

Monte Carlo Simulations of Spontaneous Ferroelectric Order in Discotic Liquid Crystals

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The demonstration of a spontaneous macroscopic ferroelectric order in liquid phases in the absence of any long-range positional order is considered as an outstanding problem of great fundamental and technological interest. We report here off-lattice Monte Carlo simulations of a system of polar achiral disklike ellipsoids which spontaneously exhibit a novel ferroelectric nematic phase which is a liquid in three dimensions, considering attractive-repulsive pair interaction suitable for the anisotropic particles. At lower temperature, the ferroelectric nematic phase condenses to a ferroelectric hexagonal columnar fluid with an axial macroscopic polarization. A spontaneous ferroelectric order of dipolar origin is established here for the first time in columnar liquid crystals. Our study demonstrates that simple dipolar interactions are indeed sufficient to produce a class of novel ferroelectric fluids of essential interest. The present work reveals the structure-property relationship of achieving long searched ferroelectric liquid crystal phases and transitions between them, and we hope these findings will help in future development of technologically important fluid ferroelectric materials.

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Conventional ferroelectric materials are solid. The development of fluid phases with an overall polar order is a goal of great fundamental and technological importance [1,2]. The least ordered conceivable ferroelectric phase is the ferroelectric nematic liquid crystal (FNLC) phase which is characterized by a spontaneous macroscopic polarization, particle mobilities typical of liquids, and complete absence of any long-range positional order. However, a practical realization of such a phase is a long-standing problem [1,2]. The currently known ferroelectric fluids are the ferroelectric smectic phases observed in systems of chiral rodlike molecules [3] and in systems of polar bent core molecules [4]. These ferroelectric smectic phases have important applications in lightweight easy-processable electrical devices for fast switching displays, rewritable memories, and nonlinear optics [5]. However, these layered smectic phases exhibit fluidity in only two spatial dimensions and clearly lack high fluidity and self-healing characteristics of a nematic liquid crystal (NLC). Chiral disk-shaped molecules can also produce a ferroelectric columnar liquid crystal phase [6]. All these currently known ferroelectric liquid crystal phases are called improper in the sense that dipole-dipole interaction does not play the major role in generating the ferroelectric order. In contrast, the possibility of proper ferroelectricity of dipolar origin in NLCs has been a topic of much discussion as it attracts great interest from both fundamental and practical viewpoints [7–18]. The still unknown FNLC phase is expected to exhibit a much faster and easier response to an external field compared to the known ferroelectric liquid crystals and hence it could open new avenues in electro-optic display technology. Theoretical studies have shown that there is no fundamental reason to forbid a ferroelectric nematic order [7–13].

A ferroelectric response was recently observed in a bent core NLC under an external field, but a ferroelectric order in the absence of the field was not achieved [19]. From computer simulation studies, it has been found that model spherical particles with a strong central dipole moment exhibit a FNLC phase in conducting surroundings [8,9,20,21]. Ferroelectric order in these systems is developed solely due to the dipolar interactions and the lack of orientational bias of the spherical particles. On the contrary, an overall polar order is very rare in systems of anisotropic molecules which spontaneously form orientationally ordered liquid crystal phases. Computer simulation studies of hard anisotropic ellipsoids, spherocylinders, and cut spheres with a permanent dipole moment have not shown a FNLC phase [9,22–24]. Similar attempts considering ellipsoidal particles interacting via attractive-repulsive Gay-Berne (GB) potential with point dipole moments have also failed to yield a ferroelectric liquid crystal [25–29]. Ayton, Wei, and Patey showed that as the length to breadth ratio decreases from unity, the tendency to form a ferroelectric nematic phase gradually decreases for hard discotic ellipsoidal particles with strong central dipoles [30]. Ayton and Patey also found that the FNLC phase can be obtained with a system of discotic hard cut spheres with a uniform distribution of axial dipoles in the central circular patch, but the assumption of uniform dipolar distribution and that of complete orientational order of disks make the system a rather idealized one [31]. A complex combination of noncentrosymmetric shape and attractive interactions was indicated as the requirement to form a polar order in tapered rodlike molecules in the absence of dipolar interactions [32]. However, the improper ferroelectric order was destroyed as the strength of an added dipole was increased [33]. Currently, the idea

