5-1982

Mean-Field Study of Molecular Tilt in Uniaxial Liquid-Crystalline Phases

M. R. Kuzma
Kent State University - Kent Campus

David W. Allender
Kent State University, dallende@kent.edu

Follow this and additional works at: https://digitalcommons.kent.edu/phypubs

Part of the Physics Commons

Recommended Citation

This Article is brought to you for free and open access by the Department of Physics at Digital Commons @ Kent State University Libraries. It has been accepted for inclusion in Physics Publications by an authorized administrator of Digital Commons @ Kent State University Libraries. For more information, please contact digitalcommons@kent.edu.
Mean-field study of molecular tilt in uniaxial liquid-crystalline phases

M. R. Kuzma and D. W. Allender
Department of Physics and Liquid Crystal Institute, Kent State University, Kent, Ohio 44242
(Received 15 June 1981)

A simple extension of McMillan’s mean-field model of the nematic- and smectic-A phases is reported. Specifically, terms proportional to fourth-order Legendre polynomials are included in the mean field. For a reasonable range of parameter choices this mean field can restrict the most probable directions of the long axis of a molecule in a smectic layer to a cone with the axis of the cone parallel to the optic axis. This result is related to recent quadrupole-magnetic-resonance observations of molecular order, and also to x-ray experiments which find that the repeat distance of the smectic layers is less than the all-trans length of the molecule. Finally, a possible connection to recent theories of the smectic-A—smectic-C transition is pointed out.

I. INTRODUCTION

In most theories of uniaxial smectic-A liquid crystals, it is assumed to be energetically favorable for the long axes of the rodlike molecules to lie perpendicular to the planes of the layer structure.1–4 Experimentally, it is well known4 that the optical axis, defining the equilibrium direction \( \hat{n}_0 \) (| \( \hat{n}_0 \) | = 1) is parallel to the wave vector \( \mathbf{q} \) (| \( \mathbf{q} \) | = \( 2\pi/d \), where \( d \) is the lattice constant) of the one-dimensional smectic-A lattice. However, this experimental observation does not necessarily justify the assumption that the molecules prefer to orient perpendicular to the layers.

Recent x-ray studies5–8 have corroborated earlier measurements9,10 of lattice constants in smectics A. These measurements indicate that in all of the compounds examined, the layer spacing \( d \) is roughly 5 to 20 percent less than the all-trans length \( l \) of the molecule under consideration.

The above experimental result (\( d/l < 1 \)) has been interpreted in four ways:

1. The molecules are tilted on the average with respect to the local director \( \hat{n} \) and are disposed in each layer to allow uniaxial symmetry around \( \hat{n} \).

2. The end chains of the molecules interdigitate or overlap in such a manner to reduce \( d \).

3. Thermally generated gauche rotations or kinks in the hydrocarbon chain act to reduce the average length of the molecule and therefore \( d \).

4. Some combination of (1) through (3).

We might expect effects (2) and (3) to be greater in homologous series which are unsymmetrical in the number of alkyl groups in the end chains, or have only one chain. This can be understood if we assume the short-range order is largely apolar, and that the central polarizable groups of the molecules tend to associate in planes. Then the excess volume due to this asymmetry can be filled by effects (2) and (3).

In this paper, we present a model for mechanism (1), namely, the tilting of molecules in a uniaxial phase. The model is based on an extension to smectic phases of the Humphries et al. formalism for nematics.13 Specifically, we include fourth-order Legendre polynomial terms \( P_4(x) \) (\( x = \cos \theta \), with \( \theta \) the angle between the optic axis and the long molecular axis), which have been much discussed in nematics,13,14 into the mean field for smectics. We find that including \( P_4(x) \) terms allows, for reasonable parameter choices, the development of an energy barrier in the mean field which tends to oppose flopping of the molecule through the director, or axis of symmetry.

In the model mean-field interaction [Eq. (3)], we find an energy barrier to flopping exists. The most probable directions for the long axes of the molecules are restricted to cones.11 Within the model, it is found that the height of the barrier is enhanced by smectic ordering and that the barrier can exist in nematic phases.

