Ferroelectric liquid crystals (FLCs) have attracted great interest from both fundamental and practical viewpoints. The existence of FLCs has been predicted in tilted chiral smectic phases by symmetry arguments. There are, however, no physical reasons why phases with other symmetry cannot be ferroelectric. It has been suggested that the ferroelectricity could be appeared in the nematic phase. Recent computer simulations have shown that a system of rod-like molecules with strong dipolar interactions can exhibit a ferroelectric nematic phase. More recently, the existence of the polar or ferroelectric nematic ordering has been experimentally observed in several achiral polymer systems.

In this Letter, we report on a complete phase diagram for the ferroelectric nematic ordering of finite-length hard spherocylinders in terms of the dipolar strength and the packing fraction of the system which exhibits a conventional isotropic-nematic, a nematic-ferroelectric nematic, and a direct isotropic-ferroelectric nematic phase transitions. The criteria for the existence of the triple and tricritical points are obtained as a function of the dipolar strength and the packing fraction.

**Phase Diagram for Ferroelectric Nematic Ordering of Hard Spherocylinders with Longitudinal Dipoles**

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The ferroelectric nematic ordering of finite-length hard spherocylinders with longitudinal dipoles is demonstrated in an extended version of the Onsager formalism. The stability analysis as well as numerical simulations were performed to obtain a complete phase diagram for the ferroelectric nematic order in terms of the dipolar strength and the packing fraction of the system. The phase diagram exhibits a usual isotropic-nematic, a nematic-ferroelectric nematic, and a direct isotropic-ferroelectric nematic phase transitions. The criteria for the existence of the triple and tricritical points are obtained as a function of the dipolar strength and the packing fraction.

**KEYWORDS:** ferroelectric nematic, longitudinal dipoles, phase diagram, triple point, tricritical point

\[
F = F_0 + k_B T \int d(1)(\rho(1)\ln\rho(1) - 1)
\]

where the index \(i\) stands for \((r_i, \Omega_i)\) of the \(i\)-th spherocylinder. Here, \(c_2(i, j)\) is the two-body direct correlation function between the \(i\)-th and \(j\)-th spherocylinders, \(\rho(i)\) the local density, and \(F_0\) the reference free energy.

In a uniform I, N, or FN phase, the local density, \(\rho(r_i, \Omega_i) = \rho(r_i, \Omega_j)\), is independent of \(r_i\) but a function of the orientation variable \(\Omega_i\). In this case, \(\rho(i) = \rho_f(\Omega_i)\) with \(\rho\) the average density and \(f(\Omega_i)\) the normalized angular distribution function. A simple mean-field form of the dipole interactions is given by

\[
U_d = -N d \cdot E = -N \frac{\rho d^2}{3\epsilon_0} \langle \cos \gamma(\Omega_1, \Omega_2) \rangle
\]

where \(\gamma(\Omega_1, \Omega_2)\) is the angle between two spherocylinders with orientations \(\Omega_1\) and \(\Omega_2\). Here, \(\epsilon_0\) and \(d\) denotes the dielectric constant in vacuum and the magnitude of the dipole moment, respectively. The electric field is given by \(E\) and \(\langle \rangle\) means the average over the angular distribution. The parameter \(P_1\) is the first-order Legendre polynomial which is directly related to the degree of the ferroelectric ordering.

We now derive the expression for the effective two-body direct correlation function \(c_2(\Omega_1, \Omega_2)\) of hard-core and dipolar interactions, \(U_d\), in terms of the packing fraction \(\eta = \rho v_0\) with the volume \(v_0\) of one spherocylinder. In a spherical approximation, the resultant form of \(c_2(\Omega_1, \Omega_2)\) is given by

\[
c_2(\Omega_1, \Omega_2) = 3\beta \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} |\sin \gamma(\Omega_1, \Omega_2)|
\]

\[
- \frac{2\eta^2}{3v_0\epsilon_0 k_BT} P_1(\Omega_1) P_1(\Omega_2),
\]

where \(\beta = (L/D)^2[\pi(1 + 3L/2D)]^{-1}\) and \(k_B\) is the Boltzmann constant.

