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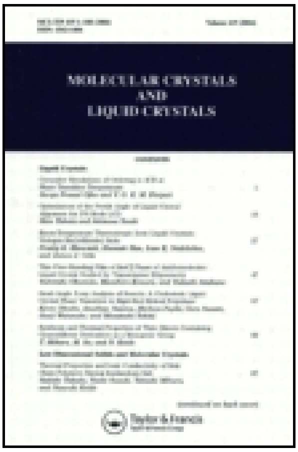

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Orientational Order in Simple Polar Liquids: Effect of the Quadrupole Moment

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Orientational Order in Simple Polar Liquids: Effect of the Quadrupole Moment

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Molecular dynamics (MD) simulations were carried out to investigate the effect of the quadrupole moment on the orientational order in polar liquids. A simple model of soft sphere with a point dipole and a linear quadrupole was employed in the current study. It is found that the quadrupole moment shifts the isotropic to ferroelectric nematic and the ferroelectric nematic to solid phase transitions to higher density. The columnar order appears at much lower temperature as compared with the pure dipole liquid.

I. INTRODUCTION

Recently, rather rich phase phenomena have been observed for the simple dipolar fluids with strong dipole interaction. The orientationally ordered phase, for example, the ferroelectric nematic phase[1] has been found when the strongly interacting dipolar spheres undergo spontaneous polarization. Under the conducting boundary condition, a single ferroelectric domain is stable. If a sample is surrounded by an insulator the ordered dipoles induce surface charge which will create a depolarizing electric field[2] whose energy is proportional to the volume of the liquid crystal and the square of polarization. Such a depolarized field makes it impossible for the liquid crystal to remain in a polarized state. As a result, two domains of opposite polarization are founded. The ferroelectric columnar phase merges at low temperatures. The ferroelectric liquid crystal phase freezes to a ferroelectric solid phase of Tetragonal 1 structure.[1] At very low temperatures, chains of dipoles aligning nose to tail are found even at very low density,[1,3–6] some systems behave like a "polymer". A minimum amount of dispersive energy is required to observe the liquid-vapor coexistence.[3,4]

Very recently, there are some parallel theoretical studies based on the reference Hypernetted-Chain (RHNC) theory[7–9] and density-functional theory.[7,10] In the simulation studies, one is limited to a finite simulation cell of periodic boundary with proper treatment of the long range interactions, that is, the Ewald sum and the reaction field from the dielectric continuum surrounding the simulation cell and its Ewald sum images. On the other hand, theories have been developed to study well defined thermodynamic systems (infinite systems) and also systems similar to those used in the simulations. It is found that the RHNC gives an isotropic to ferroelectric nematic phase transition,[7–9] which qualitatively agrees with the simulations.

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The ferroelectric liquid crystals are of potential use in making large dimensional flat display devices. Discovery of the ferroelectric liquid crystals of spherical molecules is especially exciting because this type of liquid crystal should respond to the applied field in a much faster time scale than the currently existing ones.[11-13] We are making efforts[14] to conduct studies using realistic potential in order to determine the state and molecular parameters that favour ferroelectric liquid crystals. The Gay-Berne potential[15] was used to incorporate two basic features of a realistic potential, a van der waals-like tail and an anisotropic short range core defines the molecular shape. It was shown that the orientational order was significantly enhanced by the particle shape.

Another step towards more realistic intermolecular interactions is to include higher multiple moments. It is well known that[16] the quadrupole moment has significant effects on the thermodynamics, structural, and especially the dielectric properties of liquids consisting of the multipolar molecules. The dielectric constant diverges at the isotropic to ferroelectric nematic phase transition.[1] We expect that the quadrupole moment has significant effects on the ferroelectric orientational order and phase transitions. In this paper, the molecular dynamics (MD) simulation of a simple dipole-quadrupole liquid is reported.

The remainder of this paper is divided into three parts. The model and simulation details are described in Section II, the results are given in Section III and conclusions are summarized in Section IV.