In Sec. II, we set up the mean-field model and develop the ideas of the present section. In Sec. III, we obtain theoretical isotropic-nematic-smectic-A phase diagrams which are at least topologically similar to those studied previously.1 On a representative phase diagram we plot the predicted
regions where the hopping barrier exists. We find for certain parameter ranges the hopping barrier can either jump from zero to finite values, or increase continuously from zero. In Sec. IV, we review conclusions of the model calculations, and a connection with recent theories of the smectic-$A$ to smectic-$C$ transition\textsuperscript{12,15\textendash17} is pointed out. In the Appendix, a derivation of the mean-field is given.

II. MODEL

For uniaxial nematic and smectic systems of symmetry $D_{\infty h}$, we write for the one-particle potential ($U_1$) (see Appendix)

$$U_1 = -v_0 \sum_{\mu n l} a_{\mu n l} \eta_{\mu n} \cos(\mu q z) P_l(x), \tag{1}$$

where $v_0$ equals the scale of interaction energy per molecule, and $\mu, n,$ and $l$ are positive integers. We have for identical molecules,

$$a_{\mu n l} = a_{\mu n l}. \tag{2}$$

Here the optic axis and layer normal coincide and are put in the $\hat{z}$ direction, $x = \cos \theta$, where $\theta$ is the angle between the optic axis and the long molecular axis, and $q = 2\pi/d$ is the fundamental wave number of the mass density wave. The order parameters are defined by

$$\eta_{\mu n} = \langle \cos(\mu q z) P_n(x) \rangle. \tag{2a}$$

The brackets mean a self-consistent thermal average with the distribution function

$$\rho(z,x) = \frac{e^{-U_1/kT}}{A}, \tag{2b}$$

where $A$ is the normalization constant, $k$ equals Boltzmann's constant, and $T$ equals the temperature. $U_1$ is given by Eq. (1).

By symmetry the orientation $\theta$ is equivalent to $\pi - \theta$ so that $n$ and $l$ are even. We assume only the values $\mu = 0, 1$ appear in $U_1$. This assumption is supported by the x-ray data of Als-Nielsen \textit{et al.},\textsuperscript{18} who find the higher harmonics ($\mu > 1$) do not contribute to the density wave of octyloxy-cyanobiphenyl (8OCB) when $t = (T \text{AN} - T)/T \text{AN} \geq 0$. As $t$ increases, more harmonics may appear.\textsuperscript{19} We will ignore this complication.

We want to consider the effect of the $P_4(x)$ terms on the distribution function of $\rho(z,x)$ in the nematic and smectic phases. To do this, the lowest order terms in Eq. (1) are kept, namely, $n,l = 0,2,4$ and $\mu = 0,1$. Omitting the constant $a_{000}$, we have

$$U_1 = -v_0 \left[ a_{022} \eta_{02} P_2(x) + a_{044} \eta_{04} P_4(x) + a_{102} \eta_{10} P_2(x) + a_{122} \eta_{12} \cos(qz) P_2(x) \right. \tag{3}$$

For simplicity, choose

$$a_{100} = \delta, \quad a_{122} = a_{022} = 1, \quad a_{044} = a_{144} = \epsilon, \quad \left. a_{024} = a_{042} = a_{124} = a_{142} = \gamma \epsilon. \right.$$ 

The parameter $\delta$ measures the strength of the purely translational part of $U_1$ compared to $a_{022} (= a_{122})$. The parameter $\epsilon$ controls the total $P_4(x)$ contribution to $U_1$ relative to the $P_2(x)$ contribution, and $\gamma$ is nonzero when the two-particle interactions depending on the orientation of the vector joining the molecules are included in the mean field. We restrict our parameter ranges to $|\epsilon| < 1, -0.2 < \delta < 0.5$, and $\gamma = 0$ or 1.

