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Simple model for biaxial smectic-*A* liquid-crystal phases

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We have generalized the McMillan theory of liquid crystalline smectic order in uniaxial particle fluids to biaxial particles. Upon varying the control parameter, a uniaxial nematic phase may: (i) order biaxially first, then smectically; (ii) order smectically first, then biaxially; and (iii) simultaneously order biaxially and smectically. We investigate, in the limit of complete orientational order of the molecular major axes, which of these scenarios are realized for a simple model of particles with the symmetry of rectangular parallelepipeds. We also present a generic variational derivation of the theory based on the identification of the dominant order parameters for the most ordered phase.

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I. INTRODUCTION

The quest for the elusive thermotropic biaxial nematic phase continues to arouse considerable interest and excitement. These have been stimulated by recent reports to have prepared and identified the biaxial nematic phase, in 2004 and then in 2005. In the first of these, the molecular biaxiality is thought to result from their V shape [1] while in the second the molecular tetrapode is taken to have a biaxial block shape [2]. The interest in this nematic phase stems, in part, from its potential applications, for example, in a fast switching liquid crystal display and to create biaxial compensating polymer films for displays. The excitement stems from the fact that although the existence of the biaxial nematic phase was predicted over 35 years ago [3], claims to have discovered the thermotropic phase have not been substantiated [4]. Indeed, even the most recent claims to have found thermotropic biaxial nematics do not seem to have provided absolute evidence for the biaxiality of the nematic phase [5].

The primary challenge in creating a biaxial nematic would seem to be to design a molecule of sufficient biaxiality. However, theory [6] suggests that this may not be sufficient and that it could also be necessary to cool the system to very low temperatures in order to locate the biaxial nematic. Still, Freiser [3] and others [7,8] have realized that this strategy may also fail because the uniaxial nematic will usually undergo a transition to a smectic or crystal phase before the biaxial nematic is reached. Of course, the low temperature itself is not a sufficient condition, what is really needed is a high molecular order of the major axis of the molecule, for this then allows a more effective anisotropic interaction between the minor axes. This requirement is not, however, necessarily compatible with a high molecular biaxiality because this is known to reduce the orientational order of the uniaxial nematic phase [9].

This problem for nematics may not be so severe for the smectic *A* phase for, although the molecular biaxiality does influence the smectic *A*-nematic transition [10], its influence on the major order parameter may not be so large because this is coupled to the translational order of the smectic phase [11,12]. It should, therefore, be easier to create a biaxial smectic *A* phase than the biaxial nematic especially if the system undergoes a transition directly from the isotropic phase to the smectic *A*, for then the orientational order is especially large [11]. For a biaxial smectic *A* phase formed from block-shaped molecules the structural organization is expected to be like that sketched in Fig. 1(a) with its D_{2h} symmetry. By analogy with the notation used for the two nematic phases N_{U} and N_{B}, the uniaxial smectic *A* should be denoted by SmA_{U} and its biaxial variant by SmA_{B}. In such a structure one director, say **n**, is clearly parallel to the layer normal while the other two, **l** and **m**, are in the layer plane. For a system of V-shaped molecules one possible molecular organization in a layered structure is sketched in Fig. 1(b) [13]. The mesogenic arms are tilted with respect to the layer normal, although the tilt directions alternate regularly from layer to layer. On average one director is parallel to the layer normal and the other two are parallel to the layer plane, as for the SmA_{B} phase formed from molecular blocks [see Fig. 1(a)]. The symmetry of this smectic phase is now C_{2v} and so it is appropriate to denote the phase with a symbol which indicates its polarity. One choice would be SmA_{BP} although there are other possibilities [14]. In the limit that there are no orientational correlations of the polar axes of the molecules then the phase would be apolar but it would retain its biaxiality to give a SmA_{B} phase.

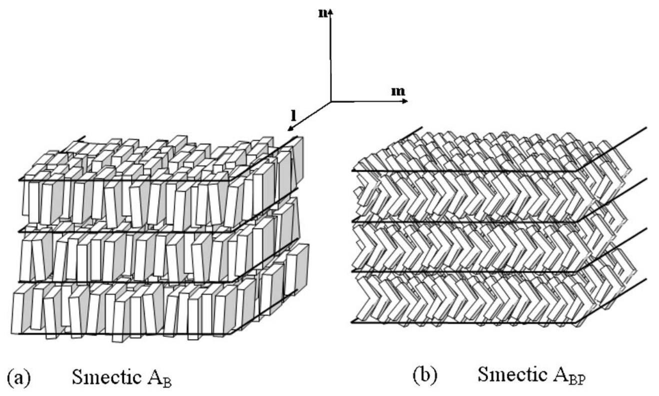
The possible existence of the apolar biaxial smectic *A* phase was first mentioned by de Gennes in the first edition of his classic book [15]. Here he attributed the suggestion to McMillan, and in a later printing, dated 1975, referred to a paper by Meyer and McMillan [16] as the source. However, this does not appear to contain any specific reference to the biaxial smectic *A* phase. The important suggestion went essentially unnoticed for several years, although in 1981 Matsushita independently predicted the existence of the SmA_{B} phase, based on a molecular field theory [17]. This theory is, in essence, a combination of that proposed by Freiser for the biaxial nematic phase [3] and the original version of McMillan's theory for the smectic *A* phase which ignores the pure translational order [11,12]. The predicted phase behavior of the system is controlled by two parameters: The molecular biaxiality, which, following Matsushita, we shall denote by

Ξ, although we note that λ is often used in theories of biaxial nematics, and α which determines the formation of the smectic structure; a relatively small region of this parameter space was explored. In general, the system can exhibit five phases, biaxial smectic *A* (SmA_B), uniaxial smectic *A* (SmA_U), biaxial nematic (N_B), uniaxial nematic (N_U), and isotropic (*I*). He discovered three specific phase sequences: SmA_B-SmA_U-N_U-*I*, SmA_B-N_U-*I*, and SmA_B-N_B-N_U-*I*. The order of the transitions was also explored; the N_U-*I* transition is first order, as expected; the SmA_U-N_U is second order, presumably because of the large nematic range [11]; and the SmA_B-SmA_U transition is largely second order, but for a narrow range of high molecular biaxialities it becomes first order. The SmA_B-N_U transition is first order and finally the SmA_B-N_B is second order. A Ginzburg-Landau theory has been developed for the biaxial smectic *A* phase [18]. This also predicts that the SmA_B-$N_B$transition to be second order; unfortunately the other transitions were not investigated with this theory.

At an experimental level the discovery of materials with an apolar biaxial smectic *A* phase has been rather limited although the systems exhibiting the polar equivalent are more extensive [19]. For both classes, however, the identification seems to have been far less problematic than for the biaxial nematic phase [4,5]. In the remainder of this paper our primary concern will be with the apolar biaxial smectic *A* phase. The first example of the SmA_B phase was discovered for a liquid crystal side group polymer [20]. The mesogenic group in the polymer was based on the biaxial disubstituted naphthalene unit and the biaxiality was enhanced by attaching it laterally through a flexible spacer to the polymer backbone. This polymer exhibits a biaxial nematic phase followed by the apolar biaxial smectic *A* phase which was identified by conoscopy and x-ray scattering. It was not until eight years later that the first claim to have observed the SmA_B phase for a low molar mass mesogen appeared [21]. The compound was a metallomesogen with a central copper atom linking two rodlike mesogenic groups to give the requisite block shape. The smectic *A* phase was formed directly from the isotropic phase and so its orientational order should be high [11]. The symmetry for the smectic *A* phase was established from that of the diamagnetic susceptibility tensor, determined using an electron spin resonance (ESR) technique, and found to be D_{2h}. Subsequently the identification of this as a SmA_B phase was checked using deuterium NMR spectroscopy and it was discovered that the smectic *A* phase had uniaxial symmetry [22] and not the biaxial that had been claimed. Two years later a similar set of metallomesogens were studied but with palladium linking the two rodlike mesogenic groups [23]. Depending on the number of dodecyloxy chains attached laterally to one of these groups the compound was found to exhibit an enantiotropic uniaxial smectic *A* phase, a monotropic SmA_U, or no smectic phase. However, when each of these compounds was mixed with about 20 mol % of the chemical inductor trinitrofluorenone, the mixtures were discovered to form the apolar biaxial smectic A phase. This phase was identified from the optical texture and the x-ray scattering patterns from monodomain samples. In between these two claims to have found the apolar biaxial smectic A phase, there was a report to have discovered a SmA_B with a totally different structure [24]. The system forming this new biaxial phase was a mixture composed of a mesogen having rodlike molecules and one composed of V-shaped molecules. The identification of the phase biaxiality was supported by, among other things, the observation of a schlieren texture when the sample was viewed normal to the smectic layers. The optical biaxiality is attributed to the arrangement of the bisector of the mesogenic arms of the V-shaped molecules parallel to the layer normal and with their planes orientationally correlated. Since the calamitic mesogen forms a bilayer smectic *A* phase, it is expected that the bisector of the arms will be aligned in equal amounts parallel and antiparallel to the layer normal, thus giving an apolar biaxial smectic *A* phase. The binary mixture behaves, therefore, in a similar manner to that for a mixture of rodlike and disclike particles which is predicted to form a biaxial nematic phase [25]. However, the biaxial nematic is found to separate into two uniaxial nematics [26], apparently unlike its smectic analog. Although this biaxial smectic *A* phase is of undoubted interest we shall not consider it any further here.