II. MODEL AND SIMULATION METHOD

The model we consider consists of soft sphere with a point dipole and a linear quadrupole in the center. In terms of the pair potential, the model can be expressed as

$$u(12) = u_{ss}(r) + u_{DD}(12) + u_{DQ}(12) + u_{QD}(12) + u_{QQ}(12) \tag{2.1}$$

where

$$u_{ss}(r) = 4\varepsilon(\sigma/r)^{12} \tag{2.2}$$

;

is the soft-sphere potential, $u_{DD}(12)$, $u_{DQ}(12)$, $u_{QD}(12)$ and $u_{QQ}(12)$ are the dipole-dipole, dipole-quadrupole, quadrupole-dipole and quadrupole-quadrupole interactions, respectively. The electrostatic interactions are long ranged, which are usually treated by the Ewald sum method,[17,18] where details for the dipole-quadrupole liquids are given by Levesque *et al.*[16] The convergence parameters in the Ewald sum were the same as previously used.[1] The MD calculations were performed at constant temperature employing the Gaussian isokinetic equations of motion[19] as described by Kusalik.[18] 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 $\Delta t^* = \Delta t/\sqrt{m\sigma^2/\varepsilon_e} = 0.0025$ (m is the mass of a particle) was employed in all calculations.

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The orientational order is described by a director $\mathbf{d}(t)$ whose instantaneous value is given by the eigenvector of the order matrix $\mathbf{Q}$ where

$$Q_{\alpha\beta}=\frac{1}{N}\sum_{i=1}^{N}\frac{1}{2}(3\mu_{\alpha}^{i}\mu_{\beta}^{i}-\delta_{\alpha\beta}), \tag{2.3}$$

where N is the number of particles in the simulation cell and μ_{α}^{i} is the α component of the unit vector $\hat{\boldsymbol{\mu}}_i$. The corresponding eigenvalue is the instantaneous second-rank order parameter P_2. The instantaneous first-rank order parameter P_1 is defined by[1,20]

$$P_1=\frac{1}{N}\left|\sum_{i=1}^{N}\hat{\boldsymbol{\mu}}_i\cdot\hat{\mathbf{d}}\right|. \tag{2.4}$$

The equilibrium pair correlation function $g(12)$ is a function of separation r and orientation of molecules, which can be expanded in the form

$$g(12)=\sum_{mnl}g^{mnl}(r)\Phi^{mnl}(12), \tag{2.5}$$

where $\Phi^{mnl}(12)$ are rotational invariants defined in earlier work.[21] In the present simulations we have calculated $g^{000}(r)$, $g^{110}(r)$, $g^{112}(r)$ and $g^{220}(r)$ providing both structural information and an alternative route to the order parameters for the liquid crystals[1]. In order to better establish the structure of orientationally ordered phases, we have calculated the longitudinal and transverse pair correlation functions, $g_{\parallel}(r_{\parallel})$ and $g_{\perp}(r_{\perp})$, respectively. Here $r_{\parallel}$ and $r_{\perp}$ are components of the interparticle vector $\mathbf{r}$ parallel and perpendicular to the director. These functions measure positional correlations in the directions parallel and perpendicular to the director and are very sensitive to any long-range spatial correlations. In order to distinguish fluid and solid phases, we calculated the mean square displacement $\langle|\mathbf{r}_i(t)-\mathbf{r}_i(0)|^2\rangle$, where $\mathbf{r}_i(t)$ is the position vector of molecule i at time t. For fluids, the mean square displacement continually increases with time and varies linearly at long times.[22] For solids, the mean square displacement becomes constant rather than continually increasing with time at long times.

III. RESULTS AND DISCUSSION

Our model can be conveniently characterized by specifying the reduced density $\rho^*=\rho\sigma^3$, the reduced temperature $T^*=kT/\varepsilon_{ss}$, the reduced dipole moment $\mu^*=(\mu^2/\varepsilon_{ss}\sigma^3)^{1/2}$, the reduced quadrupole moment $Q^*=(Q^2/\varepsilon_{ss}\sigma^5)^{1/2}$ and the reduced time, $t^*=(\varepsilon_{ss}/m\sigma^2)^{1/2}t$. The dipole moment is chosen to be the same as in previous studies[1], i.e., $\mu^*=3$. A linear quadrupole[23] is chosen with a quadrupole moment $Q^*=0.6$. Our simulations were performed for a range of densities along two isothermals, $T^*=1.35$ and $T^*=1.0$, where results for $Q^*=0.0$ have been reported[1].

