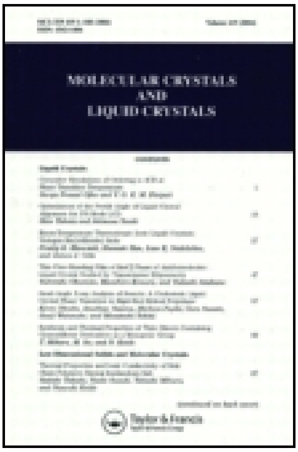

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FERROELECTRIC LIQUID CRYSTALLINE ORDERING OF RIGID RODS WITH DIPOLAR INTERACTIONS

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Abstract A mean-field model for the ferroelectric ordering of hard spherocylinders with dipolar interaction is developed within the Onsager formalism. By performing accurate numerical analyses, a complete phase diagram is obtained in terms of the dipolar strength, the number density, and the pressure of the spherocylinders, which exhibits a usual isotropic-nematic, a nematic-ferroelectric nematic, and a direct isotropic-ferroelectric nematic phase transitions. These results are in reasonable agreement with the recent computer simulations. It is also found that there exists always a direct isotropic-ferroelectric nematic phase transition above a critical dipolar strength.

INTRODUCTION

Ferroelectric liquid crystals (FLCs) have attracted great interest from both fundamental and practical viewpoints.[1] The existence of FLCs has been predicted in tilted chiral smectic phases by symmetry arguments.[2] There are, however, no reason of the principle why phases with other symmetry cannot be ferroelectric.[3,4] It has been suggested that the ferroelectricity could be appeared in the nematic phase.[4] More recently, computer simulations have shown that a system of rod-like molecules with strong dipolar interactions can exhibit a ferroelectric nematic phase.[5,6]

In this paper we report a complete phase diagram of hard spherocylinders in terms of the dipolar strength, the number density, and the pressure of the system, which exhibits a conventional isotropic-nematic (I-N), a nematic-ferroelectric nematic (N-FN), and a direct isotropc-ferroelectric nematic (I-FN) transitions. We introduce both dipole-dipole interactions and hard-core repulsions into a simple mean-field model within the Onsager formalism.[7]

At a level of a mean-field approximation, we obtain accurate angular distribution functions by numerically solving the Onsager integral equation using a simple iterative method.[8] In order to see the qualitative features of the ferroelectric ordering of hard rods, it is assumed that the aspect ratio is infinitely large, and possible electric multipolar interactions among them are negligible. Moreover, the FN phase is assumed to possess only the orientational order like a conventional N phase as argued previously.[4] Thus, the existence of ferroelectric smectic phases will not be expected in this mean-field model.

THE FREE ENERGY WITH DIPOLAR INTERACTIONS

Consider a solution of N long rod-like dipolar molecules of length L and diameter D with dipole moment $\mathbf{d}$ at temperature T. In a simple mean-field model, intermolecular interactions can be decoupled into the hard-core repulsion and dipolar interaction parts. Under these circumstances, we first construct the free energy in terms of direct correlation functions before a specific form of the intermolecular interactions is taken into consideration.

Following the density functional approach[9] and keeping the terms up to two-body correlations, the free energy is given by

$$F = F_o + k_B T \int d(1)\rho(1)[\ln \rho(1) - 1] + \frac{1}{2}\int c_2(1,2)\rho(1)\rho(2)d(1)d(2), \qquad (1)$$

where the index i stands for the coordinates, $\mathbf{r}_i$ and Ω_i, of the i-th molecule. Here $c_2(i,j)$ is the two-body direct correlation function of the i-th and j-th molecules, $\rho(i)$ the local density, and F_o the reference free energy.

