ is seen to grow continuously at the ND_{2h} - N_U transition in keeping with its second order character [28]. The final order parameter to appear is $\langle R_{22}^a \rangle$, on the formation of the C_{2h} biaxial nematic phase at T^* of 0.1497. The order parameter seems to grow continuously but steeply at the phase transition suggesting that it is second order. It is also of interest that the rate of change of the other two order parameters $\langle R_{00} \rangle$ and $\langle R_{22}^s \rangle$ with

temperature also increases when the NC_{2h} phase is formed. The behavior of the system for the larger value of λ_a of 0.31 is, as we have seen, more surprising. The first phase to appear is the uniaxial nematic which necessarily has the same transitional properties as when λ_a is 0.15. However, unlike the system with the lower value of λ_a the next order parameter to appear is $\langle R_{22}^a \rangle$ and not $\langle R_{22}^s \rangle$ expected for the biaxial nematic with D_{2h} symmetry. The symmetry of the phase with nonzero order parameters $\langle R_{00} \rangle$ and $\langle R_{22}^a \rangle$ is not known so it was designated as N_{B-} . The discontinuity in $\langle R_{00} \rangle$ and in $\langle R_{22}^a \rangle$ at the $N_{B-}-N_U$ transition for T^* of 0.2148 suggests that this is first order. At T^* of 0.1976 the third order parameter $\langle R_{22}^s \rangle$ appears growing relatively rapidly but continuously with decreasing temperature indicating that the $NC_{2h}-N_{B-}$ transition is second order. This transition can also be discerned from the change in the variation of $\langle R_{22}^a \rangle$ and $\langle R_{00} \rangle$ with the scaled temperature.

The other order parameter $\langle \tilde{D}_{00}^1 \rangle$, constructed from two pseudovectors, does not appear in the molecular field theory and so cannot be determined from the free energy. It can, however, be obtained from the singlet orientational distribution function $f(\Omega)$ calculated from the truncated potential of mean torque. Thus

$$\langle \tilde{D}_{00}^1 \rangle = \int \tilde{D}_{00}^1(\Omega) f(\Omega) d\Omega, \quad (35)$$

where

$$f(\Omega) = Q^{-1} \exp[-U_{\text{trun}}^*(\Omega)/T^*]; \quad (36)$$

here $U_{\text{trun}}^*(\Omega)$ is given by Eq. (31) and the orientational partition function Q is given by Eq. (33). The integration in Eq. (35) is taken over $O(3)$ to allow for the mirror plane in both the molecule and the phase with C_{2h} point group symmetry. However, because $\tilde{D}_{00}^1(\Omega)$ is a pseudovector this is not necessary because the average $\langle \tilde{D}_{00}^1 \rangle$ can be written as

$$\langle \tilde{D}_{00}^1 \rangle = \int_{SO(3)} D_{00}^1(\Omega) f(\Omega) d\Omega. \quad (37)$$

The temperature dependence of $\langle \tilde{D}_{00}^1 \rangle$ is shown in Fig. 3(a) calculated for $\lambda_s = 0.2$ and λ_a of 0.15; this system exhibits the phase sequence $NC_{2h}-ND_{2h}-N_U-I$. The order parameter is zero in the ND_{2h} and N_U phases but then starts to grow when the NC_{2h} phase is entered. This behavior is as we had anticipated. What we had not expected was that the behavior of the two order parameters $\langle R_{22}^a \rangle$ and $\langle \tilde{D}_{00}^1 \rangle$ would parallel each other quite so closely. That is $\langle \tilde{D}_{00}^1 \rangle$ also grows rapidly from zero and at the lowest temperature studied has reached a high value of 0.9853 which is close to the limiting value found for $\langle R_{22}^a \rangle$ but higher than this. The implication of this near equality can be seen immediately from the Cartesian versions of these two order parameters given in Eqs. (21) and (23). The difference $\langle R_{22}^a \rangle - \langle \tilde{D}_{00}^1 \rangle$ is just $4S_{xy}^{YX}/3$ and so our results show that the order parameter S_{xy}^{YX} must be small; this is certainly the case in the high order limit where it vanishes. We also show the variation of $\langle \tilde{D}_{00}^1 \rangle$ with temperature now calculated for λ_s of 0.2 and λ_a equal to 0.31 in Fig. 3(b). This parametrization is especially interesting because it yields the intermediate biaxial nematic phase N_{B-} of, as yet, unknown symmetry. The variation of $\langle \tilde{D}_{00}^1 \rangle$ in the