At about the same time computer simulation studies of model systems had also revealed the existence of the rare SmA_B phase. In the first of these investigations the intermolecular interactions were taken to be described by a biaxial variant of the Gay-Berne pair potential for uniaxial molecules [27]. This extension to the potential is especially important because it shows that there are two measures of the molecular biaxiality, one associated with the anisotropic attractive interactions and the other with the anisotropic repulsive forces. The latter are associated with the molecular shape and it is this which is usually invoked when the likelihood of a biaxial molecule forming a biaxial liquid crystal phase is considered. For the biaxial Gay-Berne mesogen it is found that when the attractive and repulsive biaxialities aid each other then a SmA_B phase is formed [8]. In contrast when they oppose then the phase sequence is found to be SmA_B-N_B-N_U-*I*. A system of hard blocks, where only the biaxiality in the anisotropic repulsive forces obtains, has been studied [28]. In this simpler, more idealistic model the simulations were facilitated by forcing the major axes of the molecules to remain parallel so that the system cannot form an isotropic phase. The phase behavior of the model system was found to be relatively rich, in a manner determined by the molecular biaxiality which is related to the ratio of the lengths of the minor axes. Depending on this ratio the phase sequence can be SmA_B-SmA_U-N_U or SmA_B-N_B-N_U. Binary mixtures were also investigated in which the components had the same biaxiality but the lengths of the major axes were different. This strategy was devised to suppress the smectic phase and so enhance the biaxial nematic range, which was successful. However, depending on the molecular biaxiality and the composition of the binary mixture the same phase sequences were observed.

In an attempt to help establish design criteria for the creation of the apolar biaxial smectic *A* phase, we have extended the molecular field theory for this phase. In particular we have derived the potential of mean force and mean torque using a variational approach which avoids the unrealistic truncation of the pair interaction implicit in other derivations.



(a) Smectic A_B (b) Smectic A_{BP}

FIG. 1. Schematic representation of the biaxial smectic phases of (a) block-shaped molecules (SmA_B), and (b) V-shaped molecules (SmA_BP).

We have also introduced a term in the potential resulting from the pure translational order. The other important feature is our attempt to relate the parameters in the theory to the molecular structure, albeit in an idealistic manner. The results of our theoretical study of the SmA_B phase are presented here and where possible contact is made with the limited range of experimental and simulation investigations of this phase. In Sec. II A we describe the order parameters needed to characterize the liquid crystal phases formed by the system and the theory based on them. The phase behavior predicted via a bifurcation analysis is then presented. The model is extended in Sec. II B to allow a more transparent relationship between the parameters occurring in the theory and the idealized molecular structure. In Sec. III we give our conclusions and the details of the variational derivation of the theory are contained in the Appendix.

II. THEORY

A. Mark I

We consider a fluid of biaxial objects of block shape and (mutually orthogonal) principal axes **a**, **b**, and **c** (see Fig. 2), and define the following microscopic tensors to describe their orientations:

$$S_{\alpha\beta} = a_\alpha a_\beta - \frac{1}{3}\delta_{\alpha\beta}, \tag{1}$$

$$B_{\alpha\beta} = b_\alpha b_\beta - c_\alpha c_\beta. \tag{2}$$

Here and in what follows, Greek subscripts denote laboratory coordinates, whereas Latin labels those for the particles. The most general form of the interaction between two such objects (to second order in $S_{\alpha\beta}$ and $B_{\alpha\beta}$) is

$$V_N(1,2) = J_0(r^{12}) + \frac{2}{3}J_2(r^{12})\mathrm{Tr}(S^1_{\alpha\beta}S^2_{\alpha\beta}) + \frac{2}{3}J_3(r^{12})\mathrm{Tr}(S^1_{\alpha\beta}B^2_{\alpha\beta} + S^2_{\alpha\beta}B^1_{\alpha\beta}) + \frac{2}{3}J_4(r^{12})\mathrm{Tr}(B^1_{\alpha\beta}B^2_{\alpha\beta}), \tag{3}$$

where $(1,2)$ denotes the set of all coordinates (position and orientation) of particles 1 and 2, $J_i \equiv J_i(r^{12})$ $(i=0,2,3,4)$ are functions (of range ξ) that do not depend on orientations but do on particle separation r^{12}, Tr denotes the trace operation, and the factors of $2/3$ have been introduced for later convenience. It is easy to show by explicit calculation that

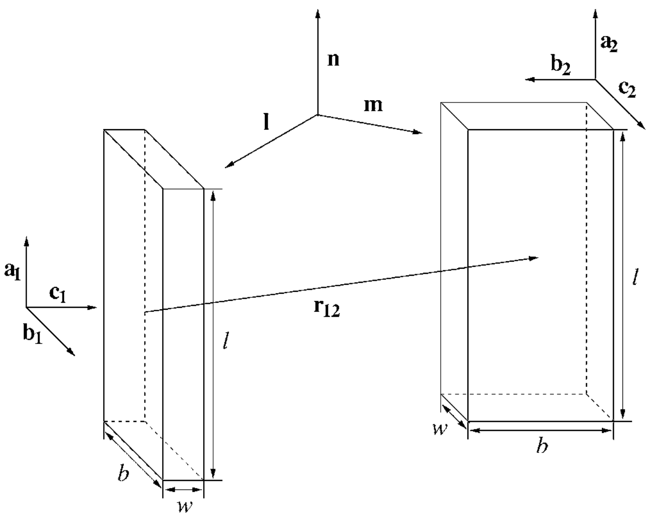


FIG. 2. Symmetry of the molecular model: biaxial parallelepipeds of edge lengths l, b, and w. **l**, **m**, and **n** are the three directors for the biaxial phase, with **n** the usual uniaxial director.

$$\begin{aligned} V_N(1,2) = {} & J_0(r^{12}) + J_2(r^{12})P_2(\mathbf{a}^1\cdot\mathbf{a}^2) + J_3(r^{12})[P_2(\mathbf{a}^1\cdot\mathbf{b}^2) \\ & - P_2(\mathbf{a}^1\cdot\mathbf{c}^2) + P_2(\mathbf{b}^1\cdot\mathbf{a}^2) - P_2(\mathbf{c}^1\cdot\mathbf{a}^2)] + J_4(r^{12}) \\ & \times[P_2(\mathbf{b}^1\cdot\mathbf{b}^2) - P_2(\mathbf{c}^1\cdot\mathbf{a}^2) + P_2(\mathbf{c}^1\cdot\mathbf{c}^2) \\ & - P_2(\mathbf{b}^1\cdot\mathbf{a}^2)], \end{aligned} \tag{4}$$

which is identical to the interaction between hard rectangular parallelepipeds introduced by Straley [29]; the same functional form was obtained by Luckhurst and coworkers [9] by a different route and is not restricted to hard particles. In the spirit of the McMillan model [11], we write the intermolecular potential appropriate to (uniaxial) *smectic A* (SmA_U) order as

$$V_S(1,2) = V_N(1,2)[1 + I_0\cos k(z^1 - z^2)], \tag{5}$$

where $I_0 > 0$ is the (constant) relative strength of the smectic part of the potential, $k = 2\pi/d$ is the wave number of a smectic phase of layer spacing d, and z^i is the coordinate of the center of mass of particle i; we have taken the z axis to be perpendicular to the layers. The sign of I_0 is chosen so that the density maximum of the smectic wave is at the center of the layer. In the remainder of this section we shall take the J_i $(i=0,2,3,4) < 0$ to be constants, i.e., in the spirit of molecular field theory we effectively replace them by their averages over r^{12}, the interparticle separation, and require that these averages be negative, so as to favor biaxial order. Accordingly, we drop their explicit r^{12} dependence: Henceforth the only positional dependence of $V_S(1,2)$ is through the term $\cos k(z^1-z^2)$.

Assuming, as seems reasonable, that the system is invariant in the xy plane, i.e., that there is nonuniformity only along z, the molecular field Helmholtz free energy difference (per unit area per layer) between ordered and isotropic (I) phases is

$$\frac{\Delta F}{Ad} = \beta^{-1}\rho\langle\ln[8\pi^2 f(z,\Omega)]\rangle + \frac{\rho^2\xi^2 d}{2}\int_0^d dz^1 \int d\Omega^1 \int_0^d dz^2 \int d\Omega^2 f(z^1,\Omega^1)V_S(z^1,\Omega^1;z^2,\Omega^2)f(z^2,\Omega^2) = \beta^{-1}\rho\langle\ln[8\pi^2 f(z,\Omega)]\rangle + \frac{\rho^2}{2}\int_0^d dz \int d\Omega\, U_{MF}(z,\Omega)f(z,\Omega), \tag{6}$$

where A is the layer surface area, $\beta=1/(k_BT)$, ρ is the number density, $\xi^2 d$ is an "interaction volume" that comes from integrating over x and y, $\Omega=(\phi,\theta,\chi)$ are the Euler angles describing particle orientation with respect to the laboratory frame, $f(z,\Omega)$ is the singlet positional-orientational distribution function giving the probability that a particle located between z and $z+dz$ has orientation in $(\Omega,\Omega+d\Omega)$, and

$$\langle\mathcal{A}(z,\Omega)\rangle = \int_0^d dz \int d\Omega\,\mathcal{A}(z,\Omega)f(z,\Omega). \tag{7}$$

The second equality in Eq. (6) defines the molecular field potential as

$$U_{\mathrm{MF}}(z,\Omega) = \xi^2 d\int_0^d dz' \int d\Omega' f(z',\Omega')V_S(z,\Omega;z',\Omega'). \tag{8}$$

