Orientational Order in Simple Dipolar Liquids: Computer Simulation of a Ferroelectric Nematic Phase

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Molecular-dynamics simulations are used to show that strongly interacting dipolar spheres can form a ferroelectric nematic phase. This is the first demonstration that dipolar forces alone can create an orientationally ordered liquid state. It is also the first time that the existence of a ferroelectric nematic phase has been established for a model fluid.

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In this Letter we describe molecular-dynamics (MD) simulations of strongly interacting dipolar spheres. It is shown that this simple model can form an orientationally ordered nematic phase and that, furthermore, this phase is ferroelectric. Although the possibility was first suggested by Born [1] many years ago, to our knowledge this is the first demonstration that dipolar forces alone can create an orientationally ordered fluid. To date the only ferroelectric liquid crystals which have been observed are chiral smectic-*C* phases [2]. However, there appears to be no fundamental reason why phases of other symmetry cannot be ferroelectric [3–5] and the possible existence of ferroelectric nematics has been suggested in the recent literature [4–6]. The present simulations establish for the first time the existence of a ferroelectric nematic state as a true *liquid* crystal phase for a completely Hamiltonian model.

We consider a dipolar soft-sphere model defined by the pair potential

$$u(12)=u_{SS}(r)+u_{DD}(12)\,, \tag{1a}$$

where

$$u_{SS}(r)=4\epsilon(\sigma/r)^{12} \tag{1b}$$

is the soft-sphere potential and

$$u_{DD}(12)=-3(\boldsymbol{\mu}_1\cdot\mathbf{r})(\boldsymbol{\mu}_2\cdot\mathbf{r})/r^5+\boldsymbol{\mu}_1\cdot\boldsymbol{\mu}_2/r^3 \tag{1c}$$

is the dipole-dipole interaction. Here ϵ and σ are parameters characterizing the soft-sphere potential, $\boldsymbol{\mu}_i$ is the dipole moment of particle i, $\mathbf{r}=\mathbf{r}_2-\mathbf{r}_1$, and r is the magnitude of $\mathbf{r}$. It is convenient to characterize dipolar soft-sphere fluids by specifying the reduced density $\rho^*=\rho\sigma^3$, the reduced temperature $T^*=kT/\epsilon$, and the reduced dipole moment $\mu^*=(\mu^2/\epsilon\sigma^3)^{1/2}$, where $\rho=N/V$, N is the number of particles, V is the volume, T is the absolute temperature, and k is the Boltzmann constant. Extensive MD studies of dipolar soft-sphere fluids have been carried out by Kusalik [7]. However, Kusalik did not look for an orientationally ordered phase and the dipole moments and state parameters he considered lie well within the isotropic region.

Our MD calculations were performed at constant temperature essentially as described by Kusalik [7], and indeed we verified our program by reproducing some of his results. The orientational coordinates of the particles were expressed in terms of quaternion parameters and the equations of motion were integrated using a fourth-order Gear algorithm. Following Kusalik, the reduced time step $\Delta t^*=\Delta t/(m\sigma^2/\epsilon)^{1/2}=0.0025$ (m is the mass of a particle) was employed in all calculations.

The possible existence of a nematic and/or ferroelectric nematic phase was monitored by calculating the usual equilibrium first- and second-rank orientational order parameters, $\langle P_1\rangle$ and $\langle P_2\rangle$, respectively. For ordinary nonferroelectric nematics $\langle P_2\rangle\neq 0$, $\langle P_1\rangle=0$. For ferroelectric nematics both $\langle P_2\rangle$ and $\langle P_1\rangle$ must be nonzero. As in previous simulations seeking isotropic-nematic transitions [8], the instantaneous second-rank order parameter P_2 was taken to be the largest eigenvalue of the ordering matrix $\mathbf{Q}$ with elements given by

$$Q_{\alpha\beta}=\frac{1}{N}\sum_{i=1}^{N}\frac{1}{2}(3\mu_\alpha^i\mu_\beta^i-\delta_{\alpha\beta})\,, \tag{2}$$

where μ_α^i is the α component of the unit vector $\hat{\boldsymbol{\mu}}_i$. The corresponding eigenvector is the instantaneous director $\hat{\mathbf{d}}$ and the instantaneous first-rank order parameter P_1 is defined by [6]

$$P_1=\frac{1}{N}\left|\sum_{i=1}^{N}\hat{\boldsymbol{\mu}}_i\cdot\hat{\mathbf{d}}\right|. \tag{3}$$

The equilibrium order parameters are the ensemble averages of P_1 and P_2.

For the axially symmetric dipolar particles we consider, the angle-dependent pair distribution function $g(12)$ can be expanded in the form

$$g(12)=\sum_{mnl}g^{mnl}(r)\Phi^{mnl}(12)\,, \tag{4}$$

where the $\Phi^{mnl}(12)$ are rotational invariants defined as in earlier work [9]. The projection $g^{000}(r)$ is the usual radial distribution function. It is also easy to show that in the nematic phase projections of the form $g^{mm0}(r)$ must obey the asymptotic relationship

$$g^{mm0}(r)\sim(2m+1)\langle P_m\rangle^2,\quad r\rightarrow\infty\,, \tag{5}$$

where $\langle P_m \rangle$ is the mth-rank order parameter. In the present simulations we have calculated $g^{110}(r)$ and $g^{220}(r)$ providing an alternative route to the order parameters and additional evidence for the formation of a ferroelectric nematic phase.