Simulations were performed with 256 particles using the Ewald-Kornfeld boundary conditions.[22] 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 collected for at least another 50,000 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 order parameters, the pressure and potential energy, are given as functions of density in Figures 1, 2 and 3, respectively. At $T^* = 1.35$ (Figures 1(a), 2(a), 3(a)), the

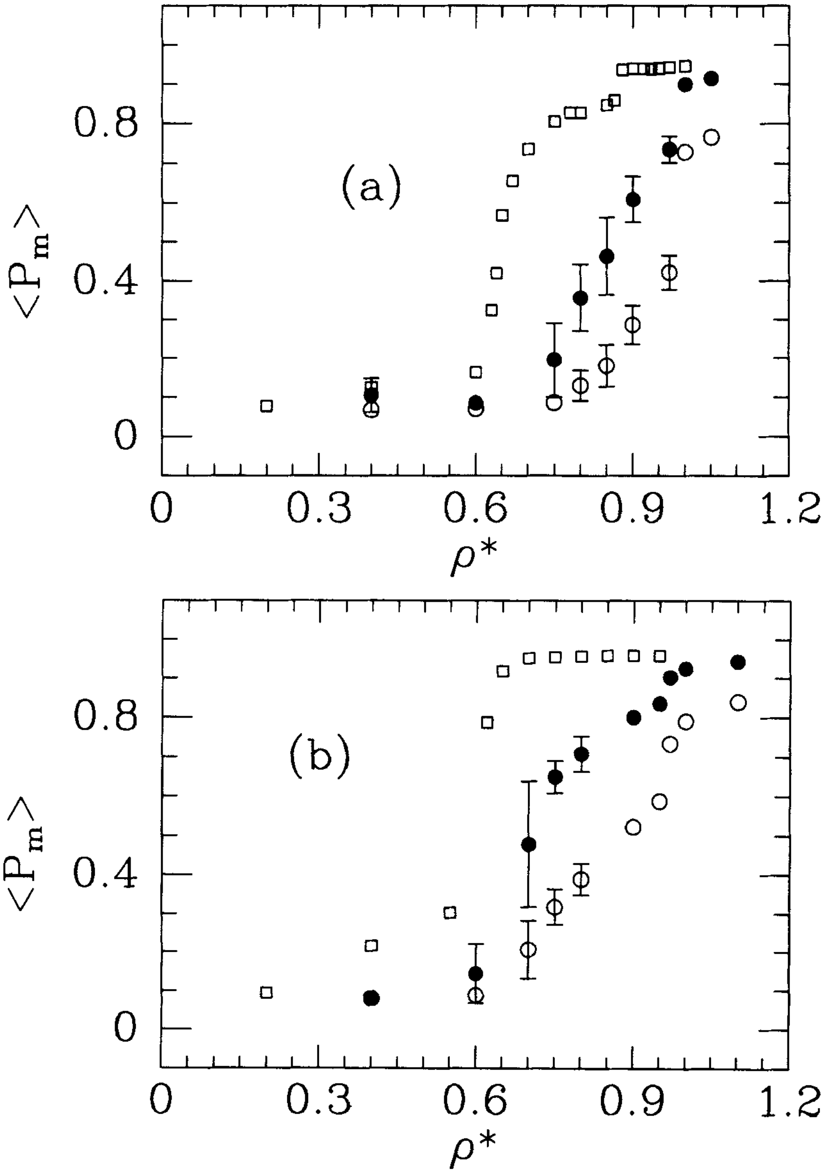

FIGURE 1 The orientational order parameters as functions of the density for (a), $T^* = 1.35$ and (b), $T^* = 1.0$. The open square, solid and open circles are $\langle P_1 \rangle$ with $Q^* = 0.0$ (pure dipole), $\langle P_1 \rangle$ and $\langle P_2 \rangle$ with $Q^* = 0.6$, respectively. The error bars represent one estimated standard deviation.