This is the potential experienced by a *single* particle due to the presence of all others: It plays a crucial role in the theory. One then obtains the positional-orientational distribution function $f(z,\Omega)$ by minimization of the free energy, subject to the constraint that $f(z,\Omega)$ be normalized to 1, $\langle 1\rangle=1$ [see Eq. (7)], leading to

$$f(z,\Omega) = \frac{\exp[-\beta\rho U_{\mathrm{MF}}(z,\Omega)]}{\int_0^d dz \int d\Omega \exp[-\beta\rho U_{\mathrm{MF}}(z,\Omega)]}. \tag{9}$$

Finding $U_{\mathrm{MF}}(z,\Omega)$ is a relatively straightforward exercise in angular momentum algebra. The final result is

$$\begin{aligned} U_{\mathrm{MF}}(z,\Omega) = {} & w_0 + w_{0s}\cos kz + (w_1 + w_{1s}\cos kz)P_2(\cos\theta) \\ & + (w_2 + w_{2s}\cos kz)\sin^2\theta\cos 2\phi + (w_3 \\ & + w_{3s}\cos kz)\sin^2\theta\cos 2\chi + (w_4 + w_{4s}\cos kz) \\ & \times\left[\frac{1}{2}(1+\cos^2\theta)\cos 2\phi\cos 2\chi \right. \\ & \left. - \cos\theta\sin 2\phi\sin 2\chi\right], \end{aligned} \tag{10}$$

where

$$w_0 = J_0\xi^2 d, \tag{11}$$

$$w_{0s} = I_0 J_0\xi^2 d\tau, \tag{12}$$

$$w_1 = \xi^2 d(J_2 S - J_3 D), \tag{13}$$

$$w_{1s} = I_0\xi^2 d(J_2\sigma_S - J_3\sigma_D), \tag{14}$$

$$w_2 = -\frac{3}{2}\xi^2 d(J_2 P - J_3 B), \tag{15}$$

$$w_{2s} = -\frac{3}{2}I_0\xi^2 d(J_2\sigma_P - J_3\sigma_B), \tag{16}$$

$$w_3 = \frac{3}{2}\xi^2 d(J_3 S - J_4 D), \tag{17}$$

$$w_{3s} = \frac{3}{2}I_0\xi^2 d(J_3\sigma_S - J_4\sigma_D), \tag{18}$$

$$w_4 = -3\xi^2 d\left(J_3 P - \frac{1}{2}J_4 B\right), \tag{19}$$

$$w_{4s} = -3I_0\xi^2 d\left(J_3\sigma_P - \frac{1}{2}J_4\sigma_B\right). \tag{20}$$

Here we have defined the order parameters

$$S = \langle P_2(\mathbf{a}\cdot\mathbf{n})\rangle = \langle P_2(\cos\theta)\rangle, \tag{21}$$

$$P = \frac{1}{3}[\langle P_2(\mathbf{a}\cdot\mathbf{m})\rangle - \langle P_2(\mathbf{a}\cdot\mathbf{l})\rangle] = -\frac{1}{2}\langle\sin^2\theta\cos 2\phi\rangle, \tag{22}$$

$$D = \langle P_2(\mathbf{b}\cdot\mathbf{n})\rangle - \langle P_2(\mathbf{c}\cdot\mathbf{n})\rangle = -\frac{3}{2}\langle \sin^2\theta \cos 2\chi\rangle, \tag{23}$$

$$\begin{aligned} B &= \frac{1}{3}[\langle P_2(\mathbf{b}\cdot\mathbf{m})\rangle - \langle P_2(\mathbf{b}\cdot\mathbf{l})\rangle - \langle P_2(\mathbf{c}\cdot\mathbf{m})\rangle + \langle P_2(\mathbf{c}\cdot\mathbf{l})\rangle] \\ &= \left\langle \left[\frac{1}{2}(1+\cos^2\theta)\cos 2\phi \cos 2\chi - \cos\theta \sin 2\phi \sin 2\chi\right]\right\rangle, \end{aligned} \tag{24}$$

$$\tau = \langle \cos kz\rangle, \tag{25}$$

$$\sigma_S = \langle P_2(\mathbf{a}\cdot\mathbf{n})\cos kz\rangle = \langle P_2(\cos\theta)\cos kz\rangle, \tag{26}$$

$$\begin{aligned} \sigma_P &= \frac{1}{3}\langle [P_2(\mathbf{a}\cdot\mathbf{m}) - P_2(\mathbf{a}\cdot\mathbf{l})]\cos kz\rangle \\ &= -\frac{1}{2}\langle \sin^2\theta \cos 2\phi \cos kz\rangle, \end{aligned} \tag{27}$$

$$\begin{aligned} \sigma_D &= \langle [P_2(\mathbf{b}\cdot\mathbf{n}) - P_2(\mathbf{c}\cdot\mathbf{n})]\cos kz\rangle \\ &= -\frac{3}{2}\langle \sin^2\theta \cos 2\chi \cos kz\rangle, \end{aligned} \tag{28}$$

$$\begin{aligned} \sigma_B &= \frac{1}{3}\langle [P_2(\mathbf{b}\cdot\mathbf{m}) - P_2(\mathbf{b}\cdot\mathbf{l}) - P_2(\mathbf{c}\cdot\mathbf{m}) + P_2(\mathbf{c}\cdot\mathbf{l})]\cos kz\rangle \\ &= \left\langle \left[\frac{1}{2}(1+\cos^2\theta)\cos 2\phi \cos 2\chi \right.\right. \\ &\qquad \left.\left. - \cos\theta \sin 2\phi \sin 2\chi\right]\cos kz\right\rangle, \end{aligned} \tag{29}$$

which are purely orientational (S, P, D, B), purely positional (τ), or mixed (σ_S, σ_P, σ_D, σ_B). In Eqs. (21)–(29), **l**, **m**, and **n** denote the directors, which are the principal axes of the *phase* (see Fig. 2). Insertion of Eq. (10) into Eq. (6) together with Eqs. (21)–(29) yields for the free energy

$$\begin{aligned} \frac{\Delta F}{Ad} &= \beta^{-1}\rho\langle \ln[8\pi^2 f(z,\Omega)]\rangle + \frac{\rho^2}{2}\Big[(w_0 + w_{0s}\tau) + (w_1 S \\ &\quad + w_{1s}\sigma_S) \;-\; 2(w_2 P + w_{2s}\sigma_P) - \frac{2}{3}(w_3 D + w_{3s}\sigma_D) \\ &\quad + (w_4 B + w_{4s}\sigma_B)\Big]. \end{aligned} \tag{30}$$

The orientational order parameters S, P, D, and B are related to the orientational order parameters $Q_{\alpha\beta}$ and $Q^b_{\alpha\beta}$, defined as the position- and orientation-weighted averages of the microscopic orientation tensors $S_{\alpha\beta}$ and $B_{\alpha\beta}$ of Eqs. (1) and (2), respectively, by

$$Q_{\alpha\beta} = \langle S_{\alpha\beta}\rangle = SQ^0_{\alpha\beta} + PD_{\alpha\beta}, \tag{31}$$

$$Q^b_{\alpha\beta} = \langle B_{\alpha\beta}\rangle = DQ^0_{\alpha\beta} + BD_{\alpha\beta}, \tag{32}$$

where

$$Q^0_{\alpha\beta} = n_\alpha n_\beta - \frac{1}{3}\delta_{\alpha\beta}, \tag{33}$$

$$D_{\alpha\beta} = m_\alpha m_\beta - l_\alpha l_\beta. \tag{34}$$

[To show that S, P, D, and B are indeed given by Eqs. (21)–(24), multiply Eqs. (31) and (32) in turn by $Q^0_{\alpha\beta}$ and $D_{\alpha\beta}$ and take the trace.] S is the usual (uniaxial) nematic order parameter of the molecular major axes **a** with respect to the director **n**; P describes the asymmetry of the fluctuations of **a** about **n**, i.e., it is a measure of phase biaxiality; and D measures the difference in order of the molecular minor axes **b** and **c** about **n** i.e., it is a measure of the molecular biaxiality. Finally, B tells how differently the molecular minor axes **b** and **c** align along **l** and **m**, i.e., it is the dominant biaxial order parameter. In the limit $S\rightarrow 1$, D and P vanish and $B\rightarrow 1$; it can be proved that in this limit $P\rightarrow B(1-S)^2$ [30]. In the remainder of this paper we shall work in the perfect (uniaxial) nematic order limit $S=1$, and accordingly neglect any terms containing D, P, σ_D, or σ_P. This is done to facilitate the numerical analysis, but we note that such an assumption is not unreasonable deep in the N_{U} phase where one expects transitions into smectic phases. In addition, it is consistent with computer simulation results for biaxial Gay-Berne mesogens by Berardi and Zannoni [8], who found (in our notation) $S\sim 0.6-0.8$. The number of order parameters in the free energy, Eq. (30), is thus reduced from an unwieldy nine to a more manageable three, on further noting that $\sigma_S \rightarrow \tau$. Moreover, when $S=1$, $\mathbf{a}^{\mathbf{i}} \| \mathbf{a}^{\mathbf{j}}$, hence $\mathbf{a}^{\mathbf{i}} \perp \mathbf{b}^{\mathbf{j}}$, $\mathbf{a}^{\mathbf{i}} \perp \mathbf{c}^{\mathbf{j}}$, ($i \neq j$) and the J_3 term vanishes, whereupon the molecular field potential becomes

$$\begin{aligned} U_{\mathrm{MF}}(z,\psi) &= (J_0 + J_2)\xi^2 d(1 + \tau I_0 \cos kz) \\ &\quad + \frac{3}{2}J_4 \xi^2 d(B + \sigma_B I_0 \cos kz)\cos 2\psi, \end{aligned} \tag{35}$$

where $\psi = \phi + \chi$ (in this limit, the two Euler angles play exactly the same role and only their sum appears). Clearly, the natural energy scale is $J_0 + J_2$, leading us to define the reduced molecular field potential as

$$\begin{aligned} U^*_{\mathrm{MF}}(z,\psi) &= \frac{U_{\mathrm{MF}}(z,\psi)}{(J_0+J_2)\xi^2 d} = 1 + \tau I_0 \cos kz \\ &\quad + \frac{3}{2}J^*_4(B + \sigma_B I_0 \cos kz)\cos 2\psi. \end{aligned} \tag{36}$$