In order to clearly distinguish fluid and solid phases, we have calculated the mean square displacement $\langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle$, where $\mathbf{r}_i(t)$ is the position of molecule i at time t. For fluids this quantity will continually increase with time varying linearly at long times according to the Einstein relationship [8]

$$2tD = \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle / 3 , \qquad (6)$$

where D is the diffusion coefficient. For solids the mean square displacement becomes constant rather than continually increasing with time.

Simulations were performed for a range of densities with $T^* = 1.35$ and $\mu^* = 3$ [10]. Periodic boundary conditions (PBC) as given by de Leeuw, Perram, and Smith [11] were applied and the dipole-dipole interactions were calculated using the Ewald summation method [12]. For all results presented here, the reaction field dielectric constant ϵ' occurring in the PBC potential [11] was taken to be infinity consistent with usual Ewald-Kornfeld boundary conditions. We would expect this choice of ϵ' to be appropriate here since the dielectric constants of the dense isotropic liquids are large and increase rapidly as the transition is approached. We have also carried out calculations with $\epsilon' = 225$ which is the approximate value of the dielectric constant estimated from our simulations at $\rho^* = 0.6$. The results obtained were qualitatively similar to those found with $\epsilon' = \infty$. In most simulations 256 particles were used but calculations with 864 particles were carried out at two densities and no significant system size dependence was found [13]. The simulations were begun with the particles randomly oriented on a face-centered-cubic lattice. Typically, the system was equilibrated for 40000 time steps and averages were then accumulated over at least another 100000 time steps. Different starting configurations (e.g., all dipoles ordered in the same direction) were also tried and all liquid-state results were found to be completely independent of the initial conditions.

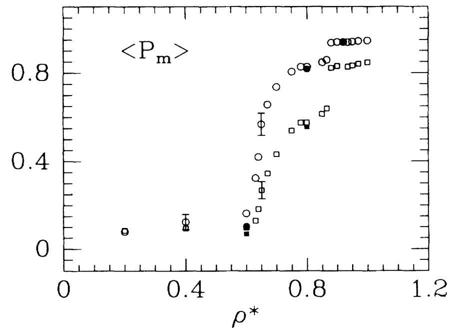

FIG. 1. The orientational order parameters as a function of density. The open circles and open squares are $\langle P_1 \rangle$ and $\langle P_2 \rangle$ obtained with 256 particles. The solid circles and solid squares are $\langle P_1 \rangle$ and $\langle P_2 \rangle$ obtained with 864 particles. The error bars represent one estimated standard deviation and are about the size of the symbols in the ordered phases.

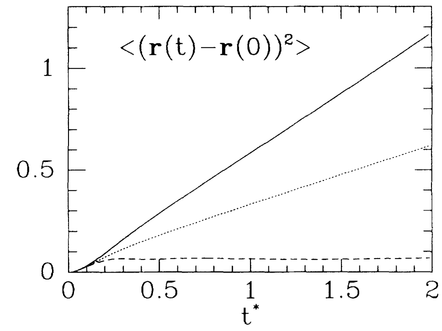

FIG. 2. The mean square displacement as a function of the reduced time t^*. The solid, dotted, and dashed curves are for $\rho^* = 0.6$, 0.8, and 0.9. The estimated errors are less than 1% for $t^* < 1$ and less than 5% for $t^* > 1$.

The order parameters as functions of density are shown in Fig. 1. It can be seen that both $\langle P_1 \rangle$ and $\langle P_2 \rangle$ increase sharply at two densities, $\rho^* \approx 0.65$ and $\rho^* \approx 0.87$, strongly indicating that two phase transitions occur [14]. The mean square displacements for $\rho^* = 0.6$, 0.8, and 0.9 are plotted in Fig. 2 and it is apparent that the system is fluid for $\rho^* = 0.6$ and 0.8 and solid for $\rho^* = 0.9$. Thus the first jump at $\rho^* \approx 0.65$ we associate with an isotropic to ferroelectric fluid transition and the second at $\rho^* \approx 0.87$ with a ferroelectric fluid to ferroelectric solid transition. The properties of the solid phase will be discussed when a fuller description of this work is published.

In order to investigate the nature of the ferroelectric fluid, we have calculated the longitudinal and transverse pair correlation functions, $g_{\parallel}(r_{\parallel})$ and $g_{\perp}(r_{\perp})$, respectively. These functions measure positional correlations in directions parallel and perpendicular to the director and are very sensitive to any spatial structure [15,16]. The results obtained gave no indication of any long-range spa-

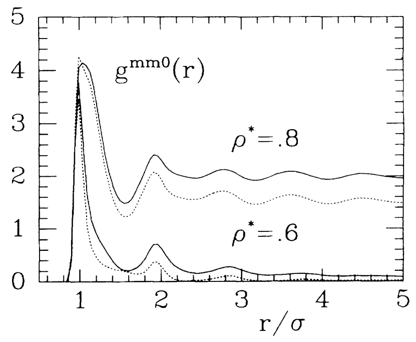

FIG. 3. The projections $g^{110}(r)$ (solid curves) and $g^{220}(r)$ (dotted curves) in isotropic and nematic phases. These results were obtained with 864 particles.