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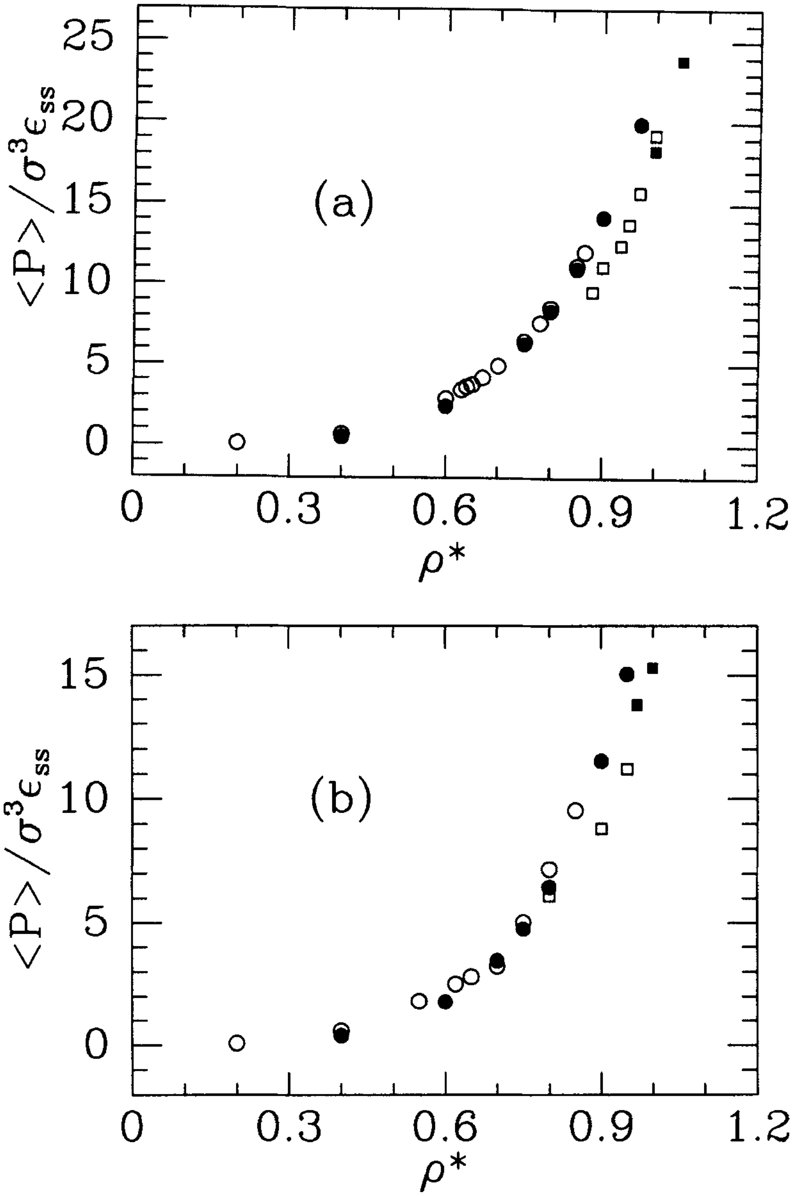

FIGURE 2 The reduced pressure as a function of the density for (a), $T^* = 1.35$ and (b), $T^* = 1.0$. The open and solid symbols are for $Q^* = 0.0$ and $Q^* = 0.6$, respectively. The circles and squares represent liquid-state and solid-state results, respectively.

isotropic to ferroelectric nematic phase transition occurs at $\rho^* \approx 0.65$ for $Q^* = 0.0$ (the pure dipole system). There is a wide density range of stable ferroelectric nematic phase from $\rho^* \approx 0.65$ to $\rho^* \approx 0.87$. A small quadrupole moment ($Q^* = 0.6$) extends the isotropic region to much higher density. There appears to be a narrow density range