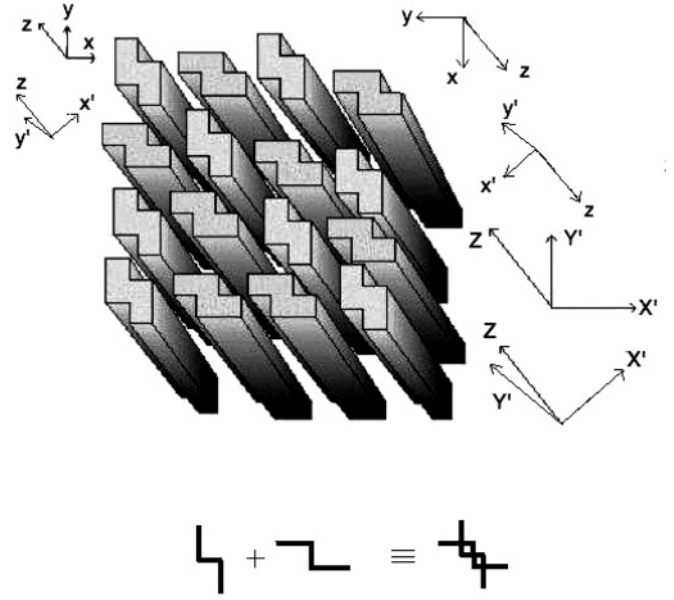


FIG. 4. A sketch of the idealized organization of molecules with C_{2h} point group symmetry in the biaxial nematic phase $ND_{2h}(\perp)$ in which the minor axes of half the molecules tend to be perpendicular to those of the other half. The axis systems $(x'y'z)$ and $(X'Y'Z)$ show the symmetry axes for this idealized ND_{2h} phase and the molecules forming it. The cross section of the average structure obtained by merging molecules in which the x axes are orthogonal is also shown.

various phases helps us to identify N_{B-} . We find that $\langle \tilde{D}_{00}^1 \rangle$ is zero in all but the low-temperature phase where the three second rank order parameters are also nonzero. This confirms our earlier assignment of this as an NC_{2h} phase. In the N_{B-} phase although the order parameter $\langle R_{22}^a \rangle$ expected for a phase with C_{2h} point group symmetry is nonzero $\langle \tilde{D}_{00}^1 \rangle$ vanishes thus suggesting that this phase does not have C_{2h} symmetry. The nonvanishing order parameter $\langle R_{22}^a \rangle$ shows, however, that the phase is biaxial and that possibly it has D_{2h} point group symmetry for which $\langle R_{22}^s \rangle$ vanishes but $\langle R_{22}^a \rangle$ and $\langle R_{00} \rangle$ are nonzero. A sketch of the molecular organization satisfying these constraints, at least in the high order limit, is given in Fig. 4.

We also show in Fig. 4 the average molecular structure obtained by internal rotation of the molecule by 180° about x and 90° about z and merging this with the original molecule. As expected this average structure has D_{2h} point group symmetry but with different rotation axes to that found for the molecules in the $D_{2h}(\parallel)$ biaxial nematic [see Fig. 1(c)]. In principle an average structure with D_{2h} symmetry could also be constructed from two molecules in which one is rotated about z with respect to the other by an arbitrary angle. However, the form of the truncated potential of mean torque for the system studied and its parametrization requires that this angle is 90° . The fact that the order parameter $\langle R_{22}^a \rangle$ is not zero but $\langle R_{22}^s \rangle$ is suggests that the choice of the laboratory and molecular axis systems is not appropriate for this particular molecular organization. Inspection of the sketch in Fig. 4 suggests that the only choice which would fit would involve a rotation of both molecular and laboratory frames about z and Z , respectively by 45° . The new axis systems are shown in Fig. 4 and now it is clear that

the molecular x' axes tend to be parallel to the new laboratory X' axis. In general, this transformation also appears to solve the problem of identifying the phase symmetry. Thus they correspond to the change of α to $\alpha \pm \pi/4$ for the laboratory frame and γ to $\gamma \mp \pi/4$ for the molecular frame. These transformations lead to a remarkable change in the functions defining the two order parameters. Thus

