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Field-induced phase transitions of simple dipolar fluids

Dongqing Wei
Centre de Recherche en Calcul Appliqué, 5160 boulevard Décarie, Bureau 400, Montréal, Québec, Canada H3X 2H9

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Molecular-dynamics simulation was used to study dipolar soft sphere fluids under a uniform external electrical field. The relevance to the structure of electrorheological fluids is discussed. It is found that a columnar phase can be induced with a small applied electric field and such a field does not alter the freezing density significantly.

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There is great interest in the structure and dynamics of electrorheological (ER) fluids [1] and ferrofluids [2]. The ER fluid consists of a suspension of colloidal particles (1–100 μm) in a solvent with low dielectric constant. Upon applying an electric field, chainlike and columnar structures are formed parallel to the field, consequently the rheological and mechanical properties change dramatically. If the electrical field exceeds a critical value the ER fluid turns into a solid whose yield stress increases as the field is further strengthened.

Recently, we have found by molecular-dynamics (MD) simulation and density-functional theory that strongly interacting dipolar soft spheres undergo spontaneous polarization to form orientationally ordered phases [3], for example, ferroelectric nematic, solid and columnar (at low temperature) phases. We address two fundamental problems: (1) dipolar forces alone can create an orientationally ordered liquid state; (2) the existence of a ferroelectric nematic and columnar phase is established, which has significant impact on our understanding of a ferroelectric liquid crystals. On the other hand, the relevance to ER fluids is obvious. The main driving force for solidification and formation of chainlike structures in the ER fluids is believed to be the dipolar interaction between the colloidal particles [1,4–6]. It is, therefore, interesting to see how sensitive the structure and dynamics of strongly interacting dipolar spheres are to the applied electric field. Valuable insight can be gained about the structure and dynamics of the ER fluids by MD simulation.

The pair potential in our model can be expressed as

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

where

$$u_{\rm SS}(r_{12}) = 4\epsilon_{\rm SS}(\sigma/r_{12})^{12} \tag{2}$$

is the soft sphere potential, and

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

is the dipole-dipole interaction. The parameters $\epsilon_{\rm SS}$ and σ characterize the soft sphere potential, $\boldsymbol{\mu}_i$ is the dipole moment of particle i, and $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ with r_{12} being the magnitude of $\mathbf{r}_{12}$. Our model can be conveniently characterized by specifying the reduced density $\rho^* = \rho\sigma^3$, the reduced temperature $T^* = kT/\epsilon_{\rm SS}$, and the reduced dipole moment $\mu^* = (\mu^2/\epsilon_{\rm SS}\sigma^3)^{1/2}$. The dipole moment is chosen to be the same as in previous studies [3], i.e., $\mu^* = 3$. All simulations are conducted at temperature $T^* = 1.35$ and under a uniform electric field. At this temperature, no stable columnar phase has been found with zero applied field [3].

The long-range dipole-dipole interactions are treated by the Ewald-sum method [7,8]. The convergence parameters in the Ewald sum are the same as previously used in [3]. The MD calculations were performed at constant temperature employing the Gaussian isokinetic equations of motion [9] as described by Kusalik [8]. The orientational coordinates of the particles were expressed in terms of the quaternion parameters and the equations of motion were integrated using a fourth-order Gear algorithm. The reduced time step $\Delta t^* = \Delta t/\sqrt{m\sigma^2/\varepsilon_{\rm SS}} = 0.0025$ (m is the mass of a particle) was employed in all calculations.

Simulations were performed with 256 particles using the usual Ewald-Kornfeld boundary conditions [10]. Runs were begun with randomly oriented particles on a face centered cubic lattice and were typically equilibrated for about 50 000 time steps. Averages were accumulated over 500 000 time steps. The standard deviations were estimated by dividing the final 50 000 time steps into ten equal blocks and assuming for statistical purposes that the block averages constitute independent measurements of the physical properties of interest.