In Eq. (3) we have omitted the terms

$$a_{102} \eta_{02} \cos(qz) + a_{104} \eta_{10} P_2(x)), \quad a_{104} \left[ \eta_{10} \cos(qz) + \eta_{10} P_4(x) \right]. \tag{4}$$

The inclusion of these terms in $U_1$, besides increasing the number of parameters, does not significantly alter the following discussion. We therefore omit them. The first term has been included in the theory of smectics $A$ by Schroeder\textsuperscript{20} and by Senbetu and WOO\textsuperscript{21}.

We want to find the extrema of the mean-field distribution function $\rho(z,x)$ as a function of $x$. Writing Eq. (3) as

$$U_1 = -v_0 \left[ A_0(x) P_2(x) + A_1(x) P_4(x) \right. \tag{4}$$

$$+ a_{124} \eta_{12} \cos(qz) P_2(x) + a_{142} \eta_{14} \cos(qz) P_2(x) + a_{104} \eta_{10} \cos(qz) \right], \tag{5}$$

where

$$A_0(z) = $\eta_{02}$ + $\gamma \epsilon \eta_{04}$ \tag{6}$$

$$\quad + \eta_{12} \cos(qz) + \eta_{14} \cos(qz), \quad \quad A_1(z) = \eta_{04} + \gamma \eta_{02} \tag{7}$$

$$\quad + \eta_{14} \cos(qz) + \gamma \eta_{12} \cos(qz). \tag{8}$$

Using Eq. (4), we find the extrema of $\rho(x,z)$ as a
function of \( x \):
\[
x = 0,
\]
or
\[
\left[ \frac{3}{7} \left( 1 - \frac{2}{5r} \right) \right]^{1/2} \equiv \tilde{x},
\]
with
\[
r = A_1(z)/A_0(z).
\]

To get \( \tilde{x} \) as a solution, we must have \( r < -0.3 \).

For \( r \geq -0.3, \rho \) has an absolute maximum at \( x = 1 \).

In Fig. 1, we have plotted the distribution function of \( x \) for the special value \( r = A_1(z = 0)/A_0(z = 0) = -0.4 \). This value of \( r \) is chosen for the sake of clarity to accentuate the maximum in Fig. 1. Setting \( z = 0 \) corresponds to the middle of a layer.

We can define the flopping barrier as \( \Delta \rho = \rho(z, x = \tilde{x}) - \rho(z, x = 1) \). Since \( \tilde{x} \) is a function of \( r = r(z) \), \( \Delta \rho \) will show the same periodicity as the density wave. \( \Delta \rho \) may even oscillate between zero and finite values. The \( P_\rho(x) \) terms in \( U_1 \) result (for \( \epsilon < 0 \)) in generally smaller values for the order parameter \( \eta_{\tilde{x}} = \langle P_\rho(x) \rangle \).

III. NUMERICAL RESULTS

We now solve the self-consistency Eqs. (2a) and (2b). To do this, we compare the free energy per molecule,
\[
\Delta F = F - F_0 = -\frac{1}{2} \langle U_1 \rangle - kT \ln A
\]

of the isotropic (\( \eta_{\mu \nu} = 0 \)), nematic (\( \eta_{00} \neq 0, \eta_{11} = 0 \)), and smectic (\( \eta_{\mu \nu} \neq 0 \)) phases. The phase with the minimum free energy is the most stable. \( F_0 \) is the free energy of the background degrees of freedom (e.g., hard-core interactions). To a good approximation, \( F_0 \) depends linearly on temperature so that, in writing \( \Delta F \), a constant volume constraint is implicitly assumed.

Four cases are considered.

(1) \( \gamma = \delta = \epsilon = 0 \); this gives McMillan's\(^1\) extension of Maier-Saupe\(^2\) for the special value \( a_{122} = \alpha = 1 \). (\( \alpha \) is McMillan's parameter.) The transition is isotropic \( \leftrightarrow \) smectic \( A \) at \( J = 0.2213 \).

(2) \( \gamma = \delta = 0, -0.5 \leq \epsilon \leq 0.2 \); Fig. 2 displays the resulting phase diagram and entropy changes (\( \Delta S \)) of the \( N-A \) and I-A transitions versus \( \epsilon \). The nematic-smectic-\( A \) transition is continuous for \( \epsilon < -0.46 \). The similarity with previous I-N-A phase diagrams is not surprising. However, it is difficult to relate directly \( \epsilon \) to molecular structure.