In a uniform I, N, or FN phase, the local density, $\rho(i) \equiv \rho(\mathbf{r}_i, \Omega_i)$, is independent of $\mathbf{r}_i$ but a function of the orientation variable Ω_i. In this case, $\rho(i) = \rho f(\Omega_i)$ with ρ the average density and $f(\Omega_i)$ the normalized angular distribution function. While the N phase is uniaxial with a cylindrical symmetry around the director $\mathbf{n}$ and a plane of symmetry perpendicular to $\pm\mathbf{n}$, the FN phase is uniaxial with a cylindrical symmetry but not with a plane of symmetry. In terms of the uniform local density $\rho(i) = \rho f(\Omega_i)$, Eq. (1) can be rewritten as

$$F/\rho k_B T = \mu_o(T) - 1 + \ln\rho + \sigma + b\rho\psi \tag{2}$$

where $\mu_o(T)$ is the chemical potential of a molecule at temperature T, $\rho = (N/V)$ is the number density, and $b = \pi/4L^2D$. Here σ describes the loss of the orientational entropy per molecule, and ψ is related to the two-body direct correlation function averaged over angular distribution function.

$$\sigma = \int f(\Omega)\ln[4\pi f(\Omega)]d\Omega, \tag{3}$$

and

$$\psi = \frac{1}{2b}\int c_2(\Omega_1,\Omega_2)f(\Omega_1)f(\Omega_2)d\Omega_1 d\Omega_2. \tag{4}$$

We now consider the dipole-dipole interaction and hard-core repulsion between two molecules, and derive the expression for the effective two-body direct correlation function $c_2(\Omega_1,\Omega_2)$. In the mean-field description, the resultant form of $c_2(\Omega_1,\Omega_2)$ is given by

$$c_2(\Omega_1,\Omega_2) = b\,[\frac{8}{\pi}|\sin\gamma(\Omega_1,\Omega_2)| - \frac{2d^2}{3b\epsilon_o k_B T}P_1(\Omega_1)P_1(\Omega_2)], \tag{5}$$

where $\gamma(\Omega_1,\Omega_2)$ is the angle between the two molecules with orientations Ω_1 and Ω_2, ϵ_o the dielectric constant in vacuum, d the magnitude of the dipole moment, k_B the Boltzmann constant, P_1 the first-order Legendre polynomial which is directly related to the degree of the ferroelectric ordering.

We then minimize the free energy with respect to $f(\Omega)$ to arrive at the integral equation

$$\ln[4\pi f(\Omega_1)] = \lambda - \rho\int c_2(\Omega_1,\Omega_2)f(\Omega_2)d\Omega_2, \tag{6}$$

where λ is the normalization constant.

Without using any functional expansions, we solve Eq. (6) numerically by the iterative method as follows:

$$f_{m+1}(\Omega) = \frac{\exp[-(q/b)\int c_2(\Omega_1,\Omega_2)f(\Omega_2)d\Omega_2]}{\int\exp[-(q/b)\int c_2(\Omega_1,\Omega_2)f(\Omega_2)d\Omega_2]d\Omega_1} \tag{7}$$

We have performed numerical iterations at different values of total elements n in polar angle θ to check that this iterative method gives results independent of n at large n. Clearly, if the iteration converges, so that $f_{k+1}(\theta) = f_k(\theta)$ for $k \geq m$, then $f_m(\theta)$ is a solution to Eq. (6). After m iteration we find that the solutions $f_m(\theta)$, independent of the initial form of $f_0(\theta)$, gives a well-defined distribution function $f(\theta)$. Convergence was assumed when the difference between the results of two successive iterations became less than at least 10^{-6}. The value of $n = 130$ was used, and typically m was on the order of 100. The formation of the N or FN phase is monitored by evaluating the usual equilibrium first- and second-rank order parameters, $\langle P_1 \rangle$ and $\langle P_2 \rangle$, where $\langle \ \rangle$ denotes the average over the angular distribution function $f(\Omega)$. Of course, for isotropic liquids, both order parameters are zero. For ordinary non-ferroelectric nematics, $\langle P_2 \rangle \neq 0$ and $\langle P_1 \rangle = 0$. For ferroelectric nematics, both $\langle P_1 \rangle$ and $\langle P_2 \rangle$ must be nonzero.

The critical concentrations in the isotropic(ρ_i), nematic(ρ_n), and ferronematic(ρ_f) phases can be found by using the condition that two of the phases have equal pressures and chemical potentials at the relevant transition when they are in stable equilibrium.

