Ferroelectric Nematic Liquid Crystals: Realizability and Molecular Constraints

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(Received 30 December 1987)

There is no fundamental reason that fluids should not be ferroelectric. However, the only knownferroelectric fluids are chiral smectic-*C* liquid crystals and related structures. We examine the possibility that molecules with permanent dipole moments can form a ferroelectric nematic phase, the least ordered conceivable ferroelectric phase. We show that reasonable electric dipole interactions between disk-shaped molecules may lead to such a phase, and calculate the phase diagram using mean-field theory. Some constraints on the constituent molecules are discussed.

PACS numbers: 64.70.Md, 36.20.Ey, 77.80.−e

A variety of molecules (mesogens) form liquid-crystalline phases.[1] Many mesogens have symmetries consistent with the formation of ferroelectric phases and nonzero electric dipole moments. Furthermore, there is no fundamental reason that ferroelectric phases should not exist. However, only the chiral smectic-*C* phase and related tilted smectic (or layered) phases have been observed to be ferroelectric.[2] Even this phase can be rigorously considered to be ferroelectric only in two dimensions because the direction of the polarization varies helically through the sample in three dimensions.

This Letter examines requirements for formation of a ferroelectric nematic (FN) phase, that is, a phase in which the only long-range order is parallel alignment of a molecular axis. We construct an effective single-particle Hamiltonian for a simple model and calculate its phase diagram using mean-field theory. This shows that the FN phase can be formed by disklike molecules which have reasonable electric dipole moments. We then consider qualitatively the effects not included in this model and the possibility that columnar phases, which have two-dimensional translational order, are ferroelectric.

First we consider a model fluid consisting of rigid, cylindrically symmetric molecules, where the orientation of the molecular symmetry axis is specified by the unit vector $\hat{\mathbf{n}}$. We assume that each molecule has an electric dipole moment μ parallel to $\hat{\mathbf{n}}$, but is otherwise symmetric under $\hat{\mathbf{n}} \leftrightarrow -\hat{\mathbf{n}}$. We neglect the effects of molecular polarizability. The usual (tensor) nematic order parameter is $Q_{\alpha\beta} = \langle \sigma_{\alpha\beta} \rangle$, where $\sigma_{\alpha\beta} = \frac{1}{2}(3n_\alpha n_\beta - \delta_{\alpha\beta})$, while the ferroelectric order parameter is $\Lambda_\alpha = \langle n_\alpha \rangle$ and the angle brackets indicate the ensemble average.

The effective single-particle Hamiltonian must be a function of scalar invariants formed from the above quantities. When the average electric field is zero, we have, to lowest order,

$$H = -a\delta_{\alpha\beta}\Lambda_\alpha n_\beta - bQ_{\alpha\beta}\Lambda_\alpha n_\beta - \tfrac{2}{3}cQ_{\alpha\beta}\sigma_{\alpha\beta} - d\Lambda_\alpha\Lambda_\beta\sigma_{\alpha\beta} - A\delta_{\alpha\beta}\Lambda_\alpha\Lambda_\beta - BQ_{\alpha\beta}\Lambda_\alpha\Lambda_\beta - \tfrac{2}{3}CQ_{\alpha\beta}Q_{\alpha\beta}, \tag{1}$$

where summation is implied over repeated Greek indices and a, b, c, d, A, B, and C are constants to be determined. Terms not containing the fields $\mathbf{\Lambda}$ and Q are irrelevant and have been omitted. Minimization of the free energy with respect to the order parameters yields $\langle \delta H/\delta\Lambda_\alpha \rangle = \langle \delta H/\delta Q_{\alpha\beta} \rangle = 0$, which results in constraints on the parameters (e.g., $A = -\frac{1}{2}a$). It follows that

$$H = -a\delta_{\alpha\beta}\Lambda_\beta(n_\alpha - \tfrac{1}{2}\Lambda_\alpha) - bQ_{\alpha\beta}\Lambda_\alpha(n_\alpha - \Lambda_\alpha) - \tfrac{1}{2}b\Lambda_\alpha\Lambda_\beta\sigma_{\alpha\beta} - \tfrac{2}{3}cQ_{\alpha\beta}(\sigma_{\alpha\beta} - \tfrac{1}{2}Q_{\alpha\beta}), \tag{2}$$

and that the average energy per particle is

$$\langle H \rangle = -\tfrac{1}{2}a\delta_{\alpha\beta}\Lambda_\alpha\Lambda_\beta - \tfrac{1}{2}b\Lambda_\alpha\Lambda_\beta Q_{\alpha\beta} - \tfrac{1}{3}cQ_{\alpha\beta}Q_{\alpha\beta}. \tag{3}$$