$$R_{22}^a(\alpha, \beta, \gamma) \xrightarrow[\text{rotations}]{\pi/4} R_{22}^s(\alpha', \beta, \gamma'), \quad (38)$$

$$R_{22}^s(\alpha, \beta, \gamma) \xrightarrow[\text{rotations}]{\pi/4} R_{22}^a(\alpha', \beta, \gamma'), \quad (39)$$

where the two rotations take place about the z and Z axes. The results of the transformation to the new molecular and laboratory frames interchanges the order parameters $\langle R_{22}^s \rangle$ and $\langle R_{22}^a \rangle$ so that in the new frames $\langle R_{22}^s \rangle$ is nonzero and now it is $\langle R_{22}^a \rangle$ that vanishes. This is just what is expected for a biaxial nematic phase with D_{2h} point group symmetry. To distinguish between the two ND_{2h} phases we have added the symbols (\parallel) and (\perp) to indicate whether the molecular minor axes are parallel or perpendicular in the biaxial nematic phase.

V. SUMMARY AND CONCLUSION

It is usually assumed either explicitly or implicitly that biaxial nematic phases possess D_{2h} point group symmetry. However, for many years it has been appreciated that biaxial phases of lower symmetry could also be formed. To aid in gaining an understanding of this behavior we have developed a molecular field theory for a biaxial nematic with C_{2h} point group symmetry constituted from molecules with the same symmetry. This theory requires a knowledge of the independent orientational order parameters for the phase. There are, in fact, nine second rank order parameters and a single pseudovector based order parameter of rank one; although it is not expected to make any significant contribution to the theory. This large number contrasts with the four second rank order parameters needed for the D_{2h} biaxial nematic composed of molecules having the same symmetry. In the theory for this phase there are just three molecular interaction parameters but this number grows to six for the C_{2h} system. The evaluation of these interaction parameters is a challenging task and the best, if not the only, model now available for this is based on the excluded volume of the molecules [4]. We have avoided this problem and reduced the complexity of the theory by retaining just the three dominant order parameters. The theory is, therefore, an extension of the Sonnet-Virga-Durand theory [38] for biaxial nematics with D_{2h} point group symmetry to those with C_{2h} symmetry. The resulting simplification reduces the number of intermolecular coefficients to just three. Two of these, λ_s and λ_a , are related to the molecular biaxiality; for molecules with D_{2h} symmetry λ_a vanishes. The appearance of the D_{2h} biaxial nematic is controlled by λ_s and that for the C_{2h} phase by λ_a . In fact, the choice of these parameters generates a very rich phase behavior with phase sequences,

$$\begin{aligned} & NC_{2h}-I, \\ & NC_{2h}-ND_{2h}(\parallel)-I, \\ & NC_{2h}-ND_{2h}(\perp)-N_U-I, \end{aligned}$$

$$\begin{aligned} & NC_{2h}-ND_{2h}(\perp)-I, \\ & NC_{2h}-ND_{2h}(\perp)-N_U-I. \end{aligned}$$

In addition, the model also reveals the existence of two biaxial nematics with D_{2h} point group symmetry. In one the minor molecular axes tend to be parallel as might be expected but in the other they tend to be perpendicular. We have yet to discover whether one D_{2h} phase can undergo a transition into the other. As Sonnet *et al.* [38] have discovered the $ND_{2h}-N_U$ transition exhibits a tricritical behavior passing from second order to first order with increasing molecular biaxiality λ_s at about 0.3 for our definition of the parameter. Similarly, we find three tricritical points, one for each of the phase maps with λ_s of 0.2, 0.3, and 0.4. For λ_s of 0.2 we find the tricritical point along the $ND_{2h}(\perp)-N_U$ transition line at $\lambda_a = 0.3$. The tricritical point for λ_s of 0.3 is found at $\lambda_a = 0.22$ along the $NC_{2h}-ND_{2h}(\parallel)$ transition line. Finally, in the phase map for $\lambda_s = 0.4$ it is located at $\lambda_a = 0.24$ along the $NC_{2h}-ND_{2h}(\parallel)$ transition line.