Using the above form of the two-body direct correlation function and rewriting the free energy, we obtain

\[
F^* = \ln \eta - 1 + \int f(\Omega)|\sin \gamma(\Omega, \Omega')| f(\Omega) d\Omega + \frac{\eta(4 - 3\eta)}{(1 - \eta)^2}
\]

\[
\times \left[ 1 + \frac{3}{2} \beta \int \int |\sin \gamma(\Omega, \Omega')| f(\Omega) f(\Omega') d\Omega d\Omega' \right]
\]
\[- \eta \int d\Omega \int d^2 P_1(\Omega) P_1(\Omega') f(\Omega) f(\Omega') d\Omega d\Omega', \quad (4)\]

where \( F^* = F/Nk_B T - \mu_0/k_B T + \ln v_0 \) with the chemical potential \( \mu_0 \) and the reduced dipole moment \( d^* = \sqrt{d^2/3v_0 k_B T} \). 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 \( \langle P_2 \rangle \), with the help of the equilibrium angular distribution function \( f(\Omega) \). The solution of \( f(\Omega) \) to the Onsager-type integral equation can be found by an iterative method.\(^{13,15}\)

For isotropic liquids, both order parameters are zero and \( \langle P_2 \rangle \neq 0 \) and \( \langle P_1 \rangle = 0 \) for ordinary non-ferroelectric nematics. For ferroelectric nematics, both \( \langle P_1 \rangle \) and \( \langle P_2 \rangle \) must be nonzero. The critical packing fraction in the isotropic (\( \eta_i \)), nematic (\( \eta_n \)), and ferronematic (\( \eta_f \)) phases can be found by using the condition that two of the phases have equal pressures and chemical potentials at the relevant transitions when they are in stable equilibrium.\(^{13}\)

Together with the phase equilibrium conditions, we carried out the stability analysis for the FN state. The stability conditions can be derived on the basis of the concept that the minimum work, which is needed to bring any small part of the system from the equilibrium state to any neighboring one, should be positive. This means that the compressibility and the minimum work under the polar environment should be

\[
\left( \frac{\partial p}{\partial \eta} \right)_{\gamma, P} = 1 + 2\eta(4 - \eta) \left[ 1 + \frac{3}{2} \beta \psi \right] - 2\eta \psi > 0,
\]

where \( p \) is the dimensionless pressure scaled \( k_B T/v_0 \), \( \psi = (\sin \gamma(\Omega, \Omega')) \), and \( \phi = d^* P_1(\Omega) P_1(\Omega') \).

\[
- \left( \frac{\partial E}{\partial \eta} \right) \approx \left( \frac{\partial \langle P_1 \rangle}{\partial d^*} \right)_{P,T} > 0,
\]

where \( P \) denotes the polarization of the system.

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 packing fraction at which \( \langle P_1 \rangle \) becomes nonzero for fixed dipolar strength. The phase diagram for \( D/L = 0.01 \) and that for \( D/L = 0.1 \) in the \( (\eta, d^*) \) plane are shown in Figs. 1 and 2, respectively. The usual I-N transition and a direct I-FN transitions are the first-order while the N-FN transition is the first-order and the second-order depending on the dipolar strength \( d^* \). The critical dipolar strength \( d^*_c \) corresponds to the I-N-FN triple point. The tricritical point for the N-FN transition is at \( d^*_t \). The packing fraction \( \eta_i \) of the isotropic phase and \( \eta_n \) 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. The order of the N-FN transition was checked by evaluating \( \langle P_1 \rangle \) as well as performing the stability analysis in the \( (p, \eta) \) plane. It was found that the orientational order parameter \( \langle P_1 \rangle \) 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 and becomes saturated with further increasing the packing fraction \( \eta \).

Figure 3 shows the triple points for the I-N-FN transition and the tricritical points for the N-FN transition as a function of the packing fraction (or dipolar strength) for several \( D/L \) ratios. For sufficiently high \( d^* \), the I-FN transition may be preempted by the isotropic-smectic transition, which is indicated by the computer simulations.\(^{60}\) In Table I, the tricritical points \( (\eta_{tr}, d^*_t) \) and the critical points \( (\eta_i, d_i) \) for the case of \( D = 5 \) \( \text{Å} \) at \( T = 500 \) K are shown.

We developed a mean-field model for a system of finite-length hard spherocylinders with longitudinal dipoles in an extended version of the Onsager formalism. The model predicts the existence of the I-N, N-FN, and a direct I-FN transitions. A complete phase diagram was obtained in terms of the dipolar strength and the packing fraction of the system. A generalized version of our model developed here when a layer order included in addition to the nematic order is applicable for predicting the phase diagrams of various dipolar systems.

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Fig. 3. The triple and tricritical points in the ($D/L, d^*$) plane for a system of hard spherocylinders with longitudinal dipoles. The solid line (with open circles) and the dashed line (with open rectangles) represent the triple (I-N-FN) points and the tricritical (the first-order to the second-order N-FN) points, respectively.

Table I. The dipole moment, $d$, for ferroelectric nematic phase considering a model with $D = 5$ Å at $T = 500$ K for various values of $D/L$. ($\eta_3$, $d_3$) and ($\eta_t$, $d_t$) are denoted triple point and tricritical point, respectively.

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<th>$\eta_t$</th>
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