Ferroelectric nematic liquid-crystal phases of dipolar hard ellipsoids

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A search for ferroelectric *nematic* liquid crystals is carried out on the basis of a simple theoretical model viewing the nonspherical polar molecules as hard ellipsoids of revolution with an embedded permanent dipole oriented along the symmetry axis. The density-dipole moment-aspect ratio phase diagram of the dipolar hard ellipsoids has been determined with the aid of an approximate density-functional theory that was shown recently to lead to good quantitative agreement with the computer simulations of the isotropic-nematic transition of hard ellipsoids. For the *dipolar* hard ellipsoids, two types of stable ferroelectric nematic phases are found for dipole moments and aspect ratios exceeding some reasonable threshold values.

A stable ferroelectric fluid could have many practical applications as an easily reorientable anisotropic fluid. Most ferroelectric materials, however, are solids with the exception of some layered[1] (chiral smectic-*C*) liquid crystals. As discussed recently,[2] there appears to be no fundamental reason why fluids could not be ferroelectric. The aim of the present investigation is to determine some of the molecular properties which could favor ferroelectricity. In order to obtain quantitative results we will use here our recent density-functional theory of orientational freezing[3] as a natural extension of the more qualitative mean-field theory used previously.[2] To keep the calculations simple, a compromise will be made with respect to the degree of realism of the molecular interactions. To this end we have focused our attention on two molecular properties which we consider essential for the possible formation of ferroelectric fluids. The basic ingredient responsible for the appearance of anisotropic fluids is well known to be the presence of anisotropic interactions between the molecules. Considerable evidence has been gained recently[4] that it is sufficient, in a first approximation, to consider only the anisotropic repulsive (steric) interactions. We will thus model the nonspherical molecules by hard ellipsoids (HE) analogous to the well-known hard-sphere (HS) model of spherical molecules.[5] For simplicity we only consider ellipsoids of revolution so that the molecular shape can be characterized by a single parameter, the breadth-to-length or aspect ratio $k = \sigma_\parallel / \sigma_\perp$, with $\sigma_\parallel$ being the diameter along the cylindrical symmetry axis and $\sigma_\perp$ the diameter in any direction perpendicular to this axis. Disk-shaped molecules correspond then to oblate ellipsoids ($0 < k < 1$) while cigar-shaped molecules correspond to prolate ellipsoids ($1 < k < \infty$). Finally, the electric polarization of the molecules, required to possibly turn the anisotropic fluid into a ferroelectric fluid, will be introduced by putting a permanent electric dipole of strength μ_0 at the center of each ellipsoid, with the dipole oriented along the molecular symmetry axis. The possible presence of higher-order electrical multipoles or of different orientations of the dipole will thus be ignored here. This approximation will be briefly referred to as the dipolar hard ellipsoid (DHE)

model analogous to the well-known dipolar hard sphere (DHS) model of spherical polar molecules.[5]

The orientational freezing of the DHE system will now be studied with the aid of the approximate density-functional theory introduced previously[3] for the study of the isotropic (*I*)–nematic (*N*) transition of HE. The results obtained there[3] for the *I*-*N* transition were in good quantitative agreement with the computer simulations of Frenkel and Mulder.[6] For the DHE system only two minor modifications of the HE theory need to be introduced. If we locate the DHE in space with the aid of the position of its center **r** and the orientation of its symmetry axis (with respect to the laboratory frame) with the aid of a unit vector **u** along the axis, then the one-body density, $\rho(\mathbf{r}, \mathbf{u})$, of a spatially uniform fluid (other phases will not be considered here) can be written, $\rho(\mathbf{r}, \mathbf{u}) = \rho h(\mathbf{u})$, with ρ the average density and $h(\mathbf{u})$ the normalized angular distribution of the molecules. The first modification stems from the fact that as a result of the absence of a top-bottom symmetry for the DHE, the general parametrization of $h(\mathbf{u})$ in terms of Legendre polynomials,[3] $h(\mathbf{u}) = \exp[\sum_l \gamma_l P_l(\mathbf{u} \cdot \mathbf{n})]$, has to admit now both odd and even values of *l*. Here **n** is the director of the uniaxial phases to which we restrict our investigation.[3] In the simplest possible approximation[3] we now have to consider a two-order-parameter distribution:

$$h(\mathbf{u}) = \frac{\exp[\gamma_1 P_1(m) + \gamma_2 P_2(m)]}{Z(\gamma_1, \gamma_2)},$$

$$Z(\gamma_1, \gamma_2) = \frac{1}{2} \int_{-1}^{1} dm \, \exp[\gamma_1 P_1(m) + \gamma_2 P_2(m)], \quad (1)$$

where $m = \mathbf{u} \cdot \mathbf{n} = \cos\theta$. Here γ_2 is the usual nematic order parameter[3] measuring the degree of alignment along **n** while γ_1 is the ferroelectric order parameter measuring the total polarization in the direction of **n**. For the *I* phase we have $\gamma_1 = \gamma_2 = 0$, while $\gamma_1 = 0$ and $\gamma_2 \neq 0$ corresponds to a *N* phase and $\gamma_1 \neq 0$ and $\gamma_2 = 0$ or $\gamma_2 \neq 0$ to a ferroelectric nematic (FN) phase. The value of these order parameters are determined by minimizing the Helmholtz free energy with respect to γ_1 and γ_2. This free-energy expression involves the unknown direct corre-

lation function (DCF) of the DHE system for which we will use the same factorization approximation as used previously[3] for the HE. The DCF of the DHE will thus be written as the product of the excluded volume of two ellipsoids of given orientation,[3] $\Sigma(\mathbf{u} \cdot \mathbf{u}')$, times the DCF of the "sphericalized" molecules, which are here DHS of the same volume as the original DHE. This is a straightforward extension of Onsager's low-density approximation[3] and its success for the I-N transition can be understood by observing that in integrated-out expressions, such as the free energy, many of the details of the DCF are irrelevant. For the excluded volume factor $\Sigma(\mathbf{u} \cdot \mathbf{u}')$, we will again use[3] the Berne-Pechukas approximation[7] while for the DCF of the DHS we will use the solution of the mean-spherical approximation (MSA) as obtained by Wertheim.[8] It is well known that the MSA for DHS is plagued with a considerable amount of thermodynamic inconsistency but better approximations would require considerably more numerical work.[5] For the sake of simplicity we have preferred approximations which lead to analytical expressions. In the MSA the DCF of DHS consists of three terms,[5] $c_{\text{DHS}} = \sum_a c_a \equiv c_{\text{HS}} + c_\Delta + c_D$, each of which can be expressed in terms of the Percus-Yevick (PY) DCF of HS, $c_{\text{PY}}(x;\eta)$, with $x = |\mathbf{r}|/\sigma_0$ the reduced distance and $\eta = (\pi/6)\sigma_0^3 \rho$ the packing fraction of HS of diameter σ_0 and density ρ. The first term of

c_{DHS} is the purely HS contribution, $c_{\text{HS}} = c_{\text{PY}}(x;\eta)$, the second is the dielectric term, $c_\Delta = \mathbf{u} \cdot \mathbf{u}' c_\Delta(x;\eta,\mu)$, and the third, c_D, the dipolar term which does not contribute to the approximate free-energy expression because the angular average of c_D with respect to $\mathbf{r}$ vanishes. The dielectric term can again be expressed in terms of the PY DCF as $c_\Delta(x;\eta,\mu) = 2\kappa[c_{\text{PY}}(x;2\kappa\eta) - c_{\text{PY}}(x;-\kappa\eta)]$, where