from both theoretical and practical points of view is that a liquid ferroelectric order cannot be discovered easily. It is essential to find appropriate microscopic interactions to design a FNLC phase. In this Letter, we report a system of attractive-repulsive achiral polar disk-shaped molecules which spontaneously produces a FNLC phase. At lower temperature, the FNLC phase condenses to a ferroelectric hexagonal columnar fluid with an axial macroscopic polarization. A spontaneous ferroelectric order of dipolar origin is established here for the first time in columnar liquid crystals. The realization of a ferroelectric columnar phase with an axial macroscopic polarization is also a long-standing puzzle in soft matter physics and chemistry. Several attempts to develop a ferroelectric columnar phase in achiral bowl-shaped and pyrimidic molecules as well as vanadyl complexes have been reported in the past 40 years [34]. However, the goal of achieving columnar liquid crystals with an axial macroscopic polarization at zero electric field and its electrical invertibility remains unsolved [35]. Such materials are considered potential candidates for ultrahigh-density memory devices, and the absence of a rational design strategy has made progress extremely difficult [36]. Computer simulation studies of dipolar spheres and disk-shaped particles have only yielded antiferroelectric columnar phases with partial or fully polarized individual columns. We report here a rare demonstration of the proper ferroelectric hexagonal columnar phase with a macroscopic polarization along the columnar axis, which might be an important step towards future development of novel ferroelectric columnar liquid crystals.

We have investigated a system of uniaxial oblate ellipsoids of revolution where each ellipsoid is embedded with two axial off-center point dipole moments. The dipoles are symmetrically placed on the equatorial plane of the ellipsoid, at equal distances from the center of the ellipsoid. The ellipsoids are interacting via a pair potential which is a sum of a modified form of the GB potential [37] and the electrostatic dipolar interactions. In the modified form for discotic liquid crystal [38], the pair potential between two oblate ellipsoids i and j is given by

$$U_{ij}^{\text{GB}}(\mathbf{r}_{ij}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) = 4\epsilon(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j)(\rho_{ij}^{-12} - \rho_{ij}^{-6}),$$

where $\rho_{ij} = [r_{ij} - \sigma(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) + \sigma_e]/\sigma_e$. Here unit vectors $\hat{\mathbf{u}}_i$ and $\hat{\mathbf{u}}_j$ represent the orientations of the symmetry axes of the molecules, $\mathbf{r}_{ij} = r_{ij}\hat{\mathbf{r}}_{ij}$ is the separation vector of length r_{ij} between the centers of mass of the ellipsoids, and σ_e is the minimum separation between two ellipsoids in a face-to-face configuration determining the thickness of the ellipsoids. The anisotropic contact distance σ and the depth of pair interaction well ϵ are dependent on four important parameters, κ , κ' , μ , ν , as defined in [38]. Here $\kappa = \sigma_e/\sigma_0$ is the aspect ratio of the ellipsoids where σ_0 is the minimum separation between two ellipsoids in a side-by-side configuration, and $\kappa' = \epsilon_0/\epsilon_e$ is the ratio of

interaction well depths in side-by-side and face-to-face configuration of the disk-shaped ellipsoids. The other two parameters, μ and ν , control the well depth of the potential. σ_0 and ϵ_0 define the length and energy scales, respectively, where ϵ_0 is the well depth in the cross configuration. The values used here to study the bulk phase behavior are $\kappa = 0.345$, $\kappa' = 0.2$, $\mu = 1$, $\nu = 3$. The value of κ is obtained from the parametrization of the GB potential that mimics the interaction between two molecules of triphenylene [39], which is known to form the core of many discotic mesogens [40]. The other parameters were chosen from previous works on discotic liquid crystals which exhibited discotic nematic and hexagonal columnar phases [29]. In the present work, two parallel dipoles are symmetrically placed on the molecular x axis (perpendicular to the symmetry axis) of each GB molecule, separated by a distance $d^* \equiv d/\sigma_0 = 0.5$ along the axis. The electrostatic interaction energy between two such dipolar ellipsoids is given by