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = k_B T \rho \, [1 + b\rho\psi], \tag{8}$$

$$\mu = -\left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu_o + k_B T \, [\ln \rho + \sigma + 2b\rho\psi]. \tag{9}$$

We shall introduce convenient dimensionless variables for the concentration, the dipole moment, pressure, and chemical potential. q denotes dimensionless concentration $b\rho$, d^* the reduced dipole moment $\sqrt{d^2/(3b\epsilon_o k_B T)}$, p the dimensionless pressure bP/k_BT, and μ the dimensionless chemical potential $(\mu - \mu_o)/k_BT + \ln b$.

NUMERICAL RESULTS AND DISCUSSION

We have found that in addition to the usual I-N transition, there exists a N-FN and a direct I-FN transitions for a system of hard spherocylinders with dipolar interactions. The phase boundaries for the I-N and I-FN transitions were determined from the coexistence conditions, and the N-FN transition was obtained by finding the critical concentration at which $\langle P_1 \rangle$ becomes nonzero for fixed dipolar strength. The phase diagram in the (q, d^*) plane is shown in Fig. 1. The usual I-N transition and a direct I-FN transitions are the first-order while the N-FN transition is the second-order ($d^* < 0.362$). The critical dipolar strength $d_c^* = 0.362$ corresponds to the I-N-FN triple point.

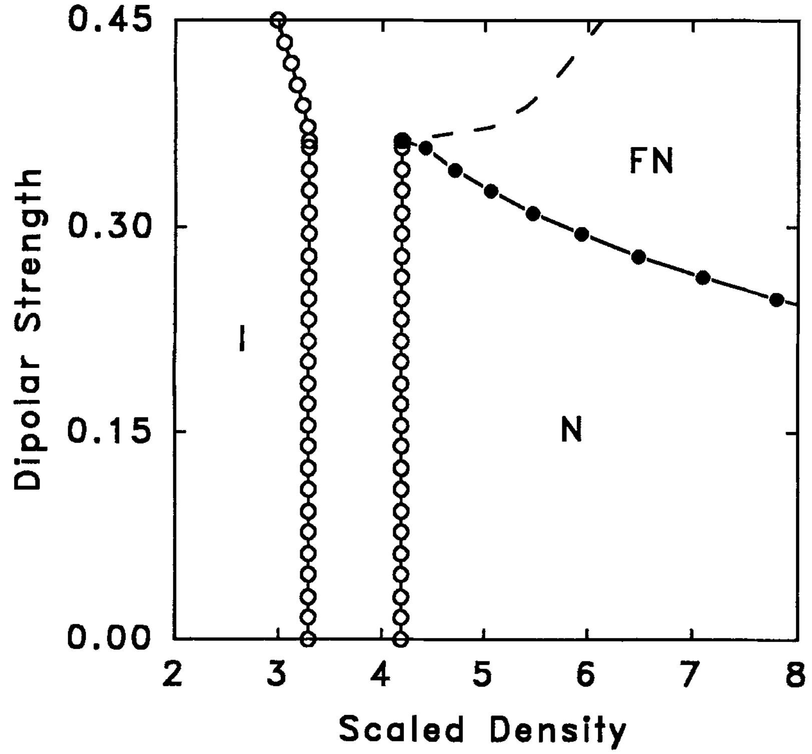

FIGURE 1 The phase diagram in the (q, d^*) plane for a system of hard spherocylinders with dipolar interactions. hard spherocylinders with dipolar interactions. The open circles and the filled circles represent the I-N and N-FN transition lines, respectively. The dotted line denotes a direct I-FN transition line.

The order of the N-FN transition was checked by evaluating $\langle P_1 \rangle$ along the pressure line for fixed d^* in the (p, q) plane. It turned out to be the second-order as reported previously.[10] The density q_i of the isotropic phase and q_n of the nematic phase at the I-N transition remain fairly constant until the dipolar strength d^* reaches at the triple point. Below the triple point, the dipolar interactions seem not to play a significant role in the I-N phase behavior, i.e., the orientational order is predominantly governed by the hard-core repulsions.[6] The dipolar term in Eq. (5) plays a role in the phase behavior once the nematic phase is well developed at relatively high concentrations.