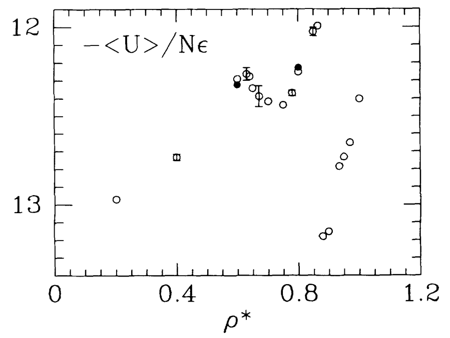

FIG. 4. The negative of the reduced potential energy as a function of density. The open and solid circles are 256 and 864 particle results, respectively. The error bars represent one estimated standard deviation and are smaller than the circles for the solid region.

tial structure and clearly showed that the orientationally ordered fluid is a ferroelectric nematic and has no columnar or smectic order.

The radial distribution function $g^{000}(r)$ also has only short-range structure in the orientationally ordered phase and resembles results for simple isotropic liquids. The projections $g^{110}(r)$ and $g^{220}(r)$ are shown in Fig. 3. We see that in the isotropic phase these functions decay becoming very small at large separations. In the ferroelectric nematic phase they become constant at large r and we have verified that the order parameters estimated from Eq. (5) are within 2% of those obtained directly.

In addition to these structural properties, we have calculated the average pressure and potential energy. The pressure was everywhere positive but within numerical accuracy it was difficult to clearly distinguish isotropic and nematic branches of the isotherm. The transition was more evident in the density dependence of the potential energy and the reduced quantity $-\langle U\rangle/N\epsilon$ is plotted in Fig. 4. The curve is clearly not monotonic and the energy decreases and then increases again as we pass through the isotropic-nematic and nematic-solid transition regions.

In summary, our simulations have shown that at least for some boundary conditions simple dipolar spheres can form a ferroelectric nematic phase. The fact that this can be accomplished with dipolar forces alone is perhaps mainly of theoretical interest since in real liquid crystals other anisotropic interactions must often dominate the dipolar contribution. However, the fact that a ferroelectric nematic phase exists in model systems strongly supports recent suggestions [4–6] that it may be possible to construct ferroelectric nematic liquid crystals.

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[1] M. Born, Sitz. Phys. Math. **25**, 614 (1916); Ann. Phys. **55**, 221 (1918). Also see G. R. Luckhurst, in *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic, London, 1979), Chap. 4.

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

[5] P. Palffy-Muhoray, M. A. Lee, and R. G. Petshek, Phys. Rev. Lett. **60**, 2303 (1988).

[6] F. Biscarini, C. Zannoni, C. Chiccoli, and P. Pasini, Mol. Phys. **73**, 439 (1991).

[7] P. G. Kusalik, J. Chem. Phys. **93**, 3520 (1990).

[8] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1989), and references therein.

[9] P. H. Fries and G. N. Patey, J. Chem. Phys. **82**, 429 (1985). The rotational invariants used here are defined by Eqs. (5) and (36) of this paper.

[10] If the particle "diameter" $\sigma=3.0$ Å and $T=298$ K, the reduced value $\mu^*=3$ corresponds to a molecular dipole moment of about 2.7 D.

[11] S. W. de Leeuw, J. W. Perram, and E. R. Smith, Annu. Rev. Phys. Chem. **37**, 245 (1986); Proc. R. Soc. London A **373**, 27 (1980); **388**, 177 (1983).

[12] In most calculations the Ewald sum parameters (as defined in [7]) employed were $R_c=0.5L$, $n_{\max}^2=54$, and $\alpha=6.4$. Tests with other parameter sets given in Table IV of [7] produced essentially identical results.

[13] For fluids with long-range forces, one must be cautious in assuming that results obtained with periodic boundary conditions would also apply to an infinite nonperiodic system. The fact that the results do not depend significantly upon sample size provides some evidence that the physical behavior of the fluid is not strongly influenced by the periodicity assumption.

[14] For a finite number of particles the order parameters are not expected to be exactly zero in the isotropic phase [R. Eppenga and D. Frenkel, Mol. Phys. **52**, 1303 (1984)]. The curves shown in Fig. 1 closely resemble those obtained in simulations of isotropic-nematic transitions for more usual models [16].

[15] A. Stroobants, H. N. W. Lekkerkerker, and D. Frenkel, Phys. Rev. A **36**, 2929 (1987).

[16] E. de Miguel, L. F. Rull, M. K. Chalam, and K. E. Gubbins, Mol. Phys. **74**, 405 (1991).