$$U_{ij}^{\text{dd}} = \sum_{\alpha, \beta=1}^2 \frac{\mu^2}{r_{\alpha\beta}^3} [(\hat{\boldsymbol{\mu}}_{i\alpha} \cdot \hat{\boldsymbol{\mu}}_{j\beta}) - 3(\hat{\boldsymbol{\mu}}_{i\alpha} \cdot \hat{\mathbf{r}}_{\alpha\beta})(\hat{\boldsymbol{\mu}}_{j\beta} \cdot \hat{\mathbf{r}}_{\alpha\beta})],$$

where $\mathbf{r}_{\alpha\beta} (= \mathbf{r}_{j\beta} - \mathbf{r}_{i\alpha})$ is the vector joining the two point dipoles $\boldsymbol{\mu}_{i\alpha}$ and $\boldsymbol{\mu}_{j\beta}$ on the molecules i and j at the positions $\mathbf{r}_{i\alpha} = \mathbf{r}_i \pm (d/2)\hat{\mathbf{x}}_i$ and $\mathbf{r}_{j\beta} = \mathbf{r}_j \pm (d/2)\hat{\mathbf{x}}_j$. Then the total interaction energy between two dipolar molecule is given by $U_{ij}^{\text{total}} = U_{ij}^{\text{GB}} + U_{ij}^{\text{dd}}$. Here we have used the reduced dipole moment $\mu^* \equiv \sqrt{\mu^2/\epsilon_0\sigma_0^3} = 0.6$, which for a molecular diameter of $\sigma_0 \approx 10 \text{ \AA}$ and an energy term $\epsilon_0 = 5 \times 10^{-15} \text{ erg}$ corresponds to 1.2 D. The long-range dipole-dipole interaction energy has been evaluated using the reaction field [41] method with dipolar cutoff radius $r_{\text{RF}}^* \equiv r_{\text{RF}}/\sigma_0 = 3.2$ and conducting boundary conditions with dielectric constant $\epsilon_{\text{RF}} = \infty$ for the system of $N = 1500$ dipolar molecules. Stability of the results against system size effect has been verified by reproduction of the ferroelectric structures at different temperatures for a quite large system of $N = 4000$ molecules with $r_{\text{RF}}^* = 5$. The robustness of the results of the reaction field method was also confirmed by simulating a system of 500 dipolar molecules with the conventional and computationally expensive Ewald sum method [41,42].

We have performed Monte Carlo (MC) simulations in the isothermal-isobaric (constant NPT) ensemble with periodic boundary conditions imposed on the systems of dipolar molecules. We have performed a cooling sequence of simulation runs along an isobar at fixed pressure $P^* \equiv P\sigma_0^3/\epsilon_0 = 100$. MC simulations of the GB ellipsoids without dipoles yielded discotic nematic and hexagonal columnar phases at the same pressure without any ferroelectric order [26]. We started the simulations from a well equilibrated isotropic liquid phase in a cubic box at $T^* \equiv K_B T/\epsilon_0 = 10.0$. We then reduced the temperature of the system sequentially to explore the phase behavior. At a