The orientational order is described by a director $\mathbf{d}(t)$

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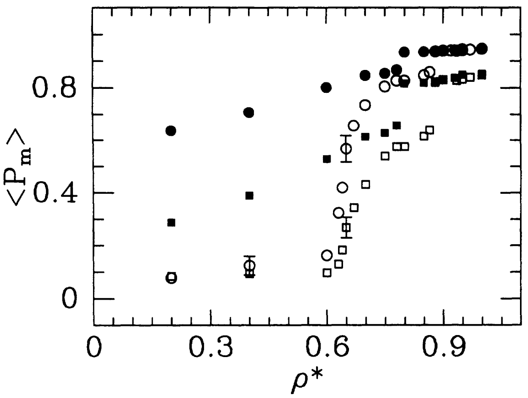

FIG. 1. The orientational order parameters as a function of the density. The open and solid symbols are for $E = 0.0$ and $E = 0.2$, respectively. The circles and squares are $\langle P_1 \rangle$ and $\langle P_2 \rangle$, respectively. The error bars represent one estimated standard deviation and are about the size of the symbols in the ordered phases.

whose instantaneous value is given by the eigenvector corresponding to the eigenvalue of largest magnitude of the order matrix $\mathbf{Q}$ where

$$Q_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{2} (3\mu_\alpha^i \mu_\beta^i - \delta_{\alpha\beta}) , \tag{4}$$

with N being the number of particles in the simulation cell and μ_α^i the α component of the unit vector $\hat{\boldsymbol{\mu}}_i$. The eigenvalue is the instantaneous second-rank order parameter P_2. The instantaneous first-rank order parameter P_1 is defined by [3, 11]

$$P_1 = \frac{1}{N} \left| \sum_{i=1}^{N} \hat{\boldsymbol{\mu}}_i \cdot \hat{\mathbf{d}} \right| . \tag{5}$$

The order parameters as functions of density are shown in Fig. 1 where the solid symbols are the results of simulations with applied field $E = 0.2$. The applied field is very small compared to a field generated by a dipole at close particle separation. As noted in our earlier publications [3], at this temperature, we observe two phase transitions without an applied field: the first sharp increase of order parameters at $\rho^* = 0.65$ in Fig. 1 is associated with an isotropic to ferroelectric nematic phase transition and the second at $\rho^* = 0.87$ is identified as a ferroelectric nematic to ferroelectric solid transition. Significant orientational ordering is observed at very low density for systems with applied field. A jump at $\rho^* = 0.8$ indicates that a phase transition occurs. The nature of the phase transition is identified by calculating the mean square displacement and the transverse pair correlation function. The mean square displacement indicates that both phases are liquid. The transverse pair correlation function at $\rho^* = 0.8$ is plotted as a function of the transverse separation in Fig. 2, which is very sensitive to columnar order. It shows clearly that the electric field induces a ferroelectric nematic to ferroelectric columnar phase transition [3] at $\rho^* = 0.8$. Within the accuracy of our results, the ferroelectric columnar to ferroelectric solid phase transition is found to occur at the same density ($\rho^* = 0.87$) as the ferroelectric nematic to ferroelectric solid transition with zero applied field.

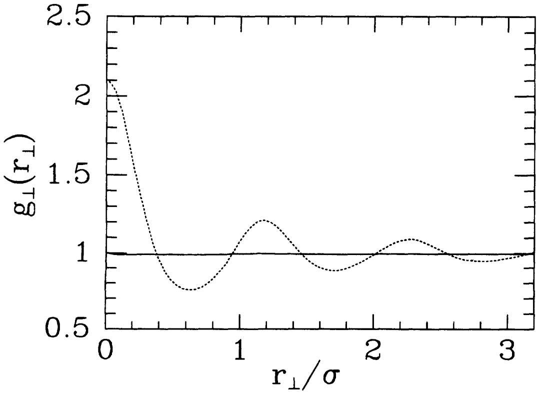

FIG. 2. The transverse pair correlation function as a function of the transverse separation. The solid and dotted lines are for $E = 0.0$ and $E = 0.2$, respectively.

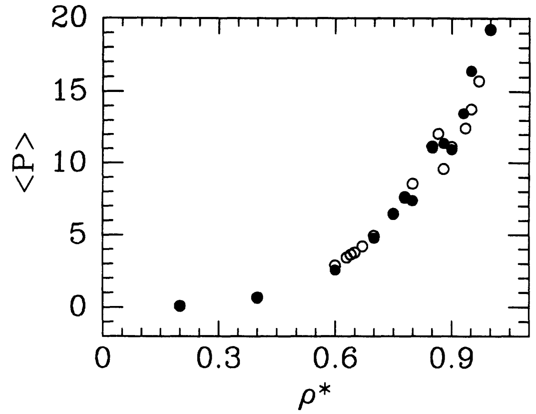

FIG. 3. The reduced pressure as a function of the density. The symbols are the same as Fig. 1.