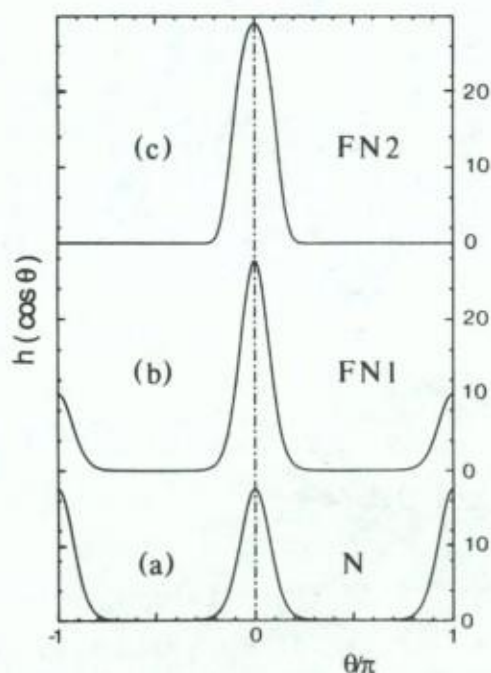FIG. 2. $\mu - \eta$ phase diagram of DHE for (a) $k = 5$ and (b) $k = 10$. Here μ is the reduced dipole strength ($\mu^2 = \beta\mu_0^2/\sigma_1^2\sigma_\parallel$) and η the packing fraction ($\eta = (\pi/6)\sigma_1^2\sigma_\parallel\rho$) of the DHE of aspect ratio $k = \sigma_\parallel/\sigma_\perp$. The different regions correspond to the isotropic (I), the nematic (N), and the two types of ferroelectric nematic ($FN1$ and $FN2$) phases.

FIG. 1. Example of the angular distribution, $h(\cos\theta)$ vs θ/π, for the three ordered phases of DHE [for the I phase, not shown here, $h(\cos\theta)$ is a constant]. (a) The N phase with equal probability for parallel ($\theta = 0$) and antiparallel ($\theta = \pm \pi$) alignment ($\gamma_1 = 0$ and $\gamma_2 \gg 1$), (b) the $FN1$ phase with a larger probability for parallel than for antiparallel alignment ($\gamma_1/0$ and $\gamma_2 \gg 1$), (c) The $FN2$ phase with a strict parallel alignment ($\gamma_1 \gg 1$). The distributions shown here correspond to $k = 10$, $\mu = 0.60$, and $\eta = 0.23$. Notice also that according to Eq. (1), $h(\cos\theta)$ is normalized with respect to $\cos\theta$.
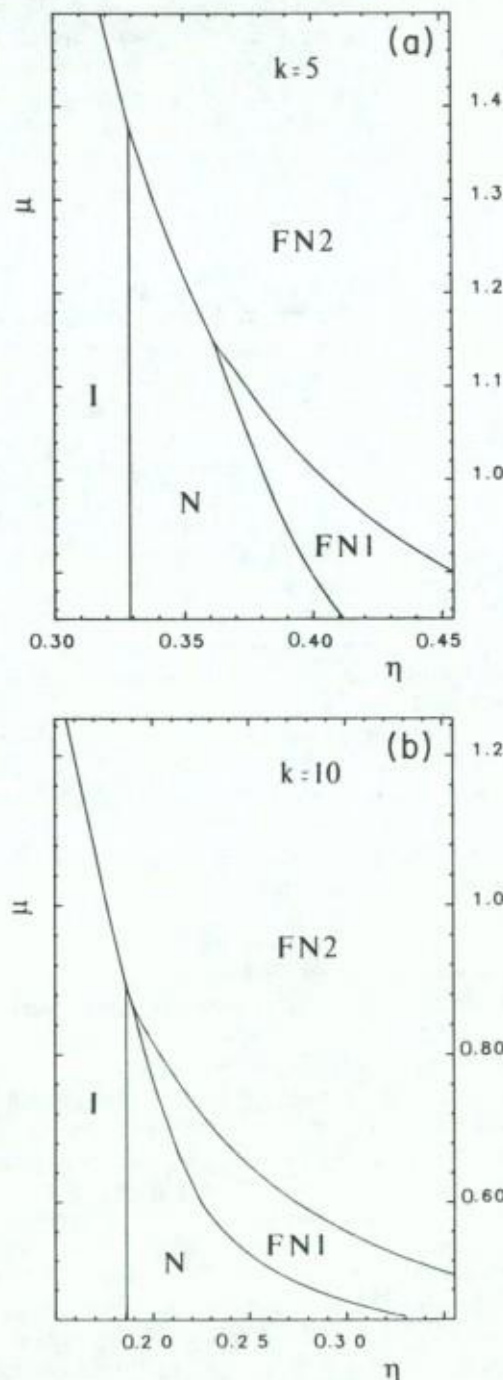
κ is given in terms of η and μ by the implicit equation $q(2\kappa\eta)-q(-\kappa\eta)=8\eta\mu^2$, where $q(\eta)=(1+2\eta)^2/(1-\eta)^4$ while $\mu=(\beta\mu_0^2/\sigma_0^3)^{1/2}$ is the reduced dipole strength ($\beta=1/k_B T$). The reduced difference is free energy per particle $(\beta/\rho)\Delta f$ between the ordered and the disordered ($\gamma_1=\gamma_2=0$) phase can then be written[3]