The model which we have developed for the biaxial nematic phase with C_{2h} point group has been considerably simplified from the complete theory. However, it still retains much of the essential physics and shows a rich phase behavior. It seems clear that there are many facets of this model which merit further exploration. It is likely that the phase maps together with orientational order parameters will prove to be a valuable aid to the interpretation of experimental studies of mesogens thought to exhibit the biaxial nematic phase with C_{2h} point group symmetry. They may also lead to a better understanding of the relationship between the principal axes for macroscopic tensorial properties and the directors for this low symmetry biaxial nematic phase.

Finally, we wish to note that in our model of C_{2h} molecules that constitute the nematic phases we have taken the $C_2(z)$ rotation axis to be parallel to the molecular long axis. This is apparent from the sketch of the molecules shown in Fig. 1 and the fact that the order parameter $\langle R_{00} \rangle$ is large and positive in all of the nematic phases. However, there is no reason why for calamitic mesogenic molecules the C_2 axis needs to be parallel to the molecular long axis. Relaxing this implicit constraint is an interesting problem, in particular to explore to what extent the nematic phases formed when the C_2 axis is parallel or perpendicular to the molecular long axis differ. This is a problem that we shall certainly return to.

ACKNOWLEDGMENTS

We are grateful to the School of Mathematics, University of Southampton for the award of a Research Scholarship to Mr. T. B. T. To. Professor G. R. Luckhurst wishes to thank Professor M. Osipov (University of Strathclyde) for a stimulating discussion, in Colmar, concerning the number of independent second rank order parameters for the biaxial nematic phase with C_{2h} symmetry. He is also grateful to Dr F. Bisi (University of Pavia) for illuminating discussions concerning the parametrization of molecular field theory using the excluded volume. Similarly, Professor S. Naemura wishes to acknowledge discussions with Professor K. Okano (Tokyo University) concerning the tensorial order parameter.

APPENDIX A

Here we wish to provide a justification for the assertion concerning the need to include a pseudovector order parameter for a biaxial nematic phase with C_{2h} point group symmetry composed of molecules having the same symmetry. Our starting point is the Cartesian supermatrix describing the orientational order of the phase. Each element in this matrix of matrices is given by [21,23]

$$S_{ab}^{AB} = \langle (3l_{aA}l_{bB} - \delta_{ab}\delta_{AB}) \rangle / 2, \quad (\text{A1})$$

where the lower case letters define the molecular axes and the upper case letters are the laboratory axes, the l_{aA} are the direction cosines between the molecular axis a and the laboratory axis A and δ_{ab} is the Kronecker delta function. If we define z to be the C_2 rotation axis in the molecule and Z that in the laboratory then the ordering supermatrix has the form

$$\mathbf{S} = \begin{pmatrix} S_{xx}^{XX} & S_{xx}^{XY} & 0 & S_{xy}^{XX} & S_{xy}^{XY} & 0 & 0 & 0 & 0 \\ S_{xx}^{YX} & S_{xx}^{YY} & 0 & S_{xy}^{YX} & S_{xy}^{YY} & 0 & 0 & 0 & 0 \\ 0 & 0 & S_{xx}^{ZZ} & 0 & 0 & S_{xy}^{ZZ} & 0 & 0 & 0 \\ S_{yx}^{XX} & S_{yx}^{XY} & 0 & S_{yy}^{XX} & S_{yy}^{XY} & 0 & 0 & 0 & 0 \\ S_{yx}^{YX} & S_{yx}^{YY} & 0 & S_{yy}^{YX} & S_{yy}^{YY} & 0 & 0 & 0 & 0 \\ 0 & 0 & S_{yx}^{ZZ} & 0 & 0 & S_{yy}^{ZZ} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & S_{zz}^{XX} & S_{zz}^{XY} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & S_{zz}^{YX} & S_{zz}^{YY} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & S_{zz}^{ZZ} \end{pmatrix}. \quad (\text{A2})$$