We have also calculated the pressure and potential energy where the contribution of explicit field terms was not included to be comparable with previous field-free calculations. For the field-free case, a weak first-order phase transition from isotropic to ferroelectric nematic and a stong first order from ferroelectric nematic to ferroelectric solid can be clearly seen from the pressure plot of Fig.

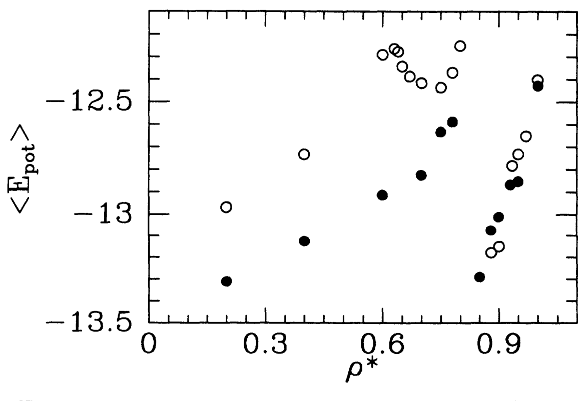

FIG. 4. The potential energy as a function of the density. The symbols are the same as Fig. 1.

3 and the potential energy plot of Fig. 4 [3]. Much larger pressure and potential energy changes are observed at the field-induced nematic to columnar phase transition. The potential energy is closely related with the orientational order parameters. At the columnar to solid transition, both order parameters and energy vary smoothly. On the other hand, there is a significant change of pressure. This is consistent with our previous results for the case of a spontaneous ferroelectric nematic to ferroelectric columnar transition at lower temperature [3].

It is not obvious how the columns of dipoles in the columnar phase pack in three dimensional space. For oblate dipolar molecules of large breath length ratio, an antiferroelectric columnar phase of two dimensional hexagonal structure is found [12]. However, this is impossible for a ferroelectric columnar phase because of the strong repulsion between dipoles in the same plane. We have found that the ferroelectric columnar phase adopts a three dimensional hexagonal structure [5]. In the ground state, the dipolar interaction energy of the hexagonal structure is slightly higher than that of tetragonal I [3, 5] [body-centered tetragonal (bct)]. It is worthwhile to note that structure of the ferroelectric solid in our simulation is also found to be tetragonal I. But the lattice constant is different from that of the ground state, probably because our study was carried out at room temperature.

In summary, the orientational order in the liquid phase is sensitive to the applied electric field. A ferroelectric columnar phase can be induced by a small applied electric field. However, the freezing density remains the same as the field-free case. In our model, particles are not polarizable. Thus some of our conclusions may not apply to real ER fluids where polarization plays an important role. We are currently working on more realistic ER fluid models.

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[1] T.C. Halsey, Science **258**, 761 (1992).
[2] H. Sollich, D. Baalss, and S. Hess, Mol. Cryst. Liq. Cryst. **168**, 189 (1989); S. Hess, J. F. Schwarzl, and D. Baalss, J. Phys.: Condens. Matter **2**, SA279 (1990).
[3] D. Wei and G.N. Patey, Phys. Rev. Lett. **68**, 2043 (1992); Phys. Rev. A **46**, 7783 (1992); Phys. Rev. E **47**, 506 (1993); **47**, 2954 (1993).
[4] J.J. Weis, D. Levesques, and G.J. Zarragoicoechea, Phys. Rev. Lett. **69**, 913 (1992).
[5] R. Tao and J.M. Sun, Phys. Rev. Lett. **67**, 398 (1991).
[6] R. Tao, Phys. Rev. E **47**, 423 (1993).
[7] S.W. de Leeuw, J.W. Perram, and E.R. Smith, Annu. Rev. Phys. Chem. **37**, 245 (1986); Proc. R. Soc. London Ser. A **373**, 27 (1980); **388**, 195 (1983).
[8] P.G. Kusalik, J. Chem. Phys. **93**, 3520 (1990).
[9] D.J. Evans and G.P. Morriss, Comput. Phys. Rep. **1**, 297 (1984); D.J. Evans, J. Chem. Phys. **78**, 3297 (1983); D.J. Evans, W.G. Hoover, B.H. Failor, B. Moran, and A.J.C. Ladd, Phys. Rev. A **28**, 1016 (1983).
[10] M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1989) and references therein.
[11] F. Biscarini, C. Zannoni, C. Chiccoli, and P. Pasini, Mol. Phys. **73**, 439 (1991).
[12] G.J. Zarragoicoechea, J.J. Weis, and D. Levesques, Phys. Rev. A **46**, 7783 (1992).