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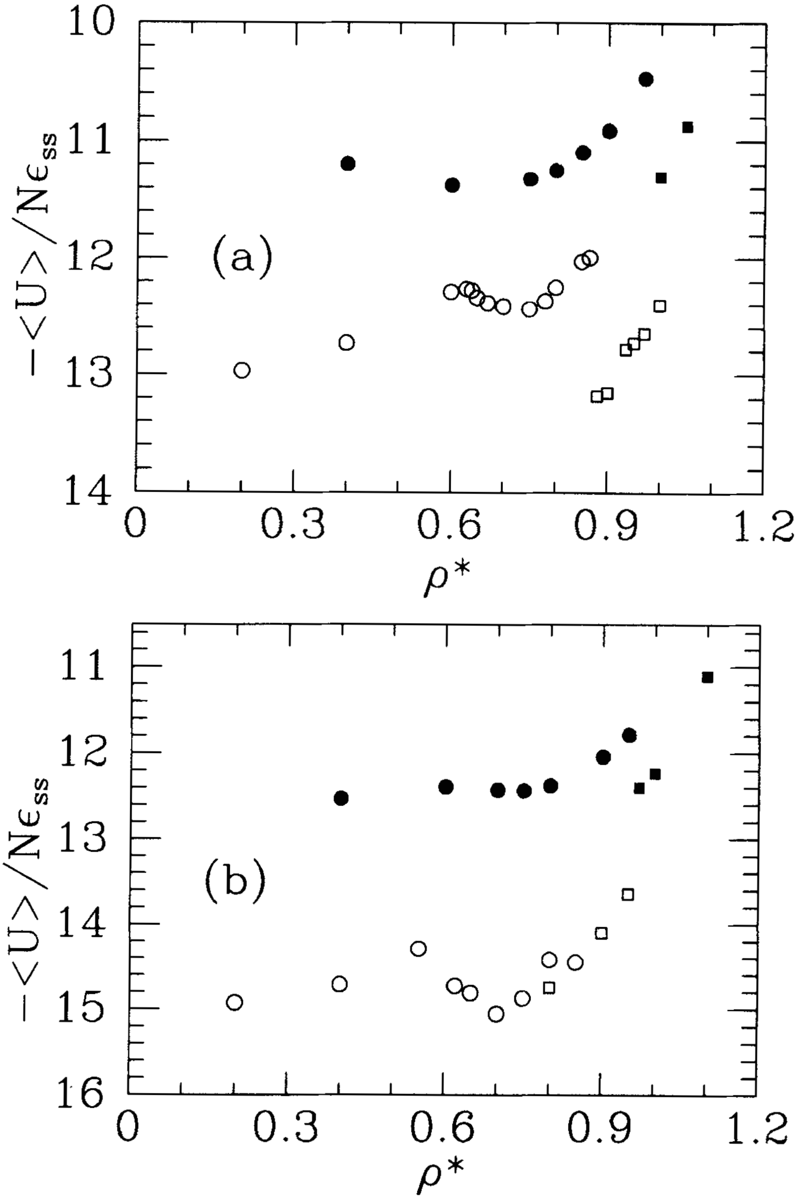

FIGURE 3 The potential energy as a function of the density for (a), $T^* = 1.35$ and (b), $T^* = 1.0$. The symbols are as in Figure 2.

near $\rho^* \approx 0.95$, where the ferroelectric nematic phase is observed. At $T^* = 1.0$ (Figure 1(b)), for $Q^* = 0.6$ (the dipole-quadrupole system), the orientational order merges at higher density compared with the pure dipole system. We have observed three phase transitions at this temperature for the pure dipole system.[1] There is an isotropic to ferroelectric nematic phase transition at $\rho^* \approx 0.6$, a nematic to columnar phase transition at $\rho^* \approx 0.7$ and a columnar to solid phase transition at $\rho^* \approx 0.8$.[1] For the dipole-quadrupole system, the isotropic phase becomes unstable with respect to the ferroelectric nematic phase at $\rho^* \approx 0.7$. There appears to be quite wide a range of stable ferroelectric nematic phase from $\rho^* \approx 0.7$ to $\rho^* \approx 0.97$. The ferroelectric nematic to solid phase transition occurs at $\rho^* \approx 0.97$. At this temperature, the ferroelectric columnar order disappears completely due to the presence of the quadrupole moment. As we pointed out in our earlier publications,[1] the transverse pair correlation function, $g_\perp(r_\perp)$is sensitive to the columnar order. An example of $g_\perp(r_\perp)$ for the dipole-quadrupole system is plotted in Figure 4. It helps one to make sure that the orientationally ordered phase is nematic rather than columnar.