In determining the number of independent order parameters of this supermatrix we note that from their definition in Eq. (A1) the diagonal submatrices are symmetric about their diagonals. In marked contrast, the two off-diagonal submatrices are not symmetric about their diagonals [39] since, for example,

$$S_{xy}^{XY} (\equiv \langle 3l_{xX}l_{yY}/2 \rangle) \quad (\text{A3})$$

clearly differs from

$$S_{xy}^{YX} (\equiv \langle 3l_{xY}l_{yX}/2 \rangle). \quad (\text{A4})$$

The nonsymmetric matrix can be written as the sum of an antisymmetric matrix and a symmetric matrix

$$\begin{pmatrix} S_{xy}^{XX} & S_{xy}^{XY} & 0 \\ S_{xy}^{YX} & S_{xy}^{YY} & 0 \\ 0 & 0 & S_{xy}^{ZZ} \end{pmatrix} \equiv \begin{pmatrix} 0 & (S_{xy}^{XY} - S_{xy}^{YX})/2 & 0 \\ -(S_{xy}^{XY} - S_{xy}^{YX})/2 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$+ \begin{pmatrix} S_{xy}^{XX} & (S_{xy}^{XY} + S_{xy}^{YX})/2 & 0 \\ (S_{xy}^{XY} + S_{xy}^{YX})/2 & S_{xy}^{YY} & 0 \\ 0 & 0 & S_{xy}^{ZZ} \end{pmatrix}. \quad (\text{A5})$$

Including this separation of the off-diagonal matrices into the supermatrix S_{ab}^{AB} results in a symmetric ordering supermatrix and an antisymmetric ordering supermatrix. The symmetric supermatrix contains 25 nonzero elements. However, allowing for the symmetry about the diagonals and the fact that the traces $\sum_A S_{ab}^{AA}$ and $\sum_a S_{aa}^{AB}$ vanish leaves a total of nine independent component order parameters. These Cartesian components are linearly related to the nine order parameters defined in terms of the Wigner functions [see Eqs (4)–(12) and (14)–(22)]. The antisymmetric ordering supermatrix contains just a single independent element since $S_{xy}^{XY} = S_{yx}^{YX}$ and $S_{xy}^{XY} = S_{yx}^{YX}$. We take this independent component to be $S_{xy}^{XY} - S_{xy}^{YX}$ [see Eq. (A5)]. The direction cosines occurring in this element can be written as the scalar products of the unit vectors defining the molecular and laboratory frames. That is

$$S_{xy}^{XY} - S_{xy}^{YX} = (3/2)\langle (\mathbf{x} \cdot \mathbf{X})(\mathbf{y} \cdot \mathbf{Y}) - (\mathbf{x} \cdot \mathbf{Y})(\mathbf{y} \cdot \mathbf{X}) \rangle, \quad (\text{A6})$$

and use of the Binet-Cauchy identity [40] allows this to be written as

$$S_{xy}^{XY} - S_{xy}^{YX} = (3/2)\langle (\mathbf{x} \wedge \mathbf{y}) \cdot (\mathbf{X} \wedge \mathbf{Y}) \rangle. \quad (\text{A7})$$

The two cross products define, in a sense, the axes \mathbf{z} and \mathbf{Z} in the molecular and laboratory frames, respectively. There is, however, a fundamental difference between the conventional axes \mathbf{z} and \mathbf{Z} which are polar vectors, that is they change sign under inversion through the center of symmetry of the respective coordinate system. In contrast the vectors defined by the cross products are axial or pseudovectors, that is they do not change sign under inversion. To distinguish between these two classes of vector we add a tilde to the pseudovectors so that the independent element of the antisymmetric supermatrix is given by

$$S_{xy}^{XY} - S_{xy}^{YX} = (3/2)\langle \tilde{\mathbf{z}} \cdot \tilde{\mathbf{Z}} \rangle. \quad (\text{A8})$$

Since neither $\tilde{\mathbf{z}}$ nor $\tilde{\mathbf{Z}}$ changes sign when inverted through the center of symmetry of their respective frames this means that the order parameter $(S_{xy}^{XY} - S_{xy}^{YX})$ is invariant under inversion and does not vanish for a molecule with C_{2h} point group symmetry in a phase having the same symmetry. This contrasts with the behavior of the analogous order parameter $\langle \mathbf{z} \cdot \mathbf{Z} \rangle$ defined in terms of the axes in the molecular and laboratory frames. These are conventional vectors and so change sign when the respective system, molecule or laboratory, is inverted through the center of symmetry. In consequence the polar order parameter $\langle \mathbf{z} \cdot \mathbf{Z} \rangle$ will change sign and so must vanish in the C_{2h} phase, unlike the pseudovector order parameter $\langle \tilde{\mathbf{z}} \cdot \tilde{\mathbf{Z}} \rangle$.