(3) \( \gamma = \epsilon = 0, -0.2 < \delta < 0.75 \); this was studied by Photinos and Saupe.\(^23\) All phases of I-N-A were obtained. Details are discussed in Ref. 22.

(4) \( \gamma = 1, -0.2 \leq \delta \leq 0.5 \), \( -0.35 \leq \epsilon \leq 0 \); this case is summarized in Fig. 3. The maximum of the distribution function (\( \tilde{x} \)) can move away from \( x = 1 \) when \( \epsilon < -0.2 \). The width of the first-order \( N-A \) region decreases to zero for \( \delta \approx 0.28 \) and \( \epsilon \approx -0.33 \). The tricritical point and the triple point coincide at point \( P \) in Fig. 3. Ronis and Rosenblatt\(^24\) recently have seen a similar occurrence for a mean-field lattice model for a smectic-\( A \) with two parameters.

FIG. 1. Distribution function (arbitrary units) of \( x = \tilde{x} = \cos \theta \) for the middle of a smectic layer. \( \tilde{x} \) is the director; \( \tilde{z} \) is the molecular long axis direction. For curve \( A, r = 0 \) and curve \( B, r = -0.4 \), see Eqs. (4) through (7).

FIG. 2. Transition temperatures \( J = kT/V_A \), and entropy changes to the smectic phase (in units of \( R_0 = Nk \)) vs model parameter \( \epsilon \) for \( \delta = \gamma = 0 \).
FIG. 3. Plot of model behavior for transitions to smectic A in the $\epsilon$-$\delta$ plane. Region A: N$\rightarrow$A second order; Region B: N$\rightarrow$A first order; Region C: I$\rightarrow$A first order. At point P the tricritical point and triple point (I-N-A) coincide.

The phase diagram for the values $\delta=0.2$ and $-0.45 \leq \epsilon \leq 0$ is shown in Fig. 4. The dotted line indicates the temperature $J_g$, above which $\bar{x}=1$, and below which $\bar{x}$ continuously decreases from one, while the heavy lines mark the points on the transition lines where $\bar{x}$ jumps discontinuously from one to smaller values. The discontinuity in the order parameters ($\eta_{1\mu\nu}$) at the transition is connected to $\bar{x}$ through Eqs. (5)–(7). In Fig. 5 the temperature dependence of $\bar{\theta}=\cos^{-1}\bar{x}$ is plotted for two values of $\epsilon$ for $\gamma=1$ and $\delta=0.2$.

IV. SUMMARY AND DISCUSSION

We have presented and solved the self-consistency equations for the specific one-particle poten-

FIG. 4. Theoretical phase diagram $J$ vs $\epsilon$ for $\delta=0.2$ and $\gamma=1$. The dashed lines (thick lines) indicate continuous (discontinuous) behavior in the maximum of the mean-field distribution function $\bar{x}$. The N-A transition is second order for $\epsilon<-0.3$. See text for details.

tial given by Eq. (3). For $\gamma=1$, $\epsilon<0.2$, and $-0.1 < \delta < 0.5$, the most probable direction of the long molecular axis is found to depend on temperature. For low enough temperatures, the most probable directions for a molecule to point are restricted to a cone with the axis of the cone parallel to the director. This behavior is caused by the development of a floating barrier in the orientational part of the mean field which reduces the probability for a molecule to orient in an interval $\Delta x$ near $x=1$ (Fig. 1). For $\gamma=0$, the floating barrier does not appear, except at unphysically small values of $J=kT/V_0$.

If we assume the smectic-A layer spacing follows $d=|\bar{x}|l\cos\theta$ for $\bar{x}<1$, then we have $d<l$ and $\Delta d/\Delta T > 0$. However, x-ray measurements in the smectic-A phase6 show $d<l$ to remain constant or slightly increase with decreasing temperature $[\Delta d/\Delta T \approx 0.01 \text{ Å/°C (Ref. 5)}]$. Steric effects, which were not included in the model, would tend to rectify the above difficulty. Their inclusion in the formalism would require the self-consistency equations to be solved at constant pressure instead of constant volume.