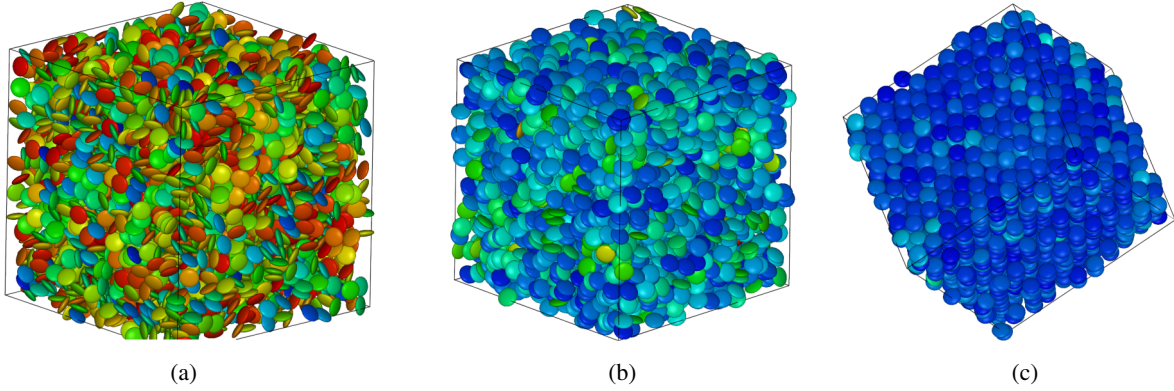


FIG. 1 (color online). Snapshots of the interesting configurations generated by MC simulations of a system of 4000 dipolar oblate GB molecules over the explored isobar at $P^* = 100$. (a) Isotropic phase at $T^* = 10.0$ with no ferroelectric order, (b) ferroelectric nematic phase with an overall macroscopic polarization at $T^* = 7.5$, (c) ferroelectric hexagonal columnar phase with an axial overall polarization at $T^* = 6.0$. The particles are color coded according to their orientation with respect to the phase director. The snapshots were generated using the graphics software QMGA [44].

given temperature, the final equilibrated configuration obtained from the previous higher temperature was used as the starting configuration. The system was equilibrated for 5×10^5 MC cycles at each state point (p^* , T^*) and 3×10^6 MC cycles were used near a transition for $N = 1500$. We have used an orthogonal simulation box where the box dimensions were varied independently during simulation of a columnar structure to fit the appropriate number of columns in the box and to reduce the possibility of cavity formation. During a MC cycle, each particle was randomly displaced and reoriented following Metropolis criteria, where the reorientation moves were performed using the Barker-Watts technique [41]. One of the three box sides was also attempted to be changed during a MC cycle. The acceptance ratios of the rototranslational moves and volume moves were adjusted to 40%. To overcome any possibility of locking in a metastable state, the particles were also allowed to attempt up-down flip moves exchanging particle tip with bottom with a 20% frequency with respect to the rototranslational MC moves. In order to fully characterize different phases of the system, various order parameters were computed. The average orientational order of the particles was monitored by the second-rank orientational order parameter P_2 defined by the largest eigenvalue of the order tensor $S_{\alpha\beta} = (1/N) \sum_{i=1}^N (1/2)(3u_{i\alpha}u_{i\beta} - \delta_{\alpha\beta})$, where $\alpha, \beta = x, y, z$ are the indices referring to three components of the unit vector $\hat{\mathbf{u}}$ along the orientation of the particles and $\delta_{\alpha\beta}$ is the Kronecker delta symbol. The value of P_2 is close to zero in the isotropic phase and tends to 1 in the highly ordered phases. The global ferroelectric order was measured by calculating the average polarization per particle P_1 defined by $P_1 = (1/N) \sum_{i=1}^N \hat{\boldsymbol{\mu}}_i \cdot \hat{\mathbf{d}}$, where $\hat{\mathbf{d}}$ is the unit vector along the direction of total macroscopic moment $\mathbf{M} = \sum_{i=1}^N \boldsymbol{\mu}_i$ and N is the number of molecules in the system. P_1 is unity in a perfectly ferroelectric phase and zero in an antiferroelectric phase and in the isotropic

phase. P_2 is therefore the indicator of global orientational order and P_1 distinguishes between ferroelectric and antiferroelectric phases. In a ferroelectric phase $P_1 \approx \sqrt{(2P_2 + 1)/3} \geq P_2$, while in an antiferroelectric phase $P_1 < P_2$. Using these criteria a ferroelectric phase can be distinguished from an antiferroelectric phase. Figure 2 shows the variation of the average order parameters $\langle P_1 \rangle$, $\langle P_2 \rangle$ as functions of temperature along the isobar for $N = 1500$ and 4000 particle systems. The phase behavior remains similar for different system size as shown in Fig. 2. Both the parameters were close to zero at high temperatures, identifying the isotropic phase. Upon cooling both of them jumped to intermediate values indicating a transition from isotropic to ferroelectric discotic nematic phase. Further cooling resulted in a gradual increase of $\langle P_1 \rangle$, $\langle P_2 \rangle$ towards unity followed by a transition to ferroelectric hexagonal columnar phase. Snapshots of the resultant configurations are shown in Fig. 1. In order to verify