The pressure and potential energy plots in Figures 2 and 3 are very useful in characterizing the phase transitions. The weak first order phase transitions, that is, isotropic to nematic, and nematic to columnar, were accompanied by a non-monotonic potential energy profile and a slight change in the slope of the pressure plot for the pure dipole case.[1] The energy and pressure change near the isotropic to nematic phase transition is less obvious for the dipole-quadrupole system. The strong first order freezing phase transition is shown by the large pressure and energy discontinuity. It is interesting to observe that the potential energy of the dipole-quadrupole system is actually less negative than that of the pure dipole, and the pressure is higher. It seems to suggest that the quadrupole moment makes molecules less attractive for the state and

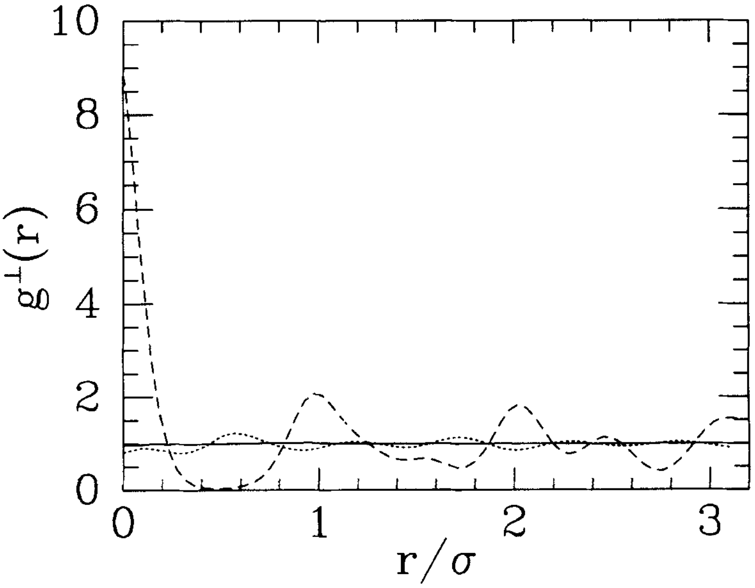

FIGURE 4 The transverse pair correlation function, $g_\perp(r_\perp)$, as a function of the transverse separation at $T^* = 1.0$. The solid, dotted and dashed lines are for $\rho^* = 0.90$ (isotropic), 0.95 (nematic), and 1.0 (solid), respectively.

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molecular parameters so given. We carefully compare various contributions to the potential energy. It is found that the potential energy due to attractive interactions, i.e., dipole-dipole, dipole-quadrupole and quadrupole-quadrupole, is actually more negative than that of the pure dipole. However it is compensated by the sharp increase of the positive contribution due to the soft sphere interaction. The pressure difference can also be explained in a similar fashion.

Yet another surprising observation comes from the fact that the freezing density of the dipole-quadrupole system is higher than that of the pure dipole. The mean square displacement as a function of time is given in Figure 5. We find that the molecules in the dipole-quadrupole system have a larger diffusion constant, which is proportional to the slope of Figure 5. This is to say that the quadrupole moment increases the mobility of molecules. It may help us understand why the nematic-solid transition occurs at higher density.

We have made efforts to locate the columnar order at a still lower temperature. For $\rho^* = 0.7$, the columnar order does not appear until $T^* = 0.4$. Figure 6 shows the structure at such a state. The split of the first peek into two separate ones is a very good indication of the columnar order. Apparently, this is related to the chain formation with dipoles aligning nose to tail and chains being arranged in a 3-D hexagonal structure. As it is shown in the projections of $g^{110}(r)$ and $g^{220}(r)$, some long-range spatial orders are present along certain inter-molecular directions.