The terms proportional to a and b in Eq. (2) depend on the sign of $\hat{\mathbf{n}}$ so that in our simple model a and b can be deduced from the average dipolar energy per particle,

$$\langle H_{d\text{-}d} \rangle = -\rho\frac{\mu^2}{2}\int G_{\alpha\beta}(\mathbf{r})n_{1\alpha}n_{2\beta}g_r(\mathbf{r},\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2)P(\hat{\mathbf{n}}_1)P(\hat{\mathbf{n}}_2)d^3r\,d^2\hat{n}_1\,d^2\hat{n}_2, \tag{4}$$

where $\mathbf{r}$ is the intermolecular separation, ρ is the number density, $g_r(\mathbf{r},\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2)$ is the radial distribution function, and $P(\hat{\mathbf{n}})$ is the singlet orientational probability distribution function. We will take this integral over a large, spherical region $r < R$; the Lorentz field coming from outside this region is usually largely canceled by the reaction field[3] and will be neglected. The dipole tensor is $G_{\alpha\beta}(\mathbf{r}) = (3r_\alpha r_\beta - \delta_{\alpha\beta})r^{-3}$ in the absence of screening and r_α is a component of $\hat{\mathbf{r}}$.

The detailed form of g_r is not established. We assume that it can be replaced by its orientationally average,

$$g(\mathbf{r}) = \int g_r(\mathbf{r},\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2)P(\hat{\mathbf{n}}_1)P(\hat{\mathbf{n}}_2)d^2\hat{n}_1\,d^2\hat{n}_2. \tag{5}$$

It follows that

$$\langle H_{d\text{-}d}\rangle = -\tfrac{1}{2}\mu^2\rho\langle G_{\alpha\beta}\rangle\Lambda_\alpha\Lambda_\beta, \tag{6}$$

where

$$\langle G_{\alpha\beta}\rangle = \int G_{\alpha\beta}(\mathbf{r})g(\mathbf{r})d^3r. \tag{7}$$

We now assume that a radially scaling transformation $\mathbf{r}' = \mathbf{r}/f(\hat{\mathbf{r}})$ exists which renders g isotropic so that $g(\mathbf{r}) = g(\mathbf{r}'f(\hat{\mathbf{r}})) = g(|\mathbf{r}'|)$. Using the fact that $g(\mathbf{r}) \to 1$ as $r \to \infty$, we find[4]

$$\langle G_{\alpha\beta}\rangle = -\int \ln(f(\hat{\mathbf{r}}))(3r_\alpha r_\beta - \delta_{\alpha\beta})d^2\hat{r}. \tag{8}$$

To first order, the average nearest-neighbor separation of molecules in the direction $\hat{\mathbf{r}}$ is well approximated[5] by

$$d(\hat{\mathbf{r}}) = \tfrac{2}{3}R_\parallel + 2R_\perp\left[1 + \frac{2}{3}\frac{\kappa-1}{\kappa+2}Q_{\alpha\beta}(3r_\alpha r_\beta - \delta_{\alpha\beta})\right].$$

Here $R_\parallel$ and $R_\perp$ are the lengths of the semimajor axes of the molecular hard core parallel and perpendicular to the symmetry axis, and $\kappa = R_\parallel/R_\perp$ is the length-to-breadth ratio. If we assume that $f(\hat{\mathbf{r}}) = d(\hat{\mathbf{r}})$, it follows, to first order, that

$$\langle G_{\alpha\beta}\rangle = -\tfrac{16}{5}\pi[(\kappa-1)/(\kappa+2)]Q_{\alpha\beta} \tag{9}$$

since $Q_{\alpha\alpha} = 0$. This result agrees well with the results of simulations.[6]