For given I_0 and $J^*_4 \equiv J_4/(J_0+J_2)$, we could now solve the consistency equations for the order parameters, Eqs. (24), (25), and (29) with angular averages defined according to Eq. (7), substitute the results into Eq. (30) (with $S=1$, $\sigma_S = \tau$, $P = D = \sigma_D = \sigma_P = 0$) and thereby compare the free energies of the different phases and locate the phase transitions. This is to explore whether any transitions are first order or continuous: We already know that the uniaxial-to-biaxial nematic transition is continuous, as (in the limit $S=1$) it is equivalent to two-dimensional nematic ordering. If any first-order transitions are found, coexistence (at constant total volume) can then be calculated using the standard double-tangent construction.

However, it is useful first to investigate the stability of the (assumed perfectly ordered) uniaxial nematic phase relative to either biaxial nematic or smectic fluctuations, as a function of the interaction parameters. This can be carried out analytically using bifurcation analysis, and serves as a check on any future numerical work. Following Mulder [31], we write the positional-orientational distribution function as a power series in the small parameter ϵ

$$f(z,\psi) = f^{(0)}(z,\psi) + \epsilon f^{(1)}(z,\psi) + \epsilon^2 f^{(2)}(z,\psi) + \cdots, \quad (37)$$

where

$$f^{(0)}(z,\psi) = \frac{1}{2\pi d}, \quad (38)$$

is the positional-orientational distribution function of the perfectly ordered uniaxial nematic phase, and $f^{(1)}(z,\psi)$ and $f^{(2)}(z,\psi)$ are determined by substituting Eq. (37) into Eq. (9) and equating terms of the same order in ϵ

$$f^{(1)}(z,\psi) = -\frac{\beta^*\rho\xi^2 d}{2\pi d}\left[\tau^{(1)} I_0 \cos kz + \frac{3}{2}J_4^*(B^{(1)} + \sigma_B^{(1)} I_0 \cos kz)\cos 2\psi\right], \quad (39)$$

$$\begin{aligned} f^{(2)}(z,\psi) = &-\frac{\beta^*\rho\xi^2 d}{2\pi d}\left[\tau^{(2)} I_0 \cos kz + \frac{3}{2}J_4^*(B^{(2)} + \sigma_B^{(2)} I_0 \cos kz)\cos 2\psi\right] \\ &+ \frac{(\beta^*\rho\xi^2 d)^2}{4\pi d}\left[\tau^{(1)} I_0 \cos kz + \frac{3}{2}J_4^*(B^{(1)} + \sigma_B^{(1)} I_0 \cos kz)\cos 2\psi\right]^2. \end{aligned} \quad (40)$$

Here, we have defined $\beta^* = \beta(J_0 + J_2)$ and

$$B^{(k)} = \int_0^d dz \int_0^{2\pi} d\psi \cos 2\psi f^{(k)}(z,\psi), \quad (41)$$

$$\tau^{(k)} = \int_0^d dz \int_0^{2\pi} d\psi \cos kz f^{(k)}(z,\psi), \quad (42)$$

$$\sigma_B^{(k)} = \int_0^d dz \int_0^{2\pi} d\psi \cos 2\psi \cos kz f^{(k)}(z,\psi). \quad (43)$$

Equation (39) is a linear eigenvalue equation for $f^{(1)}(z,\psi)$—the bifurcation equation—that gives the bifurcation points from the uniaxial nematic to the other phases. The symmetry of the latter is that of the corresponding eigenfunctions.

The sharp-eyed reader will not have failed to notice that this bifurcation analysis also involves expanding what Mulder [31] calls the "control parameter" λ, which in our case corresponds to $\beta^*\rho\xi^2 d \equiv \beta^*\rho^*$, in a power series in ϵ similar to Eq. (37). Identification of the actual physical control parameter requires that we specify a molecular model for this system. In a thermotropic liquid crystal, λ will typically be the temperature (or, equivalently, β) and ρ can be regarded as a constant, since it follows, but does not trigger, the transitions (although one could also conceivably keep the temperature constant and vary the density). On the other hand, for a liquid crystal composed of hard bodies treated at the level of Onsager theory [32], the intermolecular potential $V_S(1,2)$ of Eqs. (5) and (8) is replaced by $\beta^{-1}M(1,2)$, with $M(1,2)$ the Mayer function, the temperature drops out and the control parameter is simply the density. In order to retain full generality, in the remainder of this section we simply set $\lambda = \beta^*\rho^*$ and substitute its expansion

$$\lambda = \lambda^{(0)} + \epsilon\lambda^{(1)} + \epsilon^2\lambda^{(2)} + \cdots \quad (44)$$

into Eqs. (39) and (40). The first of these thus acquires its "standard" bifurcation equation form (with $\beta^*\rho^*$ replaced by $\lambda^{(0)}$), whose associated eigenvalues yield the instabilities, as we shall see presently. Because we are assuming perfect uniaxial nematic order with respect to the z axis, the eigenfunctions take the simplest possible forms.

(1) Bifurcation into the biaxial nematic (N_B) phase: The eigenfunction is $f^{(1)}(z,\psi) = \mathcal{C}\cos 2\psi$ and the instability occurs for

$$\lambda_c^{(0)} = -\frac{4}{3J_4^*}. \quad (45)$$

(2) Bifurcation into the uniaxial smectic ($\mathrm{Sm}A_\mathrm{U}$) phase: The eigenfunction is $f^{(1)}(z,\psi) = \mathcal{C}\cos kz$ and the instability occurs for

$$\lambda_c^{(0)} = -\frac{2}{I_0}. \quad (46)$$

(3) Bifurcation into the biaxial smectic ($\mathrm{Sm}A_\mathrm{B}$) phase: The eigenfunction is $f^{(1)}(z,\psi) = \mathcal{C}\cos 2\psi \cos kz$ and the instability occurs for

$$\lambda_c^{(0)} = -\frac{8}{3I_0 J_4^*}. \quad (47)$$

In all cases, $\mathcal{C}$ is a constant to be determined; it is different for each situation. Note that we do not consider the N_B-$\mathrm{Sm}A_\mathrm{B}$ transition, which is certainly possible in such systems (as we shall see later): Its study would require investigating the stability of the N_B phase with respect to smectic fluctuations.

The requirement that $\lambda_c^{(0)} > 0$ implies that a direct transition from N_U to $\mathrm{Sm}A_\mathrm{B}$ is only possible if J_4^* and I_0 have opposite signs. Recall that the sign of I_0 sets the phase of the smectic wave (i.e., the location of the density maximum either at the center of the layer or at the edges) and is otherwise unimportant, whereas J_4^* must be negative in order to favor biaxial order [see Eq. (4)]. From Eqs. (45)–(47) it is then readily concluded that:

(i) If $I_0 > 0$, there is no N_U-$\mathrm{Sm}A_\mathrm{U}$ transition

(a) If $I_0 < 2$, the N_U phase becomes unstable with respect to the N_B phase at $\lambda_c^{(0)} = -4/(3J_4^*)$.

(b) If $I_0 > 2$, the N_U phase becomes unstable with respect to the $\mathrm{Sm}A_\mathrm{B}$ phase at $\lambda_c^{(0)} = -8/(3I_0 J_4^*)$.

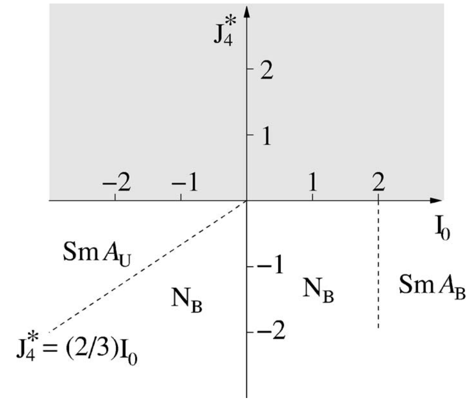


FIG. 3. Diagram showing the regions of instability, on increasing $\lambda^{(0)}$, of the uniaxial nematic ($N_{\rm U}$) phase relative to the biaxial nematic ($N_{\rm B}$), uniaxial smectic (Sm$A_{\rm U}$) and biaxial smectic (Sm$A_{\rm B}$) phases, as a function of the potential parameters I_0 and J_4^*. We do not concern ourselves with the hatched region, where $J_4^*>0$ and the molecular minor axes tend to align perpendicular, rather than parallel, to one another, hence no biaxial phases (in the usual sense) are expected to exist.

(ii) If $I_0<0$, there is no $N_{\rm U}$-Sm$A_{\rm B}$ transition

(a) If $|J_4^*|<(2/3)|I_0|$, the $N_{\rm U}$ phase becomes unstable with respect to the Sm$A_{\rm U}$ phase at $\lambda_c^{(0)}=-2/I_0$.