We have introduced these order parameters using the Cartesian language since this leads logically to the definition of the pseudovector order parameter. However, this and the polar order parameter can also be written in terms of Wigner functions. Thus

$$\langle \mathbf{z} \cdot \mathbf{Z} \rangle = \langle D_{00}^1 \rangle \quad (\text{A9})$$

and

$$\langle \tilde{\mathbf{z}} \cdot \tilde{\mathbf{Z}} \rangle = \langle \tilde{D}_{00}^1 \rangle, \quad (\text{A10})$$

where the tilde again indicates the definition in terms of pseudovectors for the molecule and for the phase. The consequence of this is that $\langle D_{00}^1 \rangle$ will change sign on inverting through the center of symmetry in the C_{2h} phase and so this polar order parameter will vanish. This contrasts with the behavior of the pseudovector order parameter which does not change sign on inversion and so does not vanish in a C_{2h} phase composed of molecules with the same symmetry. We note that Mettout [17] has also considered the pseudovector and polar order parameters based on rank one Wigner functions.

APPENDIX B

Here we show in a little detail that, based on the C_{2h} point group symmetry of the molecules, there are just six nonzero components of the interaction supertensors u_{2mn} [20].

(a) The molecules comprising the system are identical and so

$$u_{2mn} = u_{2nm}, \quad (\text{B1})$$

where the subscript m refers to molecule 1 and n refers to molecule 2.

(b) The internal energy $\langle U \rangle$ constructed from the invariants in Eq. (24) is real so that [20]

$$u_{2mn}^* = (-)^{m+n} u_{2-m-n}. \quad (\text{B2})$$

(c) The $C_2(z)$ element of C_{2h} requires that for u_{2mn} the subscripts m and n can only take values 0 and ± 2 .

These three constraints lead to the following six independent nonzero components of the interaction supertensor u_{2mn} ,

$$(1) u_{200},$$

$$\left. \begin{array}{l} (2) u_{202} = u_{220}, \\ (3) u_{20-2} = u_{2-20}, \end{array} \right\} \begin{array}{l} \text{These components are related} \\ \text{by } u_{202}^* = u_{20-2} \text{ and} \\ u_{220}^* = u_{2-20}. \end{array}$$

$$\left. \begin{array}{l} (4) u_{222}, \\ (5) u_{2-2-2}, \\ (6) u_{22-2} = u_{2-22}. \end{array} \right\} \begin{array}{l} \text{These components are related} \\ \text{by } u_{222}^* = u_{2-2-2}. \end{array}$$

The two components given against (6) are real since $u_{22-2}^* = u_{2-22}$.

Although these six independent components were obtained by symmetry based arguments it is possible that transformation to a new molecular frame by rotation about the $C_2(z)$ axis could reduce the number further. We have explored this possibility and it seems to be feasible. Rotation of the axis system about z through an angle γ causes the components of the supertensor to change according to

$$u'_{2mn} = u_{2mn} \exp[i(m+n)\gamma]. \quad (\text{B3})$$

Here the prime denotes the value following the rotation. In order for, say, λ_0 [see Eq. (30)] to vanish we require

$$u_{222} \exp(i4\gamma) - u_{2-2-2} \exp(-i4\gamma) = 0. \quad (\text{B4})$$

To solve this equation for γ we write

$$u_{222} = a_{222} + ib_{222}, \quad (\text{B5})$$

and since u_{2-2-2} is u_{222}^* then

$$u_{2-2-2} = a_{222} - ib_{222}. \quad (\text{B6})$$

Substitution of these two results into Eq. (B4) then gives the rotation angle making λ_0 vanish as

$$\tan 4\gamma = -b_{222}/a_{222}. \quad (\text{B7})$$

Similar arguments show that for γ_a to be zero the rotation angle is

$$\tan 2\gamma = -b_{220}/a_{220}, \quad (\text{B8})$$

and for γ_s to be zero requires

$$\tan 2\gamma = a_{220}/b_{220}. \quad (\text{B9})$$

Thus the three coefficients can be made to vanish but not simultaneously, each requires a different angle of rotation. This could simplify the complete molecular field theory to some extent. In addition, it would provide an unambiguous way in which to define the x and y molecular axes. In contrast, the more important relative coefficient λ_a cannot, in general, be made to vanish. We shall return to this possibility as well as other ways of simplifying the problem in a subsequent paper [41].

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