Comparing Eqs. (3), (6), and (9), we find $a = 0$ and

$$b = -\mu^2\rho\tfrac{16}{5}\pi[(\kappa-1)/(\kappa+2)]. \tag{10}$$

Thus b is positive and ferroelectricity is favored only for oblate (disklike) particles. if we choose $\hat{\mathbf{z}}$ parallel to $\mathbf{\Lambda}$, the effective single-particle Hamiltonian is

$$H = -bS\Lambda(n_z - \Lambda) - \tfrac{1}{2}b\Lambda^2\sigma - cS(\sigma - \tfrac{1}{2}S), \tag{11}$$

where $\Lambda = \Lambda_z$, $S = Q_{zz}$, and $\sigma = \sigma_{zz}$. Solution of the self-consistent equations $\Lambda = \langle n_z\rangle$ and $S = \langle\sigma\rangle$ yields $c = 4.54kT_{\mathrm{NI}}$, where T_{NI} is the temperature of the nematic-isotropic transition for weak dipolar interactions ($b = 0$), and the complete resulting phase diagram shown in Fig. 1.

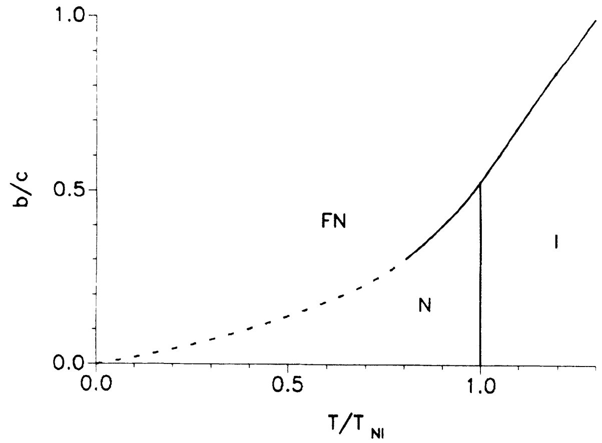

FIG. 1. Phase diagram showing the isotropic (I) nematic (N) and ferroelectric-nematic (FN) phases. Solid lines indicate first-order transitions; dashed lines, second-order transitions. The I-N-FN triple point occurs at $b/c = 0.525$. For $T_{\mathrm{NI}} = 300$ K, $\rho = 1\times10^{27}$ m^{-3}, and $\kappa = 0.2$, we find that this requires a dipole moment of 5.2 D, which is readily accessible.

Successive orientational transitions in crystals have been calculated by Krieger and James.[7] Lei[8] has suggested that this calculation applies to liquid crystals formed from bowl-shaped molecules. Their effective Hamiltonian differs from ours in that they assumed that $a \neq 0$ and $b = 0$. In contrast we expect the ferroelectric phase only if $b > 0$, because of coupling between the order parameters S and Λ. In addition, if there are no (or only weak) interactions between S and Λ we expect that fluctuations will be important and may considerably change the transition temperature as dipole-dipole interactions do not directly result in nonzero bend and twist elastic constants.

Arguments similar to those given above suggest that parallel alignment is favored by interactions between transverse dipoles on rodlike molecules. Experimental evidence for this is provided[9] by recent observations of Kirkwood correlation factors in excess of unity. This tendency might lead to a ferroelectric biaxial nematic.[10]

We now consider some effects which may significantly alter the behavior. If the molecules are chiral the ordering direction will twist, as in a cholesteric liquid crystal,[1] resulting in a helielectric phase. If the molecules are nonchiral, symmetry arguments,[11] confirmed by experiments on two-dimensional tilted chiral smectics,[12] show that the FN phase is stable to small deformations only if the tendency of the order parameter to splay in the ordered state is small enough. This tendency results from asymmetric or wedge-shaped molecules and, if large enough, results in modulated polar phases.