(b) If $|J_4^*|>(2/3)|I_0|$, the $N_{\rm U}$ phase becomes unstable with respect to the $N_{\rm B}$ phase at $\lambda_c^{(0)}=-4/(3J_4^*)$.

These results are summarized in Fig. 3. Figure 4 shows the order parameters versus the control parameter λ for each of the cases labeled 1–3 previously, Eqs. (45)–(47), obtained by solving Eqs. (24), (25), and (29) iteratively with the positional-orientational distribution function given by Eqs. (9) and (35); 16-point Gauss-Legendre quadrature [33] was used to perform the integrations over z and ψ. All of the transitions appear to be continuous; those from the $N_{\rm U}$ phase occur at the $\lambda_c^{(0)}$ found from the bifurcation analysis.

We conclude that our model exhibits $N_{\rm B}$, Sm$A_{\rm U}$, and Sm$A_{\rm B}$ phases, as well as the $N_{\rm U}$ phase. It remains to relate the potential parameters J_i ($i=0,2,4$) and I_0 to particle properties. However, it turns out that this is difficult to do for I_0 within our "decoupling" approximation, Eq. (5), whereby we simply took the smectic potential $V_S(1,2)$ to equal the nematic potential $V_N(1,2)$ times a single harmonic with the layer periodicity [34]. In the next section we propose a more sophisticated version of the theory which is free from this shortcoming.

B. Mark II

As a generalization of the extended McMillan model pair potential, Eq. (5) of the preceding section, we propose (in the limit of perfect uniaxial order, $S=1$, $\mathbf{a^1}=\mathbf{a^2}=\mathbf{n}$)

$$\begin{aligned} V_S(1,2) &= J_0(r^{12}) + J_4(r^{12})P_2(\mathbf{b}^1\cdot\mathbf{b}^2) \\ &\quad + \frac{1}{2}J_5(r^{12})[P_2(\hat{\mathbf{u}}^{\mathbf{12}}\cdot\mathbf{a}^1)+P_2(\hat{\mathbf{u}}^{\mathbf{12}}\cdot\mathbf{a}^2)] \\ &= J_0(r^{12}) + J_4(r^{12})P_2(\mathbf{b}^1\cdot\mathbf{b}^2) + J_5(r^{12})P_2(\hat{\mathbf{u}}^{\mathbf{12}}\cdot\mathbf{n}), \end{aligned} \tag{48}$$

where $\mathbf{r^{12}}$ is the vector connecting the centers of mass of particles 1 and 2, $r^{12}=|\mathbf{r^{12}}|$, and $\hat{\mathbf{u}}^{\mathbf{12}}=\mathbf{r^{12}}/r^{12}$. Now we do not preaverage the distance dependence of the coefficients multiplying the functions of the relative orientations of the two particles, which is essential for relating these coefficients to particle properties.

In Eq. (48), the term proportional to $J_5(r^{12})$ explicitly describes a coupling between the molecular major axes $\mathbf{a^1}$ and $\mathbf{a^2}$ and the intermolecular vector $\mathbf{r^{12}}$. As discussed by several authors (see, e.g., [35–37]), this term is absent in the original McMillan theory, which as a result does not contain any

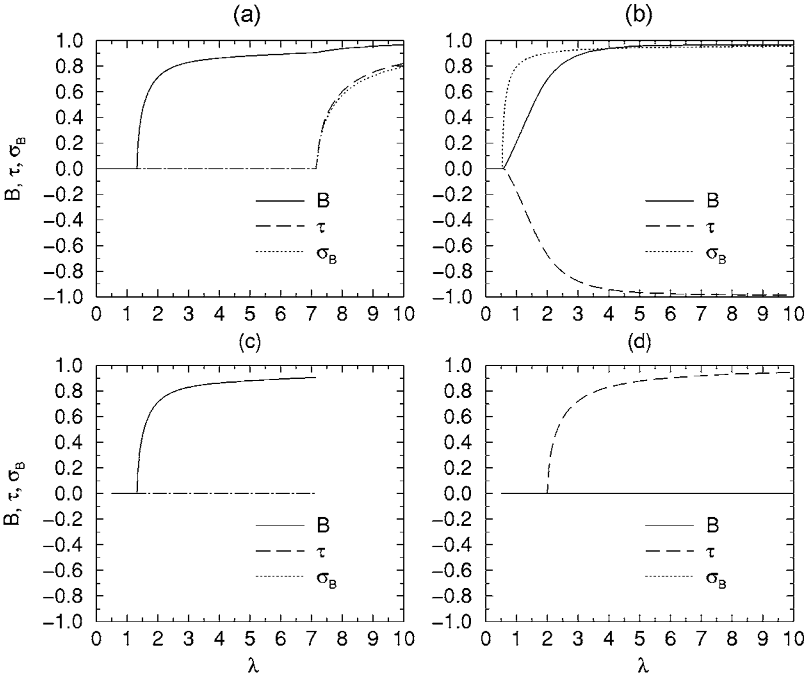


FIG. 4. Order parameters B, τ, and σ_B versus the control parameter λ. (a) $I_0=1$, $J_4^*=-1$: $N_{\rm U}$-$N_{\rm B}$ transition at $\lambda\approx1.33$, and $N_{\rm B}$-Sm$A_{\rm B}$ transition at $\lambda\approx7.11$. (b) $I_0=2.5$, $J_4^*=-2$: $N_{\rm U}$-Sm$A_{\rm B}$ transition at $\lambda\approx0.54$. (c) $I_0=-1$, $J_4^*=-1$: $N_{\rm U}$-$N_{\rm B}$ transition at $\lambda\approx1.33$. (d) $I_0=-1$, $J_4^*=-0.5$: $N_{\rm U}$-Sm$A_{\rm U}$ transition at $\lambda\approx2.0$. All of the transitions from the perfectly aligned $N_{\rm U}$ phase appear to be continuous and occur at $\lambda\simeq\lambda_c^{(0)}$ found from Eqs. (45)–(47). The $N_{\rm B}$-Sm$A_{\rm B}$ transition in (a) also appears continuous, but cannot be located using the bifurcation analysis performed in this paper: One would need to study the stability of the $N_{\rm B}$ phase with respect to a perturbation with Sm$A_{\rm B}$ symmetry.

energy term that favors the orientation of the molecular major axes (and hence of the director) along the smectic layer normal. For any two molecules 1 and 2 in the same smectic layer, such a term would be minimized when the major axes $\mathbf{a_1}$ and $\mathbf{a_2}$ are mutually parallel and the intermolecular vector $\mathbf{r}^{12}$ is perpendicular to them, i.e., parallel to the layer, thereby forcing the molecular major axes to be normal to the smectic layer. It should be noted that this term appears naturally as a part of the general van der Waals interaction between two molecules, namely, due to the induction interaction between the permanent dipole of molecule 1 and the isotropic part of the polarizability of molecule 2 [35]. The same term appears in the systematic expansion of the hard-core repulsion potential for two anisotropic molecules [35,38,39].

In order to derive an interaction with the symmetry appropriate to biaxial objects, we resort, as suggested before, to the model of hard parallelepipeds of dimensions (l,b,w). Note that by so doing we are *not* restricting ourselves to hard-body fluids: Rather, the particle dimensions l, b, and w should be interpreted as the strengths of different terms in the interparticle potential. However, it is particularly useful that, at the level of pairwise interactions, this can be identified with (k_BT times) the Mayer function. We follow Straley [29] and find $J_0(r^{12})$, $J_4(r^{12})$, and $J_5(r^{12})$ by requiring that the assumed form of the potential, Eq. (48), reproduce the excluded volumes of two particles when any two of their principal axes coincide:

$$J_0(r^{12}) = \frac{1}{3\beta}\left[\Theta(r^{12}-w) - \Theta(r^{12}-l) - \Theta(r^{12}-b) + 2\Theta\left(r^{12} - \frac{1}{2}(w+b)\right)\right], \tag{49}$$

$$J_4(r^{12}) = \frac{2}{3\beta}\left[\Theta(r^{12}-w) - \Theta\left(r^{12}-\frac{1}{2}(w+b)\right)\right], \tag{50}$$

$$J_5(r^{12}) = \frac{2}{3\beta}[\Theta(r^{12}-l) - \Theta(r^{12}-b)], \tag{51}$$

where $\Theta(x)=-1$ if $x<0$, $\Theta(x)=0$ if $x>0$ is the step function. Equation (48) with $J_0(r^{12})$, $J_4(r^{12})$, and $J_5(r^{12})$ thus determined is then used to interpolate the potential for arbitrary relative particle orientations. The accuracy of this interpolation scheme has been assessed in the case of V-shaped particles ("hard boomerangs") [40], for which errors do not exceed 40%.