We can qualitatively examine the influence of steric effects by appealing to the Monte Carlo calculations of Coldwell et al.,25 who monitor the free energy of a system of hard three-dimensional spherocylinders with their centers constrained to a plane. This corresponds to a single perfectly or- dered smectic layer. As the areal density is increased, the axes of the rods on the average tend to align perpendicular to the plane as expected. Generalizing to a three-dimensional system of spherocylinders at closest packing densities, we have $d \leq l$ due to the slight overlap allowed by the spherical end caps of the cylinders. Vieillard-Baron26 started from just such a smecticlike state in obtaining an equation of state for the three-dimensional spheroidal...
cylinder system.

Combining these ideas, we may then view the constancy of $d$ in the $A$ phase as a balance between energetic and entropic effects: the energetic effects favoring tilting, as described within the above model; and the entropic effects favoring alignment perpendicular to the layer increasing the inplane translational entropy, as described in the steric models.

The discontinuity of $\eta_{02} = \langle P_2(x) \rangle$ at the N-I transition ($\eta_{02}^{\text{trans}}$) decreases as $|\epsilon|$ increases ($\epsilon < 0$). If $\epsilon = 0$, $\eta_{02}^{\text{trans}} = 0.429$, while, for example, at the point ($\epsilon = -0.2$, $\gamma = 1$, $\delta = 0$), $\eta_{02}^{\text{trans}} = 0.18$. This reduction in $\eta_{02}^{\text{trans}} (T = T_N)$ is enhanced for $\gamma > 0$ but is still present for $\gamma = 0$. Deviations of the model molecules from cylindrical symmetry can also lower $\eta_{02}$ at the nematic-isotropic transition.

Other mean-field potentials can display the hopping barrier behavior. For instance, an extension of Straelsey's derivation of a $D_2$ symmetry orientational field to a $C_{2x}$ orientational field allows for the appearance, in this biaxial field, of a hopping barrier if the value of the nematic order $\eta_{02} < 1$. However, in view of the large number of order parameters involved not even including coupling to the smectic density wave, this approach loses its practicality.

Measurements of $\eta_{04}$ are to our knowledge not available for the compounds studied in Refs. 5 and 7. Some references to the experimental techniques for measuring $\eta_{04}$ are summarized in Table 1.

In Refs. 29 through 31, $\eta_{04}$ was found to be negative over a portion of the nematic range. The range of parameters investigated, we found $\eta_{04} > 0$. Prasad and Venugopalan along with Jen et al. have explicitly found $\eta_{04} > 0$ in a smectic-A phase, and it is plausible to assume $\eta_{04} > 0$ for smectic phases in general.

An observation of the onset of finite $\bar{\Theta}$ has been made in recent quadrupole magnetic resonance experiments. The order matrix for uniaxial phases measured by these experiments on deuterated molecules is

$$S_{ij} = \frac{1}{2} \left( 3(\hat{n} \cdot \hat{x}_i)(\hat{n} \cdot \hat{x}_j) - \delta_{ij} \right),$$

where $\hat{x}_k$ are molecular axes. This order matrix can, of course, be diagonalized by an appropriate choice of molecular axes. However, it has been found that the molecular axes which diagonalize $S_{ab}$ in the nematic phase are not necessarily the same axes which diagonalize $S_{ab}$ in the smectic-A phase. (For some materials they may be the same.) In effect, what happens is that the axis which wants to align with $\hat{n}$ (at angle $\bar{\Theta}$ with respect to the long axis of a cylindrical molecule) must be chosen as a molecular axis in order to diagonalize $S_{ab}$. This axis is not unique for the cylindrical molecules we have chosen to study for simplicity, but would be for biaxially shaped molecules. Thus, the off-diagonal order measured in quadrupole magnetic resonance (QMR) experiments, or equivalently the angle between the molecular axes which diagonalize the order matrix in the nematic and smectic phases is a measure of the angle $\bar{\Theta}$.