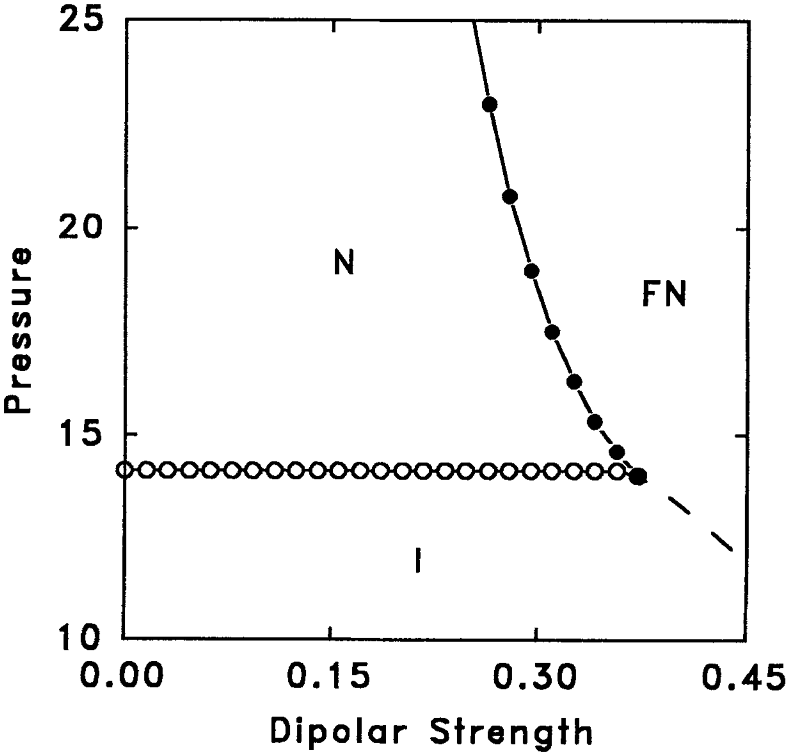

FIGURE 2 The phase diagram in the (d^*, p) plane for a system of hard spherocylinders with dipolar interactions. The open circles and the filled circles represent the I-N and N-FN transition lines, respectively. The dotted line indicates the direct I-FN transition.

For $d^* > 0.362$, a direct I-FN transition occurs. However, the shape of the I-FN transition line is physically unrealistic since for fixed q the FN phase becomes separated into the I and FN with increasing d^*. This is precisely consistent with the criterion for the breakdown of the Onsager approximation.[11] For relatively short rod-like molecules, higher orders in both D/L and direct correlation functions should be taken into account to correctly describe the I-FN phase behavior.

A phase diagram along the phase boundaries in the (d^*, p) plane is shown in Fig. 2. Note that $p = bP/k_BT$, $d^* = \sqrt{d^2/(3b\epsilon_o k_BT)}$. The pressure along the I-N phase boundary remains constant until the dipolar strength $d^* \leq 0.362$. However, the pressure at the N-FN transition decreases with increasing the dipolar strength d^*.