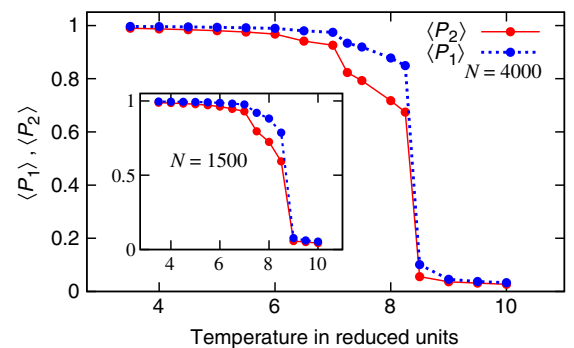


FIG. 2 (color online). Evolution of the average order parameters against reduced temperature T^* at constant pressure $P^* = 100.0$ for $N = 1500$ (inset) and $N = 4000$: polarization $\langle P_1 \rangle$ (blue dotted line); second-rank order parameter $\langle P_2 \rangle$ (red solid line). The systems develop a macroscopic ferroelectric order for $T^* \leq 8.5$ ($N = 1500$) and $T^* \leq 8.25$ ($N = 4000$).

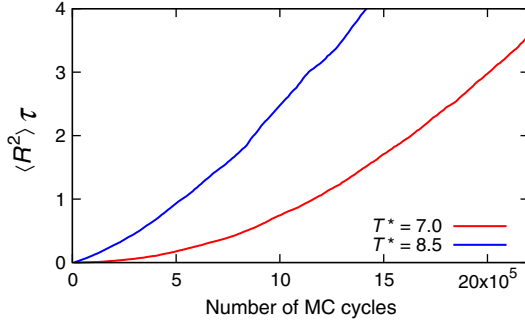


FIG. 3 (color online). Mean-squared displacement $\langle R^2 \rangle_\tau$ against MC cycles for the FNLC phase at $T^* = 8.5$ and for the ferroelectric hexagonal columnar phase at $T^* = 7.0$ for the system of $N = 1500$ dipolar particles.

the fluidity of the ferroelectric phases, we calculated the mean square displacement as follows: $\langle R^2 \rangle_\tau = (1/N) \times \sum_{i=1}^N [\mathbf{r}_i(\tau) - \mathbf{r}_i(0)]^2$, where $\mathbf{r}_i(\tau)$ is the position vector of the i th particle after completion of τ MC cycles. In the ferroelectric nematic and hexagonal columnar phases, the mean square displacement steadily increased with increasing τ indicating fluid behavior. The corresponding plots of $\langle R^2 \rangle_\tau$ are shown in Fig. 3.

For a proper structural analysis of the resultant ferroelectric phases, we calculated important distribution functions as required. Figure 4(a) shows the radial distribution function $g(r^*)$ for various temperatures for the system of 4000 molecules. The flatness in $g(r^*)$ at $T^* = 10$ reflects the structurelessness of the isotropic liquid even at short range. At $T^* = 8.25$, it shows the absence of any long-range positional order in the FNLC phase. Considerable structure in $g(r^*)$ at $T^* = 6$ indicates the formation of a more ordered columnar phase. The columnar distribution function $g_c(r_{\parallel}^*)$, which is a measure of positional order within a single column, is shown in Fig. 4(b). The periodic nature of $g_c(r_{\parallel}^*)$ confirms the periodic stacking of molecules in the columnar phases. At $T^* = 6$, $g_c(r_{\parallel}^*)$ decays algebraically; the peak values are found to decrease as