Also of particular interest is the result of Ref. 7 that $d$ remains practically constant throughout both the smectic-A and smectic-C phases ($d_A \approx d_C \approx 27.7 \, \text{Å}$). In the $B$ phase the layer spacing jumps to $d_B \approx 28.9 \, \text{Å}$, which is essentially the all-trans length of the molecule.

In some current theories of the $A$-$C$ transition, the existence of tilted molecules in the $A$ phase has been assumed. In our model, we neglect short-range order so that each molecule is treated as if it makes a random azimuthal angle $\phi$ with respect to some axis perpendicular to the layer normal.

In the $A$ phase we might expect short-range order in the $\phi$ angles to be important for length scales less than a characteristic length $l_B$. We can estimate $l_B$ within a layer from the analogy of the two-dimensional spin wave $XY$ model to the $A$-$C$ transition. It is found to be

$$l_B \approx a \exp \left( \frac{\pi K a}{kT} \right) \quad T > T_{AC}. \quad (9)$$

Choosing the elastic constant $K \approx 10^{-6} \, \text{dyn} \, \text{cm}$ (bulk value), molecular width $a \approx 5 \, \text{Å}$, and $T \approx 300 \, \text{K}$, we get $l_B \approx 40a = 200 \, \text{Å}$, which is to be regarded as a lower bound for $l_B$ since interactions between the layers encourage long-range order to develop in the $\phi$ angles both parallel and perpendicular to the layers as $T \to T_{AC}$.15
The subscript $B$ on $l_B$ indicates that Eq. (9) can also be regarded as the length over which biaxial correlations (at least within a layer) are strong. If we use optics to determine whether a system is uniaxial or biaxial then when the condition $\lambda >> l_B$ holds, the system will be optically uniaxial. $\lambda$ is the wavelength of visible light in the medium.

Thus, the tilt angle $\tilde{\theta} = \cos^{-1} \tilde{x}$, barring chain kinking, etc., is essentially unobservable in the $A$ phase except by indirect means such as the layer spacing. Nonzero $\tilde{\theta}$ in the $A$ phase may further contribute to an already small scattering of light when the momentum transfer vector $\tilde{q}$ of thermal fluctuations has a nonzero component normal to the layers. This effect might be observable, but difficult to separate out from scattering due to volume dilations.

If there is negligible change in layer spacing through the $A$-$C$ transition, then it would be reasonable to expect that for homeotropic alignment in the $A$ phase, the undulation instability, caused by the contraction of the layers, should be very weak or even absent for the compounds used in Refs. 5 and 7. Experimental observation of this might be complicated by the possible first-order nature of the $A$-$C$ transition in these compounds.

Although it is outside the scope of this paper, a further problem that should be considered is an estimation of the elastic constants. Several authors have employed different methods for calculating the splay, twist, and bend constants, $K_{11}$, $K_{22}$, and $K_{33}$, respectively, for the nematic phase. Essentially, these methods use the mean-field approximation and are parametrized by some molecular property.

Since the two-particle interaction has energy terms favoring nonparallel molecular alignment, it might appear that one or more of the elastic constants ($K_{ij}$) are negative. However, in the mean-field approximation the molecules are regarded as statistically independent and as our phase diagrams illustrate, the free energy does show that the nematic and smectic phases are stable if no deformations are allowed.

If deformations are allowed then we note that Priest considered a general two-particle potential including $P_2$ and $P_4$ interactions of opposite sign in estimating the elastic constants. He found that all the $K_{ij}$ were positive. Thus, we expect that an inherent instability does not occur in our model.

In the smectic-$A$ phase $K_{11}$ (splay) is the only relevant constant since $K_{22}$ and $K_{33}$ diverge. Priest's formulas for $K_{11}$ should not undergo major modification and we also expect from the above argument that $K_{11} > 0$ for the smectic-$A$ phase of our model. It would of course be useful to carry out a quantitative estimation of the elastic constants, in particular, the dilution modulus $\tilde{B}$, as well as the $K_{ii}$.

The authors wish to acknowledge useful discussions and assistance from Dr. A. deVries, Dr. J. W. Doane, and Dr. A. Saupe.