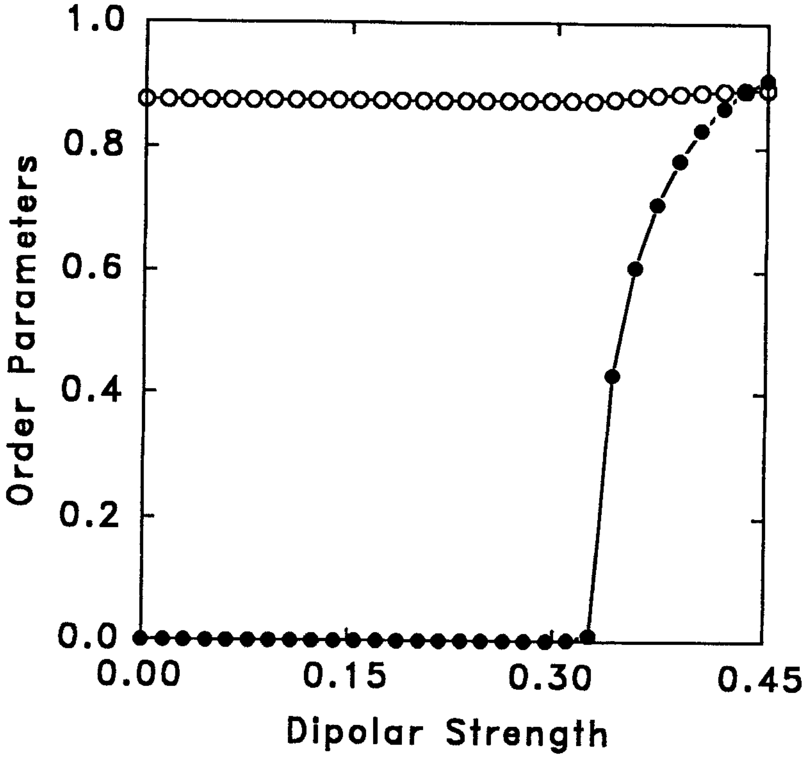

FIGURE 3 The orientational and ferroelectric order parameters for fixed $q = 5$ as a function of the dipolar strength. The open circles and the filled circles represent $\langle P_1 \rangle$ and $\langle P_2 \rangle$, respectively.

For sufficiently high d^*, the I-FN transition may be preempted by the isotropic-smectic transition, which is indicated by the computer simulations.[6] In our case, we assume that our system possesses no positional order; the states with only orientational order, neither with translational order nor with true crystalline symmetry. Therefore, the existence of any smectic ferro- or antiferro-electric phase would not be expected within this model.[12,13]

Fig. 3 shows two order parameters, $\langle P_1 \rangle$ and $\langle P_2 \rangle$ for fixed $q = 5.0$ as a function of the dipolar strength d^*. The orientational order parameter $\langle P_2 \rangle$ slightly increases on passing the N-FN transition, implying that the dipolar interactions do not significantly affect the degree of the orientational order. However, the ferroelectric order parameter $\langle P_1 \rangle$ abruptly increases at the N-FN ($d^* = 0.33$) and becomes saturated with further increasing the dipolar strength d^*.

CONCLUDING REMARKS

We developed a mean-field model for a system of hard spherocylinders with dipolar interactions within the Onsager formalism. The model predicts the existence of the I-N, N-FN, and a direct I-N transitions. In all cases we obtained qualitatively correct results, which agree with the recent computer simulations. A complete phase diagram is obtained in terms of the dipolar strength, the number density, and the pressure of the dipolar system. It was also found that there exists the I-N-FN triple point located at $d^* = 0.362$. In the phase diagram, the N-I and I-FN transitions is the first-order whereas the N-FN transition is the second-order. The model proposed here is applicable for a system of dipolar molecules, possessing only the orientational degree of freedom. We believe, however, that the above limitation doesn't influence the main features of the results for the N-FN and I-FN transitions.

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REFERENCES

1. For a comprehensive discussion, see J. W. Goodby, et al., Ferroelectric Liquid Crystals (Gordon and Breach, Philadelphia, 1991).
2. R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, J. Phys. (Paris) Lett. 36, L69 (1975).
3. R. H. Tredgold, J. Phys. D 23, 119 (1990).
4. P. Palffy-Muhoray, M. A. Lee, and R. G. Petschek, Phys. Rev. Lett. 60, 2303 (1988).
5. F. Biscarini, C. Zannoni, C. Chiccoli, and P. Pasini, Mol. Phys. 73, 439 (1991).
6. D. Wei and G. N. Patey, Phys. Rev. Lett. 68, 2043 (1992).
7. L. Onsager, Ann. Acad. Sci. (N. Y.) 51, 627 (1949).
8. S.-D. Lee and R. B. Meyer, J. Chem. Phys. 84, 3443 (1986).
9. See G. R. Luckhurst, The Molecular Physics of Liquid Crystals Ed., G. R. Luckhurst and G. W. Gray (Academic Press, London, 1979), Chap. 4, and references therein.
10. J. L. Colot, X.-G. Wu, H. Xu, and M. Baus, Phys. Rev. A 38, 2022 (1988).
11. S.-D. Lee, J. Chem. Phys. 87, 4972 (1987).
12. J. J. Weis, D. Levesque, and G. J. Zarragoicoechea, Phys. Rev. Letts. 69, 913 (1992).
13. D. Levesque, J. J. Weis, and G. J. Zarragoicoechea, Phys. Rev. E 47, 496 (1993).