Bearing in mind the need to give a microscopic interpretation of the terms driving (biaxial) smectic order, we expand Eq. (48) in a Fourier series (normalized by the interaction volume, which we now take to be w^3—later we shall use w as our unit of length), with the result

$$V_S(1,2) = \frac{1}{2}[J_0^0 + J_4^0 P_2(\mathbf{b^1}\cdot\mathbf{b^2})] + [J_0^1(k) + J_4^1(k)P_2(\mathbf{b^1}\cdot\mathbf{b^2}) + J_5^1(k)]\cos k(z^1-z^2) + \cdots, \tag{52}$$

where

$$J_0^0 = \frac{\pi}{9\beta w^3}(4l^3 - 3b^3 + 5w^3 + 3bw^2 + 3b^2w), \tag{53}$$

$$J_4^0 = \frac{\pi}{9\beta w^3}(-b^3 + 7w^3 - 3bw^2 - 3b^2w), \tag{54}$$

$$J_0^1(k) = \frac{1}{3\beta w^3}\left[\mathcal{E}_k(l) - \mathcal{E}_k(b) + \mathcal{E}_k(w) - 2\mathcal{E}_k\left(\frac{1}{2}(b+w)\right)\right], \tag{55}$$

$$J_4^1(k) = \frac{2}{3\beta w^3}\left[\mathcal{E}_k(w) - \mathcal{E}_k\left(\frac{1}{2}(b+w)\right)\right], \tag{56}$$

$$J_5^1(k) = \frac{2}{3\beta w^3}[\mathcal{F}_k(l) - \mathcal{F}_k(b)], \tag{57}$$

and

$$\mathcal{E}_k(x) = \frac{4\pi}{k^3}(kx\sin kx + \cos kx - 1), \tag{58}$$

$$\mathcal{F}_k(x) = 2\pi\left[\frac{6\sin kx}{k^3} - \frac{6}{k^2}\int_0^x \frac{\sin ky}{ky}dy + \frac{2}{k}\left(\frac{\sin kx}{k^2} - \frac{x\cos kx}{k}\right)\right]. \tag{59}$$

It should be noted that J_0^0, J_4^0, $J_0^1(k)$, $J_4^1(k)$, and $J_5^1(k)$ are purely geometrical factors: They are functions of the particle dimensions (l,b,w) and of the smectic wave-number k.

By exploiting the analogy with the derivation in the preceding section, from Eq. (52) we arrive at the molecular field potential

$$U_{\mathrm{MF}}(z,\psi) = \frac{1}{2}w^3\left(J_0^0 + \frac{1}{4}J_4^0\right) + w^3\left[J_0^1(k) + \frac{1}{4}J_4^1(k) + J_5^1(k)\right]\tau\cos kz + \frac{3}{8}w^3\left[\frac{1}{2}BJ_4^0 + \sigma_B J_4^1(k)\cos kz\right]\cos 2\psi. \tag{60}$$

Now the natural energy scale is $(J_0^0 + J_4^0/4)/2$, leading to the reduced molecular field potential

$$U^*_{\mathrm{MF}}(z,\psi) = \frac{U_{\mathrm{MF}}(z,\psi)}{\frac{1}{2}(J_0^0 + J_4^0/4)w^3} = 1 + \left[J_0^{1*}(k) + \frac{1}{4}J_4^{1*}(k) + J_5^{1*}(k)\right]\tau\cos kz + \frac{3}{8}\left[\frac{1}{2}BJ_4^{0*} + \sigma_B J_4^{1*}(k)\cos kz\right]\cos 2\psi, \tag{61}$$

where $J_i^{j^*} = J_i^j/(J_0^0 + J_4^0/4)/2$ $(i=0,4,5;\ j=0,1)$, and to the reduced inverse temperature $\beta^* = \beta(J_0^0 + J_4^0/4)/2$, Comparing Eqs. (60) and (61) with its counterparts for the Mark I theory, Eqs. (35) and (36) respectively, we notice the more complex form of the k dependence of the former, as well as the expected enhancement of smecticity due to the $J_5^1(k)$ term. Furthermore, Eqs. (60) and (61) has the same general structure as Eq. (A22), which is derived using a variational procedure, but in addition incorporate molecular detail.

Bifurcation analysis again yields the instabilities of the N_{U} phase with respect to the N_{B}, SmA_{U}, and SmA_{B} phases, as before. The control parameter is now [see the discussion following Eqs. (41)–(43)] $\lambda=\beta^*\rho w^3\equiv\beta^*\rho^*$.

(1) Bifurcation into the N_{B} phase occurs at

$$\lambda_c^{(0)}=-\frac{32}{3J_4^{0*}}. \tag{62}$$

(2) Bifurcation into the SmA_{U} phase occurs at

$$\lambda_c^{(0)}=-\frac{2}{J_0^{1*}(k)+\frac{1}{4}J_4^{1*}(k)+J_5^{1*}(k)}. \tag{63}$$

(3) Bifurcation into the SmA_{B} phase occurs at

$$\lambda_c^{(0)}=-\frac{32}{3J_4^{1*}(k)}. \tag{64}$$

Note that the values of the control parameter at the bifurcations into the SmA_{U} and SmA_{B} phases depend on k, the smectic wave vector. This is not a free parameter in the theory: It must be selected so as to minimize the free energy at each transition into a smectic phase. It is possible in principle, though extremely cumbersome, rigorously to determine k for each (l,b,w) in this manner. We have, however, opted for a simpler route: An exploratory numerical investigation revealed that the control parameter at which the N_{U} phase becomes unstable with respect to the SmA_{U} phase is smallest for $1.3l\lesssim d\lesssim 1.6l$; so we simply took $d=2\pi/k=1.5l$. This obviously assumes that the preferred wavelength of the smectic phase does not depend on whether it is biaxial or not, and is greater than the block length. The latter is supported by the simulation of [28], where (although not reported) the layer spacing is about 1.25 times the block length [41].

The resulting stability diagram is shown in Fig. 5. Figure 6 plots the order parameters versus the control parameter λ, for four choices of (l,b,w) marked with white circles in Fig. 5; details of the numerical calculations are as for Theory Mark I. It is readily seen that the N_{U} phase destabilizes into a SmA_{U} phase if the molecular blocks are rather elongated ($l/b\lesssim 0.5$), and into a N_{B} phase if they are more squat ($l/b\lesssim 0.5$). However, because we are assuming perfect nematic order of the molecular axes of length l, the region $l\lesssim b$ is perhaps physically less meaningful. The SmA_{B} phase is only favored along the boundary between the SmA_{U} and N_{B} phases, i.e, when $l/b\sim 0.5$. Our findings are qualitatively consistent with those of Vanakaras *et al.* ([28], Figs. 1 and 2), who used the exact second-virial theory [32], together with Monte Carlo simulations, for one- and two-component mixtures of hard, blocklike molecules: For the single-component system, the transition from the N_{U} phase is into the SmA_{U} phase at small molecular biaxiality, and into the N_{B} phase at large molecular biaxiality; only at a single value of the biaxiality is the transition direct into the SmA_{B} phase. In the simulations reported in [28], the single-component system consists of blocks with D_{4h} symmetry with one of their axes perfectly aligned along the main director (in our notation, $l=b=1$), hence lying along the diagonal of Fig. 5, and variable ratio of the lengths of the **b** and **c** axes ($1/r$ in their notation, b/w in ours), which introduces the biaxiality. They saw a N_{U}-$\mathrm{N_B}$ transition for $r\gtrsim 15$ ($b/w\lesssim 0.067$ in our notation), which is outside the range of Fig. 5. Still, it is important to realize that this diagram only includes the transitions that can occur from the N_{U} phase: Further transitions from the SmA_{U} and N_{B} phases into the SmA_{B} might yet occur at higher densities/lower temperatures, see Fig. 6.

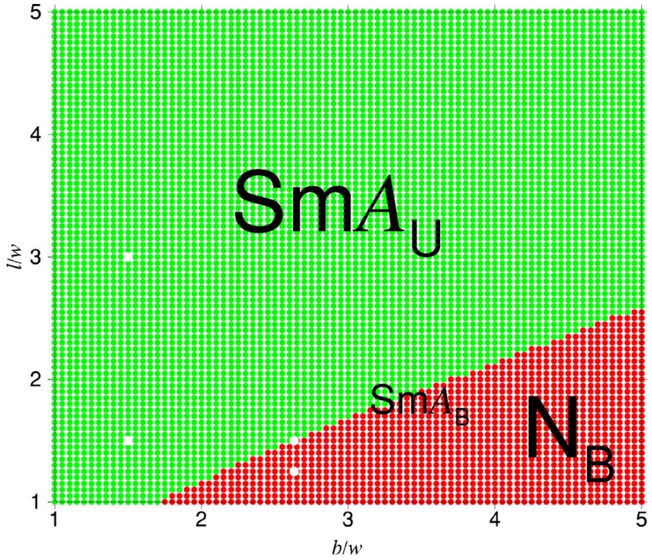


FIG. 5. (Color online) Diagram showing the regions of instability, on increasing the control parameter $\lambda=\rho w^3/k_{\mathrm{B}}T$, of the uniaxial nematic (N_{U}) phase relative to the biaxial nematic (N_{B}), uniaxial smectic (SmA_{U}), and biaxial smectic (SmA_{B}) phases, as a function of particle length l and breadth b, for the layer spacing $d=1.5l$. We do not concern ourselves with the region $l/w,b/w<1$, where ordering occurs at very high densities/low temperatures and is likely preempted by transitions into solid phases. This diagram should be interpreted as follows: Take a system characterized by a certain pair of values $(l/w,b/w)$ and compress it/cool it from its N_{U} phase; if it lies in the top region of the diagram, then its first instability is relative to the SmA_{U} phase: If it lies in the bottom right region of the diagram, its first instability is relative to the N_{B} phase; finally, if it lies along the boundary between the two regions, its first instability is relative to the SmA_{B} phase. Further instabilities may occur at higher densities/lower temperatures, but these are not captured by the present diagram. The white circles are the locations of the four systems whose order parameters are plotted in Fig. 6.