Essentially any disklike molecule which has a dipole along its axis also has other differences between the top and bottom of the disk, i.e., chemical and shape differences. Typically the free energy is larger when dissimilar chemical structures (e.g., polar and oily) are in contact. Thus chemically dissimilar tops and bottoms of the disk are expected to discourage ferroelectricity. Steric interactions between asymmetry molecules also generally disfavor ferroelectric nematics. Consider the orientation-dependent second virial coefficient,

$$B(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2) = -\tfrac{1}{2}\int d^3r\left(e^{-\beta v(\mathbf{r},\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2)}-1\right), \qquad (12)$$

where v is the interaction potential. Ferroelectric nematics are favored if B is smaller when the mesogens are parallel ($\hat{\mathbf{n}}_1=\hat{\mathbf{n}}_2$) than when they are antiparallel ($\hat{\mathbf{n}}_1=-\hat{\mathbf{n}}_2$). We have evaluated this integral for hard-core interactions and a wide variety of shapes. For many anisotropic shapes, including a variety of bowls, $B(1) > B(-1)$ [often $B(1)\sim 1.3B(-1)$] so that ferroelectricity is disfavored. We speculate that $B(1)>B(-1)$ in general for hard-core interactions between solids of rotation. There are exceptions to this rule for shapes other than solids of rotation, e.g., linked cones constrained by the links to have the same orientation[13] (like an egg carton). Shapes known to us with this property seem unlikely to be ferroelectric except in a more ordered phase than a uniaxial nematic, e.g., a biaxial nematic or columnar phase. Thus asymmetries other than the dipole both discourage ferroelectric phases and encourage modulated polar phases.

Dipolar interactions large enough to form the FN phase will alter the translational distribution of mesogens. If a disk has a longitudinal dipole consisting of opposite charges above and below the center of the disk, then the interaction energy between disks will be minimized when the disks are as close as is consistent with interactions, oriented parallel along a line joining their centers. If all configurations for which the energy is within the thermal energy of this minimum have essentially the same spatial separation between the mesogens, we expect a more ordered phase than the nematic, a columnar phase or a crystal with two- or three-dimensional translational order. This tendency to form states with broken translational symmetry is decreased if the charges form off-center or tilted dipoles, a number of small dipoles, or a very different pattern of charges above and below the disk, and if the charges cannot approach each other too closely. Columns are encouraged if the molecules pack better when they have particular spatial separations, as do many asymmetric shapes such as bowls.

Finally we do not expect most columnar phases formed by disk-shaped molecules to have polar order, i.e., to be ferroelectric or antiferroelectric. We consider only systems in which there is translational order perpendicular to the columns and no translation order parallel to the columns; i.e., states with liquid-crystalline but not crystalline symmetry. Disklike molecules known to exhibit liquid-crystalline phases are characteristically rigid cores surrounded by flexible tails.[14] We do not expect that these flexible tails distinguish between parallel and antiparallel alignment of disks in neighboring columns and will concentrate on Coulomb interactions.

Columnar phases of chiral, tilted mesogens will be ferroelectric if there is no more than one rotation axis which leaves the average mesogen positions unchanged. This is the reason why the chiral smectic-*C* phase is ferroelectric.[2] With the exclusion of this possibility, interactions between the mesogens must be large enough for a ferroelectric phase to result.

The formation of columns will substantially increase Coulomb and steric interactions which tend to align the disks in each column, so that it is reasonable to expect consecutive disks to be parallel in each column and we consider only such phases. Note, however, that the dipole-dipole interactions may be overwhelmed by other interactions and, in fact, antiferroelectric dimers in (tilted) columns have been observed.[15] In any case the dipole-dipole interaction is not sufficiently long ranged to result in long-range order in a column in the absence of interactions between the columns.[16] Therefore the formation of polar states in which the disks are aligned parallel in each column with some polar ordering perpendicular to the columns requires that the intercolumn interactions be large enough. However, if intracolumn interactions are too large crystalline phases would be expected.

The polar intercolumn interactions are small compared to intracolumn interactions. If a dipole is held fixed and another dipole is translated freely along a line parallel to its moment the average interaction energy is zero. Therefore the Coulomb interaction between columns with the average dipoles along the columns results in a weak tendency for polar order, depending on the intercolumn pair distribution function. The intercolumn dipole interaction is relatively weak and expected intercolumn distribution functions make the effective interaction substantially smaller. Therefore it is not expected that columnar phases formed from disks with a symmetry axis parallel to the columns will have polar order.