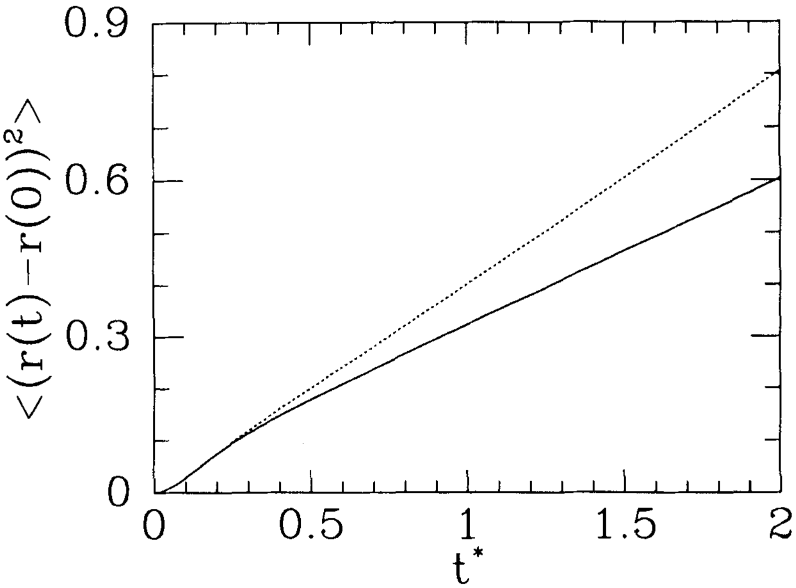

FIGURE 5 The mean square displacement as a function of t^* at $T^* = 1.35$ and $\rho^* = 0.8$. The solid and dotted lines are for $Q^* = 0.0$ (pure dipole), 0.6, respectively.

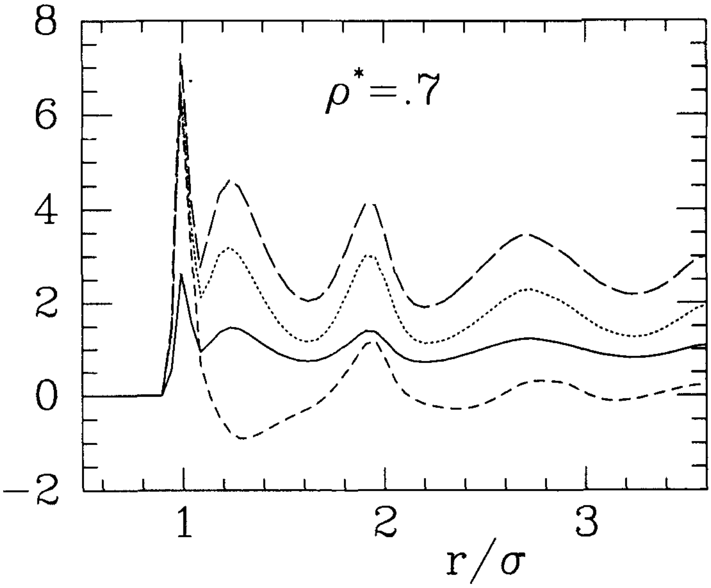

FIGURE 6 Projections of the pair distribution functions at $T^* = 0.4$ and $\rho^* = 0.7$. The solid, dotted, short-dash and long-dash curves are for $g^{000}(r)$, $g^{110}(r)$, $g^{112}(r)$ and $g^{220}(r)$, respectively.

IV. SUMMARY AND CONCLUSION

Molecular dynamics simulations were used to study the effect of quadrupole moment on the orientational order in polar liquids. This is part of our continuing efforts to search for the state and molecular parameters that favour the ferroelectric liquid crystal phases. Simulations were carried out along the same two isothermal lines as were done in the studies cited in (1). It is shown that the quadrupole moment shifts the isotropic to ferroelectric nematic and the ferroelectric nematic to solid phase transitions to higher density, compared with results for pure dipole liquids. The columnar order for the pure dipole liquid at $T^* = 1.0$ is completely demolished by the quadrupole moment $Q^* = 0.6$. It merges only at a very low temperature, for example, at $T^* = 0.4$ for $\rho^* = 0.7$. In the current study, the Ewald-Kornfeld boundary conditions[22] are used, evidently, only single domain ferroelectric phases were found. The domain structures under other boundary conditions, which have been observed for the pure dipole case[1] are of interest to our future simulations.

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