III. CONCLUSIONS

We have constructed simple models for the mesogenic behavior of particles with the symmetry of rectangular parallelepipeds, by combining and extending earlier theories by McMillan [11] and by Straley [29]. All of our calculations

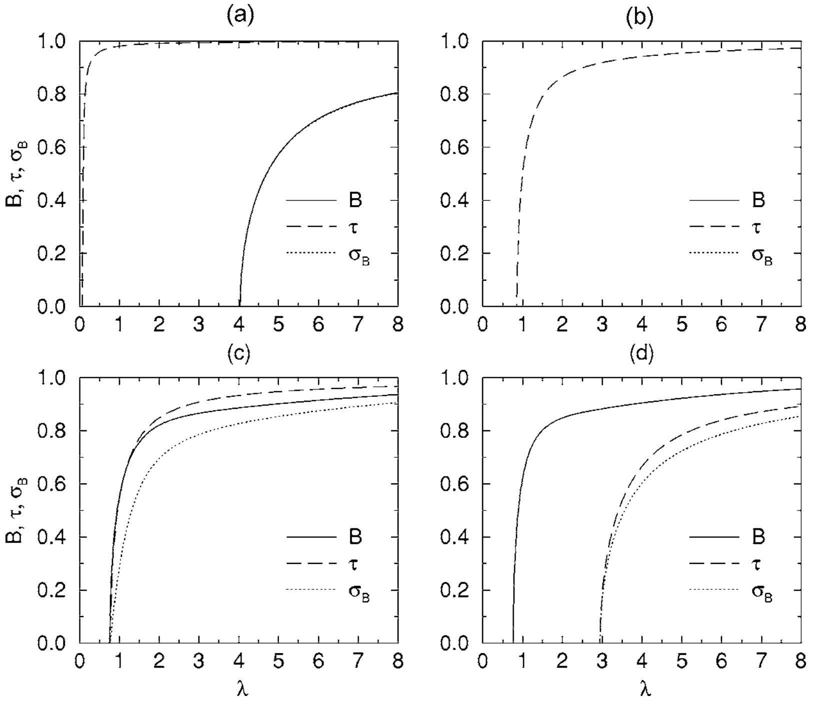


FIG. 6. Order parameters B, τ, and σ_B versus the control parameter λ. (a) $l/w=3$, $b/w=1.5$: N_{U}-SmA_{U} transition at $\lambda \approx 0.08$, and SmA_{U}-SmA_{B} transition at $\lambda \approx 4.04$. (b) $l/w=1.5$, $b/w=1.5$: N_{U}-SmA_{U} transition at $\lambda \approx 0.86$. (c) $l/w=1.5$, $b/w=2.63$: N_{U}-SmA_{B} transition at $\lambda \approx 0.77$. (d) $l/w=1.25$, $b/w=2.63$: N_{U}-N_{B} transition at $\lambda \approx 0.77$, and N_{B}-SmA_{B} transition at $\lambda \approx 2.96$. All of the transitions from the perfectly aligned N_{U} phase appear to be continuous and occur at $\lambda \simeq \lambda_c^{(0)}$ found from Eqs. (62)–(64). The SmA_{U}-SmA_{B} transition in (a) and the N_{B}-SmA_{B} transition in (d) also appear continuous, but cannot be located using the bifurcation analysis performed in this paper: One would need to study the stability of the SmA_{U} or N_{B} phases with respect to a perturbation with SmA_{B} symmetry.

have been performed in the limit of complete orientational order of the particle major axes: we do not believe this simplification to be too restrictive, as simulations by Berardi and Zanoni of a related system [8] suggest that the degree of uniaxial order close to transitions into biaxial phases can be quite high.

We have found that our particles preferentially form a uniaxial smectic A phase when their temperature is lowered from the uniaxial nematic phase, rather than order biaxially. A direct N_{U}-SmA_{B} transition can only occur for a special ratio of interparticle interaction parameters, as in the simulations of Vanakaras *et al.* [28], and is, therefore, unlikely to be observed. However, our results do not rule out the possibility of a SmA_{U}-SmA_{B} transition at lower temperatures.

ACKNOWLEDGMENTS

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APPENDIX: A VARIATIONAL DERIVATION OF A MOLECULAR FIELD THEORY OF THE BIAXIAL SMECTIC *A* PHASE

The variational analysis starts with the orders parameters characterizing the phase and in particular the dominant order parameters. To establish the complete set of order parameters we expand the singlet positional-orientational distribution function $f(z,\Omega)$ in a complete set of basis functions. Recall that here z is the translational coordinate, giving the position of the molecular center of mass along an axis parallel to the layer normal, and Ω denotes the set of Euler angles relating the molecular and laboratory frames. For the translational coordinate we choose the Chebyshev polynomials, $\cos(2\pi pz/d)$, where p is a positive integer and d is, as before, the layer spacing, or periodicity, of the smectic phase. The basis functions for the orientations are taken to be $R^L_{mn}(\Omega)$, which is the symmetry-adapted linear combination of Wigner rotation matrices $D^L_{mn}(\Omega)$ [8]

$$R^L_{mn}(\Omega) = \frac{1}{4}\delta_{L\ \mathrm{even}}\delta_{m\ \mathrm{even}}\delta_{n\ \mathrm{even}}[D^{L\ *}_{mn}(\Omega) + D^{L\ *}_{-mn}(\Omega) + D^{L\ *}_{m-n}(\Omega) + D^{L\ *}_{-m-n}(\Omega)]. \tag{A1}$$

In addition to being restricted to even values, m and n are also positive and the $R^L_{mn}(\Omega)$ are real and orthogonal. The singlet distribution function can be written as an expansion in these complete basis sets as [43]

$$f(z,\Omega) = \sum_{L,m,n,p} f_{Lmn,p}\cos\left(\frac{2\pi pz}{d}\right)R^L_{mn}(\Omega). \tag{A2}$$

The expansion coefficients can be determined by using the orthogonalities of the basis functions and are found to be

$$f_{Lmn,p} = \frac{2L+1}{8\pi^2 d}\left\langle \cos\left(\frac{2\pi pz}{d}\right)R^L_{mn}(\Omega)\right\rangle, \tag{A3}$$

where the angular brackets denote an ensemble average. The complete set of order parameters allowing for the symmetry of both the phase and the molecules are the averages $\langle\cos(2\pi pz/d)R^L_{mn}(\Omega)\rangle$, where L, m, and n take even values and p takes all integer values including zero. This clearly constitutes an extremely large number of order parameters but experiment and simulation suggest that in the vicinity of the phase transitions the dominant order parameters are those with $L=2$ and $p=0$, together with such values of m and n as are compatible with $L=2$. In other words, the dominant pure translational order parameter is

$$\tau = \left\langle \cos\left(\frac{2\pi z}{d}\right) \right\rangle \tag{A4}$$

while there are four second-rank pure orientational order parameters

$$R_{200} = \langle R^2_{00}(\Omega) \rangle = \left\langle \frac{1}{2}(3\cos^2\theta - 1) \right\rangle \equiv S, \tag{A5}$$

$$R_{202} = \langle R^2_{02}(\Omega) \rangle = \sqrt{\frac{3}{8}} \langle \sin^2\theta \cos 2\chi \rangle \equiv -\frac{1}{\sqrt{6}} D, \tag{A6}$$

$$R_{220} = \langle R^2_{20}(\Omega) \rangle = \sqrt{\frac{3}{8}} \langle \sin^2\theta \cos 2\phi \rangle \equiv -\sqrt{\frac{3}{2}} P, \tag{A7}$$

$$R_{220} = \langle R^2_{22}(\Omega) \rangle = \left\langle \frac{1}{4}(1+\cos^2\theta)\cos 2\phi \cos 2\chi - \frac{1}{2}\cos\theta \sin 2\phi \sin 2\chi \right\rangle \equiv \frac{1}{2} B. \tag{A8}$$

In addition, there are four mixed translational-orientational order parameters which we denote by

$$\sigma_{200} = \left\langle \cos\left(\frac{2\pi z}{d}\right) R^2_{00}(\Omega) \right\rangle \equiv \sigma_S, \tag{A9}$$

$$\sigma_{202} = \left\langle \cos\left(\frac{2\pi z}{d}\right) R^2_{02}(\Omega) \right\rangle \equiv -\frac{1}{\sqrt{6}} \sigma_D, \tag{A10}$$

$$\sigma_{220} = \left\langle \cos\left(\frac{2\pi z}{d}\right) R^2_{20}(\Omega) \right\rangle \equiv -\sqrt{\frac{3}{2}} \sigma_P, \tag{A11}$$

$$\sigma_{222} = \left\langle \cos\left(\frac{2\pi z}{d}\right) R^2_{22}(\Omega) \right\rangle \equiv \frac{1}{2} \sigma_B. \tag{A12}$$

These nine order parameters are more than sufficient to characterize the four phases with which we are concerned, namely, uniaxial nematic (N_{U}), biaxial nematic (N_{B}), uniaxial smectic *A* (SmA_{U}), and biaxial smectic *A* (SmA_{B}). The nonzero order parameters for these phases are as follows:

N_{U}: R_{200} and R_{202}.

N_{B}: R_{200}, R_{202}, R_{220}, and R_{222}.

SmA_{U}: R_{200}, R_{202}, τ, σ_{200}, and σ_{202}.

SmA_{B}: R_{200}, R_{202}, R_{220}, R_{222}, τ, σ_{200}, σ_{202}, σ_{220}, and σ_{222}.