APPENDIX

Here we derive the mean field Eq. (1a) and define the parameters $\epsilon$, $\delta$, and $\gamma$. The two-particle energy between uniaxial molecules referenced to an arbitrary coordinate system $(\tilde{x}\tilde{y}\tilde{z})$ is

$$U_{12} = \sum_{n\lambda=0}^{\infty} \sum_{m=-n\lambda}^{n\lambda} \begin{bmatrix} n & I & \lambda \\ m & -m & 0 \end{bmatrix} B_{\mu\lambda}(r_{12}) Y_{\mu\lambda}(\theta,0) \times Y_{mn}(\Omega) Y_{-m}(\Omega_2),$$

$$n + I > \lambda > |n - I|.$$  \hspace{1cm} (A1)

The factor in large parentheses is the Wigner coefficient. $\tilde{r}_{12}$ is the vector pointing from molecule 1 to molecule 2. ($r_{12} = |\tilde{r}_{12}|$.)

Choosing the $\tilde{z}$ axis of the external coordinate system parallel to $\pm \hat{n}$ (or parallel to an applied magnetic field), we set $\Omega_i = (\theta_i \varphi_i)$, $i = 1, 2$ as the orientation of molecule $i$ relative to the coordinate system $(\tilde{x}\tilde{y}\tilde{z})$. Subscripted coordinates $(\tilde{x}_i \tilde{y}_i \tilde{z}_i)$ denote the molecular coordinated system.

For $\lambda > 0$, the interaction energy depends on the direction of $\tilde{r}_{12}$. If we hold molecule 1 fixed and average molecule 2 isotropically around a sphere centered at molecule 1, we find that only the term $\lambda = 0$ is nonzero by orthogonality of the spherical harmonics $Y_{lm}$. The Wigner coefficient becomes

$$\begin{bmatrix} n & I & 0 \\ m & -m & 0 \end{bmatrix} = \delta_{lm} (-1)^n \delta_{m}(2n + 1)^{-1/2},$$

so that $n = I$.

With this fact in mind, we return to Eq. (A1). If
we let $\theta_1$ and $\theta_2$ be near zero ($|\hat{z} \cdot \hat{n}| \approx 1$), and have $|r_{12}| \gg l$ (l molecular length), then rotations of $\phi_1$ and $\phi_2$ have little effect on $U_{12}$. Averaging over $\phi_1$ and $\phi_2$ we get

$$
\langle U_{12} \rangle_{\phi,\phi_2} = \sum_{nl} b_{nl}(r_{12}, \theta_2) P_n \times (\cos \theta_1) P_l(\cos \theta_2),
$$

(A2)

where

$$
b_{nl}(r_{12}, \theta_2) = \sum_{m} \sum_{n=-l}^{n+l} \bar{B}_{ml}(r_{12}) P_m(\cos \theta_2).
$$

(A3)

The bar over $B$ means we have absorbed the Wigner coefficient and $Y_{nm}$ normalization factors into $B$. At this point Humphries et al. multiply Eq. (A2) by a function $n(r_{12}, \theta_2)$ = $n'(r_{12}, \theta_2)$. They equate $n'(r_{12})$ to a radial correlation function, and $n'(\theta_2)$ to a correlation function for $\theta_2$. This is a questionable procedure. Further difficulties arise if lattice order and orientational order are strongly coupled. We circumvent the introduction of a correlation function and just average Eq. (A2) over a plane of area $A$ perpendicular to the director $(\hat{n})$. This assumes there is no long-range order in the plane. Equation (A2) becomes

$$
\langle U_{12} \rangle_p = \langle \langle U_{12} \rangle_{\phi,\phi_2} \rangle_A
= \sum_{nl} c_{nl}(z_{12}) P_n(\cos \theta_1) P_l(\cos \theta_2),
$$

(A4)

where

$$
c_{nl}(z_{12}) = \frac{1}{A_0} \int dA \ b_{nl}(r_{12}, \theta_2),
$$

(A5)

$A_0$ is the area of plane, and $z_{12} = r_{12}\cos \theta_r$.