$$\frac{\beta}{\rho}\Delta f = \int d\mathbf{u}\, h(\mathbf{u})\ln h(\mathbf{u})$$
$$-\frac{\eta}{2}\sum_{\alpha=\text{HS},\Delta} I_\alpha(\bar{\eta};\mu)[H_\alpha(\gamma_1,\gamma_2)-H_\alpha(0,0)] \,, \quad (2)$$

where

$$\eta I_\alpha(\bar{\eta};\mu)=\rho \int d\mathbf{r}\, c_\alpha\left[\frac{|\mathbf{r}|}{\sigma_0};\bar{\eta},\mu\right] \,, \quad (3)$$

$$H_\alpha(\gamma_1,\gamma_2)=\int d\mathbf{u} \int d\mathbf{u}'\, h(\mathbf{u})(\mathbf{u}\cdot\mathbf{u}')^{n_\alpha}\Sigma(\mathbf{u}\cdot\mathbf{u}')h(\mathbf{u}') \,, \quad (4)$$

with $n_\alpha=0$ ($n_\alpha=1$) for the $\alpha=\text{HS}$ ($\alpha=\Delta$) term of the DHS DCF. In Eq. (3), $\bar{\eta}=\bar{\eta}(\eta,k)$ is, moreover an effective density somewhat smaller than η and determined in such a way that the HS DCF of the I phase evaluated at the density $\bar{\eta}$ will mimic[3] the sphericalized DCF of the ordered phase of density η. In order to fix $\bar{\eta}$ we use again[3] the rescaling of the contact distances defined implicitly by $c_{\text{PY}}(1;\eta)=c_{\text{PY}}(x(k);\bar{\eta})$, with $x(k)=k$ when $k\leq 1$ and $x(k)=1/k$ when $k\geq 1$. The three terms in the right-hand side of Eq. (2) are seen then to favor respectively the I, N, and FN phases. Minimizing now Eq. (2) with respect to γ_1 and γ_2, for a given value of k, μ, and η, we find four different stable phases. An example of the corresponding angular distributions is shown in Fig. 1. The phase diagram in the $\mu-\eta$ plane is shown in Fig. 2 for $k=5$ and $k=10$. It is seen that below a threshold value of μ (typically for $\mu<0.35$ when $k=10$) only I-N transitions are observed. Above this threshold we find free energy minima corresponding, besides to the I and N phases, to two types of FN phases. The latter consist of a FN1 phase with considerable antiferroelectric order; but a small net polarization (see Fig. 1) and a FN2 phase with a strong ferroelectric order and hence a large polarization (see Fig. 1). All transitions appear to be first-order except for the N-FN1 transition which is second order, at least within the present numerical accuracy. The FN1 phase appears only for the intermediate μ values. For values of μ above the N-FN1-FN2 triple point value, the N-phase transforms directly into the FN2 phase when increasing η, whereas above the I-N-FN2 triple point value the N phase disappears as a thermodynamically stable phase. When increasing the molecular excentricity (i.e., increasing k) the FN phases are pushed towards lower values of μ and η. For instance, the I-N-FN2 triple point which for $k=5$ corresponds to $\mu=1.38$ and $\eta=0.33$ is shifted to $\mu=0.89$ and $\eta=0.19$ for $k=10$ and to $\mu=0.80$ and $\eta=0.13$ for $k=15$, while the two triple points come also closer one to another (see Fig. 2). The FN phases occur then well below the densities for which the other phases not considered here (e.g., the smectic or solid phases) are expected to become stable.[9] To favor ferroelectricity one should thus look for molecules[10] with a sufficiently high dipole moment ($\mu\gtrsim 0.3$) and a sufficiently large excentricity ($k\gtrsim 7$).

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