$r_{\parallel}^{*- \eta}$, with $\eta = 0.6$ giving the best fit, indicating a quasi-long-range columnar order. As the temperature is lowered, $g_c(r_{\parallel}^*)$ exhibits long-range periodic structure. The small peaks for r^* , $r_{\parallel}^* < 0.5$ in $g_c(r_{\parallel}^*)$ and in $g(r^*)$ describe the finite probability of short-range face-to-face ordering in the FNLC phase. Figure 4(c) shows the perpendicular distribution function $g(r_{\perp}^*)$, which is a measure of translational order in the plane orthogonal to the orientation of the disk-shaped molecules. $g(r_{\perp}^*)$ at $T^* = 8.25$ remains essentially flat for the FNLC phase. At $T^* = 6$ and 7, three peaks for $r_{\perp}^* < 2$ with ratio close to $1:\sqrt{3}:2$ indicates hexagonal columnar packing. For temperatures below $T^* = 5.5$, we observed a transformed $g(r_{\perp}^*)$. The peak around $r_{\perp}^* = 1$ splits into two, which is a signature for quasihexagonal order [43]. The overall structure of $g(r_{\perp}^*)$ is quite similar to the crystalline orthorhombic phase reported in [43]. We conclude that, at low temperatures, there is a transition from a ferroelectric columnar hexagonal phase to a ferroelectric orthorhombic crystal phase.

We have also verified the occurrence of these ferroelectric phases for small changes in shape anisotropy. For $\kappa = 0.45$ and $\kappa = 0.30$, the system shows all the ferroelectric phases as described above for $\kappa = 0.345$. However, at $\kappa = 0.25$ we observe a direct isotropic to ferroelectric columnar transition. The occurrence of the ferroelectric fluid phases is also verified for small changes in dipolar separation. For $d^* = 0.4$ the system reproduces both the ferroelectric fluids described above for $d^* = 0.5$ and for $d^* = 0.8$ there is greater probability of sticking of the ellipsoids as the terminal dipoles can reach very near to each other.

In summary, the present study demonstrates that a simple pair interaction between polar disk-shaped molecules is sufficient to produce a ferroelectric nematic liquid and a fluid ferroelectric hexagonal columnar phase, even in the absence of any noncentrosymmetric geometry or chirality of the constituent molecules. In this work, we have attempted to identify the molecular origin of two

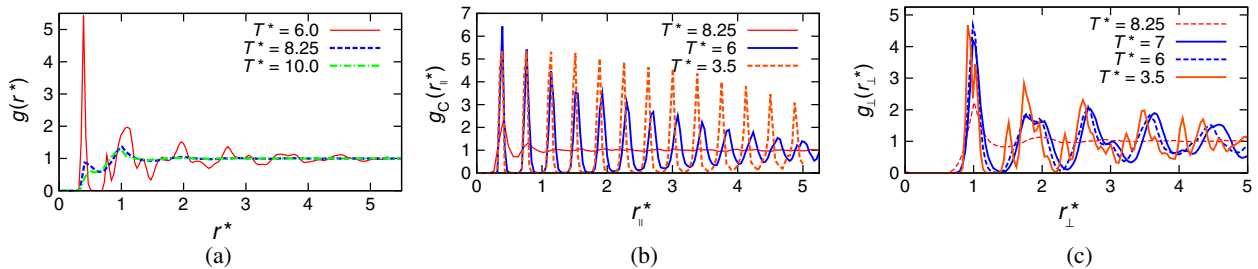


FIG. 4 (color online). (a) Radial distribution function $g(r^*)$ at three different temperatures: $T^* = 10.0$ (I) (green dot-dashed line), $T^* = 8.25$ (FNLC) (blue dashed line), $T^* = 6.0$ (FCol_h) (red solid line). (b) Columnar distribution function $g_c(r_{\parallel}^*)$ at three different temperatures: $T^* = 8.25$ (FNLC) (red solid line), $T^* = 6.0$ (FCol_h) (blue solid line), $T^* = 3.5$ (FCr) (red dashed line). (c) Perpendicular distribution function $g_{\perp}(r_{\perp}^*)$ at four different temperatures: $T^* = 8.25$ (FNLC) (red dashed line), $T^* = 7.0$ (FCol_h) (blue solid line), $T^* = 6.0$ (FCol_h) (blue dashed line), $T^* = 3.5$ (FCr) (red solid line). The symbols I stands for isotropic, FNLC stands for ferroelectric nematic liquid crystal phase, FCol_h stands for ferroelectric columnar hexagonal phase, and FCr stands for ferroelectric orthorhombic crystal phase.

interesting long sought after phases to gain insight into the future development of novel ferroelectric fluid materials.

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