The ensemble average of the energy ($E$) of $N$ uniaxial molecules in volume $V$ is

$$
E = \frac{n^2}{2} \int d^3r_1 \frac{d\Omega_1}{4\pi} \int d^3r_2 \frac{d\Omega_2}{4\pi} \langle U_{12} \rangle_p \times \rho(r_1, \theta_1) \rho(r_2, \theta_2) g(r_{12}, \Omega_1, \Omega_2),
$$

(A6)

where $n = N/V$, $\rho(r, \Omega)$ is the one-particle distribution function, $g$ is the indirect pair correlation function, and $U_{12}$ is given by Eq. (A1).

In the mean-field approximation, we set $g = 1$, use $\langle U_{12} \rangle_p$ in place of $U_{12}$, and let $\rho(r, \Omega) \rightarrow \rho(z, \theta)$ to arrive at

$$
E = \frac{n^2}{2} \int d^3r_1 \frac{d\Omega_1}{4\pi} \int d^3r_2 \frac{d\Omega_2}{4\pi} \langle U_{12} \rangle_p \times \rho(z_1, \theta_1) \rho(z_2, \theta_2),
$$

(A7)

$$
\frac{E}{N} = \frac{1}{2V} \int d^3r_1 \frac{d\Omega_1}{4\pi} U_1(z_1, \theta_1) \rho(z_1, \theta_1),
$$

(A8)

so that

$$
U_1(z_1, \theta_1) = n \int d^3r_2 \frac{d\Omega_2}{4\pi} \langle U_{12} \rangle_p \rho(z_2, \theta_2).
$$

(A9)

To make a connection with Eq. (1) of Sec. II, we expand the $c_{nl}(z_{12})$ in a Fourier series as

$$
c_{nl}(z_{12}) = \sum_{\mu} c_{\mu nl} e^{-i\mu z_{12}}.
$$

(A10)

Since by symmetry the system is invariant under $z_{12} \rightarrow -z_{12}$, we get

$$
c_{\mu nl} = c_{-\mu nl}.
$$

(A11)

Equations (A3), (A5), and (A10) relate the $c_{\mu nl}$ to volume integrals of the intermolecular interaction functions $B_{ml}(r_{12})$. Using Eqs. (A4), (A10), and (A11), we arrive at

$$
\langle U_{12} \rangle_p = \sum_{nl\mu} c_{\mu nl} \eta_{\mu n} \cos(\mu q z_{12}) P_n(\cos \theta_1) P_l(\cos \theta_2).
$$

(A12)

Substituting this into Eq. (A9), we have

$$
U_1 = n \sum_{nl\mu} c_{\mu nl} \eta_{\mu n} \cos(\mu q z_{12}) P_n(\cos \theta_1) P_l(\cos \theta_2),
$$

(A12)

where

$$
\eta_{\mu n} = \langle \cos \mu q z P_n(\cos \theta) \rangle,
$$

(A13)

and the brackets are a thermal average with

$$
\frac{\rho(z, \theta)}{A} = \frac{e^{-\mu U_1(z, \theta)/kT}}{V}.
$$

Equations (A12) and (A13) are Eqs. (1a) and (2a), respectively, in the text.

Comparing Eq. (A12) and (1a), we have

$$
c_{\mu nl} = -\frac{V_0}{n} a_{\mu nl}.
$$

Reference to Eq. (3b) allows identification of the parameters. The parameter $\gamma$ is nonzero when we include two-particle interactions which depend on
\( \theta_n \), i.e., when \( n \neq l \). For simplicity we choose \( \gamma = 0 \) or 1. The parameter \( \delta \) controls the purely translational part of \( U_1 \). The parameter \( \epsilon \) controls the \( P_4(x) \) contributions to \( U_1 \) relative to the \( P_2(x) \) part.

Values of \( B_{nl}^m \left( \frac{r_{12}}{r} \right) \) have been calculated by Sweet and Steele\(^\text{44} \) for simple linear molecules. They show all \( B_{nl}^m \) with \( n \) and/or \( l = 4 \) are soft-core repulsive and approximately the same order of magnitude.

---