If the disks are tilted from the column axis the dipoles will have a component perpendicular to the columns. If we assume that the intercolumn pair distribution is uniform, the effective intercolumn interaction favors parallel dipoles if the separation is parallel to the dipoles and antiparallel dipoles if the separation is perpendicular to the dipoles. Therefore phases are expected in which the dipoles in the plane perpendicular to the columns are antiferromagnetically ordered, and ferroelectric in-plane order seems unlikely. Depending on the spatial variation of the tilt this will result in either ferroelectric or antiferroelectric ordering along the columns.

Finally, note that disks bonded together with flexible spacers to form polymers or oligomers in such a way that successive monomers tend to point in the section (as in egg cartons[13]) may form columnar phases. This bonding will yield a substantial intercolumn interaction and so if the intracolumn alignment interaction (Coulombic or steric) is large enough the columnar phases will be ferroelectric.

We have argued that, with careful molecular design, disk-shaped molecules will form nematic liquid crystals which are also ferroelectric. Such systems, as the least ordered conceivable ferroelectric phases, might have considerable application as easily reorientable anisotropic fluids. Columnar phases which are ferroelectric, or at least have polar order, may also form. Some constraints on molecules which will form such phases have been discussed.

Support from the National Science Foundation through Grant No. DMR8614093 (R.G.P.) and from the Natural Sciences and Engineering Research Council of Canada (P.P.-M.) and useful conversations with R. B. Akins, B. Bergersen, D. A. Dunmur, G. Patey, D. R. Perchak, P. L. Taylor, and K. M. Wiefling are gratefully acknowledged.

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[1] See, e.g., S. Chandrasekhar, *Liquid Crystals* (Cambridge Univ. Press, New York, 1977).

[2] R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, J. Phys. (Paris), Lett. **36**, L69 (1975).

[3] See, e.g., John G. Kirkwood, in *John Gamble Kirkwood Collected Works,* edited by R. H. Cole (Gordon and Breach, New York, 1965), Vol. 2, p. 53.

[4] P. Palffy-Muhoray and D. A. Balzarini, Can. J. Phys. **59**, 375 (1981).

[5] P. Palffy-Muhoray, D. A. Balzarini, and D. A. Dunmur, Mol. Cryst. Liq. Cryst. **110**, 315 (1984).

[6] D. Frenkel, private communication.

[7] T. J. Kreiger and H. M. James, J. Chem. Phys. **22**, 796 (1954).

[8] Lin Lei, Mol. Cryst. Liq. Cryst. **146**, 41 (1987); L. M. Leung and Lin Lei, Mol. Cryst. Liq. Cryst. **146**, 71 (1987).

[9] K. Toriyama and D. A. Dunmur, Mol. Phys. **56**, 479 (1985).

[10] B. Bergersen, D. A. Dunmur, P. Palffy-Muhoray, and R. G. Petschek, unpublished.

[11] G. A. Hinshaw, Jr., and R. G. Petschek, Phys. Rev. B **37**, 2133 (1988), and references therein.

[12] See, e.g., C. Rosenblatt, R. B. Meyer, R. Pindak, and N. A. Clark, Phys. Rev. A **21**, 140 (1980); N. A. Clark, D. H. Van Winkle, and C. Muzny, private communication.

[13] R. B. Akins, private communication. We do not view this description as an introduction of "egg-cartonic" or oothecatic [from the greek *ωιον* (egg) *θηκη* (case)] phases.

[14] S. Chandrasekhar, in *Advances in Liquid Crystals,* edited by Glenn H. Brown (Academic, New York, 1982), Vol. 5, p. 47ff.

[15] P. Weber, D. Guillon, and A. Skoulios, J. Phys. Chem. **91**, 2242 (1987); D. Guillon, A. Skoulios, and J. Malthete, Europhys. Lett. **3**, 67 (1987).

[16] See, e.g., L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1958), p. 482.