The next stage in the variational analysis to construct the molecular field theory is to obtain the Helmholtz free energy [12,15]. This is built from the internal energy and the entropy. The internal energy is constructed from linear combinations of products of the order parameters and suitable tensorial weighting factors reflecting the strength of the molecular interactions. For the dominant order parameters that we have identified the molar internal energy is

$$U = -\frac{N_A}{2}\left[u\tau^2 + \sum_{m,n,r} (1+\delta_{2m})(1+\delta_{2n})(1+\delta_{2r}) \times (u_{2mn} R_{2rm} R_{2rn} + u'_{2mn} \sigma_{2rm} \sigma_{2rn}) \right]. \tag{A13}$$

The delta functions have been included to ensure that the expansion coefficients u_{2mn} are equivalent to those in the molecular field theory developed from the pair potential written in terms of Wigner rotation matrices [9].

The notation is not straightforward, even though we have resisted the temptation to give it in its most general form. Thus u, which relates to the pure translational interactions, could be written as $u_{000,1}$; similarly, u_{2mn} would at the most general level be $u_{2mn,0}$, and u'_{2mn} would be $u_{2mn,1}$. Clearly further simplifications would be possible but we wish to retain contact with the notation adopted for the order parameters. The molar entropy is related to the singlet translational-orientational distribution function by

$$S = -N_A k_B \int f(z,\Omega) \, \text{In}\, f(z,\Omega) dz d\Omega. \tag{A14}$$

The molar Helmholtz free energy is then

$$F = -\frac{N_A}{2}\left[u\tau^2 + \sum_{m,n,r} (1+\delta_{2m})(1+\delta_{2n})(1+\delta_{2r})(u_{2mn} R_{2rm} R_{2rn} + u'_{2mn} \sigma_{2rm} \sigma_{2rn}) \right] + N_A k_B \int f(z,\Omega) \, \text{In}\, f(z,\Omega) dz d\Omega. \tag{A15}$$

At this stage the singlet distribution function is unknown but can be determined by the requirement that the free energy is a minimum with respect to variations in $f(z,\Omega)$. This minimization is subject to various constraints, namely, that the distribution function is normalized:

$$\int f(z,\Omega) dz d\Omega = 1, \tag{A16}$$

and that the order parameters are related to the distribution function by

$$R_{2mn} = \int R^2_{mn}(\Omega) f(z,\Omega) dz d\Omega, \tag{A17}$$

$$\tau = \int \cos\left(\frac{2\pi z}{d}\right) f(z,\Omega) dz d\Omega, \tag{A18}$$

$$\sigma_{2mn} = \int \cos\left(\frac{2\pi z}{d}\right) R^2_{mn}(\Omega) f(z,\Omega) dz d\Omega. \tag{A19}$$

The minimization gives the singlet distribution function as

$$f(z,\Omega) = Q^{-1} \exp[-\beta U(z,\Omega)], \tag{A20}$$

where the partition function is

$$Q = \int \exp[-\beta U(z,\Omega)]dz d\Omega. \tag{A21}$$

The potential of mean torque and mean force $U(z,\Omega)$ is found to be

$$U(z,\Omega) = -\Bigg[\sum_{m,n,r}(1+\delta_{2m})(1+\delta_{2n})(1+\delta_{2r})u_{2mn}R_{2rm}R^2_{rn}(\Omega) + u\tau\cos\left(\frac{2\pi z}{d}\right) + \sum_{m,n,r}(1+\delta_{2m})(1+\delta_{2n}) \times(1+\delta_{2r})u'_{2mn}\sigma_{2rm}\cos\left(\frac{2\pi z}{d}\right)R^2_{rn}(\Omega)\Bigg]. \tag{A22}$$

This has the same general structure as Eq. (60) but not the same level of detail: Because it was derived from a single-particle potential, its coefficients cannot be straightforwardly related to molecular properties.

For comparison with our other derivation of this potential we now give the specific coefficients of the various terms.

(1) Pure orientational

$$-(u_{200}R_{200}+2u_{220}R_{202})R^2_{00}(\Omega), \tag{A23}$$

$$-(2u_{202}R_{200}+4u_{222}R_{202})R^2_{02}(\Omega), \tag{A24}$$

$$-(2u_{200}R_{220}+4u_{220}R_{222})R^2_{20}(\Omega), \tag{A25}$$

$$-(4u_{202}R_{220}+8u_{222}R_{222})R^2_{22}(\Omega). \tag{A26}$$

Nota bene (N. B.) because the molecules are identical the coefficients obey the equality $u_{2mn}=u_{2nm}$ [9].

(2) Pure translational

$$-u\tau\cos\left(\frac{2\pi z}{d}\right), \tag{A27}$$

(3) Mixed translational/orientational: Given the structure of these terms the specific forms for them are analogous to those for the orientational terms [see Eqs. (A23)–(A26)], and so

$$-(u'_{200}\sigma_{200}+2u'_{220}\sigma_{202})\cos\left(\frac{2\pi z}{d}\right)R^2_{00}(\Omega), \tag{A28}$$

$$-(2u'_{202}\sigma_{200}+4u'_{222}\sigma_{202})\cos\left(\frac{2\pi z}{d}\right)R^2_{02}(\Omega), \tag{A29}$$

$$-(2u'_{200}\sigma_{220}+4u'_{220}\sigma_{222})\cos\left(\frac{2\pi z}{d}\right)R^2_{20}(\Omega), \tag{A30}$$

$$-(4u'_{202}\sigma_{220}+8u'_{222}\sigma_{222})\cos\left(\frac{2\pi z}{d}\right)R^2_{22}(\Omega). \tag{A31}$$

These results should, of course, reduce to the forms already derived for the potential in simpler systems. These simpler systems include

(1) Maier-Saupe for uniaxial molecules in a uniaxial phase [42]. For this the only non-zero coefficient is u_{200} and the only nonzero order parameter is R_{200}, which gives the potential

$$U(\Omega) = -u_{200}R_{200}R^2_{00}(\Omega). \tag{A32}$$

(2) McMillan for uniaxial molecules in a uniaxial smectic A phase [15]. The nonzero coefficients are now u_{200}, u, u'_{200}, which together with the order parameters that vanish give the potential as

$$U(z,\Omega) = -u_{200}R_{200}R^2_{00}(\Omega) - u\tau\cos\left(\frac{2\pi z}{d}\right) - u'_{200}\sigma_{200}\cos\left(\frac{2\pi z}{d}\right)R^2_{00}(\Omega). \tag{A33}$$

(3) Luckhurst-Zannoni-Nordio-Segre for biaxial molecules in a uniaxial nematic phase [9]. The nonzero strength parameters are u_{200}, u_{220} $(=u_{202})$, and u_{222}, yielding the potential as

$$U(\Omega) = -(u_{200}R_{200}+2u_{220}R_{202})R^2_{00}(\Omega) - (2u_{202}R_{200} + 4u_{222}R_{202})R^2_{02}(\Omega). \tag{A34}$$

(4) Averyanov-Primak for biaxial molecules in a uniaxial smectic *A* phase [10]. This combines McMillan's [11] and the Luckhurst *et al.* [9] theories

$$U(\Omega) = -(u_{200}R_{200}+2u_{220}R_{202})R^2_{00}(\Omega) - (2u_{202}R_{200} + 4u_{222}R_{202})R^2_{02}(\Omega) - u\tau\cos\left(\frac{2\pi z}{d}\right) - u'_{200}\sigma_{200}\cos\left(\frac{2\pi z}{d}\right)R^2_{00}(\Omega) - (2u'_{202}\sigma_{200} + 4u'_{222}\sigma_{202})\cos\left(\frac{2\pi z}{d}\right)R^2_{02}(\Omega). \tag{A35}$$

(5) Straley [29] as well as Boccara, Mejdani, and de Seze [6] for biaxial molecules in a biaxial nematic phase

$$U(\Omega) = -(u_{200}R_{200}+2u_{220}R_{202})R^2_{00}(\Omega) - (2u_{202}R_{200} + 4u_{222}R_{202})R^2_{02}(\Omega) - (2u_{200}R_{220}+4u_{220}R_{222})R^2_{20}(\Omega) - (4u_{202}R_{220}+8u_{222}R_{222})R^2_{22}(\Omega). \tag{A36}$$

The complete theory of biaxial molecules in a biaxial smectic *A* phase that we have derived, gives the Helmholtz free energy as

$$F = \frac{N_A}{2}\Bigg[u\tau^2 + \sum_{m,n,r}(1+\delta_{2m})(1+\delta_{2n})(1+\delta_{2r})u_{2mn}R_{2rm}R_{2rn} + \sum_{m,n,r}(1+\delta_{2m})(1+\delta_{2n})(1+\delta_{2r})u'_{2mn}\sigma_{2rm}\sigma_{2rn}\Bigg] - N_A k_B \ln Q. \tag{A37}$$

The order parameters for the system are then those that minimize this free energy, with the partition function Q determined from the four-dimensional integral in Eq. (A21) and the potential $U(z,\Omega)$ in Eq. (A22).

These calculations can be simplified if needed, by invoking the following two approximations. First, the two biaxial order parameters R_{202} (molecules) and R_{220} (phase) can be set to zero since simple molecular field theory and simulations show that they are small, certainly in comparison with R_{200} and R_{222} [44]. The other approximation was proposed by Kventsel, Luckhurst, and Zewdie [12] as a way of simplifying McMillan's theory [11], and that is to replace the mixed order parameter by the product of the two pure order parameters, i.e.,

$$\sigma = \tau S, \tag{A38}$$

which for the biaxial system becomes

$$\sigma_{2mn} = \tau R_{2mn}. \tag{A39}$$

This approximation is found to be good for uniaxial Gay-Berne molecules [45]. With these two approximations the number of order parameters is reduced to just three, namely, R_{200}, R_{222}, and τ, which are sufficient to describe the N_{U}, N_{B}, SmA_{U}, and SmA_{B} phases.

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