

## Ferroelectric and dipolar glass phases of noncrystalline systems

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In a recent Letter [Phys. Rev. Lett. **75**, 2360 (1995)] we briefly discussed the existence and nature of ferroelectric order in positionally disordered dipolar materials. Here we report further results and give a complete description of our work. Simulations of randomly frozen and dynamically disordered dipolar soft spheres are used to study ferroelectric ordering in noncrystalline systems. We also give a physical interpretation of the simulation results in terms of short- and long-range interactions. Cases where the dipole moment has one, two, and three components (Ising, *XY*, and *XYZ* models, respectively) are considered. It is found that the Ising model displays ferroelectric phases in frozen amorphous systems, while the *XY* and *XYZ* models form dipolar glass phases at low temperatures. In the dynamically disordered model the equations of motion are decoupled such that particle translation is completely independent of the dipolar forces. These systems spontaneously develop long-range ferroelectric order at nonzero temperature despite the absence of any fine-tuned short-range spatial correlations favoring dipolar order. Furthermore, since this is a nonequilibrium model, we find that the paraelectric to ferroelectric transition depends on the particle mass. For the *XY* and *XYZ* models, the critical temperatures extrapolate to zero as the mass of the particle becomes infinite, whereas for the Ising model the critical temperature is almost independent of mass, and coincides with the ferroelectric transition found for the randomly frozen system at the same density. Thus in the infinite mass limit the results of the frozen amorphous systems are recovered. [S1063-651X(97)03807-5]

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### I. INTRODUCTION

Computer simulations of fluids of strongly interacting dipolar spheres have established the existence of a stable ferroelectric liquid crystal phase [1,2]. The phase is truly fluid in that it exhibits long-range orientational (ferroelectric) order, but only short-range spatial correlations. Interestingly, the local spatial correlations found in these ferroelectric fluids were similar to those in the ferroelectric tetragonal-*I* lattice, which is the lattice structure believed to be the low-temperature ferroelectric solid phase for dense dipolar hard spheres [3]. The translational mobility of the particles in the fluid phase allowed specific short-ranged correlations to build up, and the system spontaneously polarized. From these results, it was believed that the establishment of a ferroelectric liquid phase was largely driven by well-tuned specific short-range spatial correlations [4].

On the other hand, experimental systems of near spherical  $\text{Fe}_3\text{O}_4$  magnetic particles in a frozen nonmagnetic solvent [5–7], which interact via magnetic dipole moments, do not exhibit a dipole-driven ferromagnetic phase upon cooling, but, rather, develop magnetic irreversibilities similar to the situation in random magnetic systems known as spin glasses [8]. In these systems, the particles are frozen at random locations at all temperatures, but above a certain temperature the particle dipoles can freely rotate [9]. The simplest interpretation of these results is that the lack of fine-tuned spatial correlations inhibit the formation of long-range ferroelectric order, while the large degree of randomness in the

positions lead to random frustration for the dipolar interactions and, consequently, to the formation of a “dipolar glass” at low temperature. The anisotropic nature of the dipolar interaction would lead one to expect that the glass transition in these frozen ferrofluids is of thermodynamic (as opposed to purely dynamic) origin, and hence occurs at a nonzero glass transition temperature  $T_g$  characterized by a divergent spin-glass susceptibility [8,10].

To summarize, the naive picture that emerges is that some crystalline lattices (e.g., body-centered-cubic, face-centered-cubic, tetragonal-*I*) and some dipolar fluids can spontaneously develop long-range ferroelectric order [11] because they have “suitable” spatial correlations. On the other hand, low-density randomly frozen dipolar systems lack these correlations, exhibit random frustration, and therefore have dipolar glass ground states [12]. Also, we would expect that dilution of the dipoles on a crystalline lattice, which displays ferroelectric order for full occupation, will eventually lead to a transition from ferroelectric order to dipolar glass below a critical occupation density, again due to the increase build up of random frustration with decreasing dipole density [5,13].

However, in recent papers, Zhang and Widom [14,15] proposed a mean-field theory that predicts ferroelectric phases in dipolar systems that lacked any specific spatial correlations, provided the density of the particles,  $\rho$ , was above a critical value  $\rho_c$ . They considered amorphous solids of dipolar hard spheres where the particles were free to rotate, but were frozen at random sites. Specifically, they assumed complete randomness where the radial distribution function,  $g(r)$ , describing the probability that two particles are separated by a distance  $r$ , was set to  $g(r) = 1$  for  $r > \sigma$ , where  $\sigma$  is the diameter of the sphere. Their prediction of ferroelectric phases in dipolar systems that lack any specific

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spatial correlations suggests that a well-tuned short-range structure may not be necessary for ferroelectric phase formation. Although the experimental results on frozen ferrofluids seem to contradict this assertion, Zhang and Widom suggested that the experimental dipole density was possibly too low (i.e., below  $\rho_c$ ) for ferroelectric order, and hence a dipolar glass state was found.

The role of short-range spatial correlations on ferroelectric phase formation is still not well understood. The question of whether or not dense spatially disordered dipolar materials can have ferroelectric phases was briefly discussed in Ref. [16]. In this paper, the effect of spatial disorder on the phase behavior of dense dipolar systems is investigated with molecular dynamics (MD) and Monte Carlo (MC) simulations. Systems where the dipole vector has one, two, and three components are considered and we refer to these as the Ising,  $XY$ , and  $XYZ$  models, respectively. The fundamental forces that promote and destroy ferroelectric order in dipolar systems are identified and discussed.

The remainder of this paper is organized as follows. In Sec. II we briefly discuss the generic temperature vs density phase diagram one might expect to find for diluted ferroelectric lattices and amorphous dipolar systems. In Sec. III, the models and simulation methods employed are described. Section IV is concerned with ferroelectric and dipolar glass ordering found in amorphous frozen dipolar systems. A simulation technique devised to study orientational order in spatially random media is introduced in Sec. V. The results of these “dynamically disordered” simulations offer significant insight into the observed behavior of both dipolar fluids [1,2] and the dipolar amorphous solids [5–7,14]. A mean-field theory which describes the ferroelectric transition when only reaction field interactions are present is given in Sec. VI. This helps us understand the competition between the long-range reaction field interactions and shorter-ranged contributions to the energy. This competition is a key feature determining whether or not a system displays ferroelectric order. Finally, our main results and conclusions are summarized in Sec. VII.

## II. TEMPERATURE-DENSITY PHASE DIAGRAM IN RANDOM DIPOLAR SYSTEMS

It is useful to briefly discuss the temperature  $T$  vs density  $\rho$  phase diagram (sketched in Fig. 1) that one might expect to observe in random dipolar systems based on our current understanding of randomly frustrated magnetic spin glasses [5,8,13,17].

First, consider a Bravais lattice (e.g., body-centered-cubic), where all sites are occupied by an  $n$ -component classical dipole such that  $\rho = \rho_{\max}$ . We will assume here that the positions of the particles at the lattice sites are fixed. At high temperature, the system is in a disordered paraelectric phase (see Fig. 1). For a perfect lattice (all sites occupied), a transition to a long-range ferroelectric phase occurs at some critical temperature,  $T_c$  [18]. As the system is diluted, a ferroelectric phase remains observable for sufficiently large  $\rho > \rho_c$ , but with  $T_c$  decreasing as more sites are vacated and  $\rho$  decreases. In addition, the zero-temperature polarization  $P(T=0)$  decreases from its full value at  $\rho = \rho_{\max}$  as  $\rho$  approaches  $\rho_c$  from above. Based on work on spin glasses

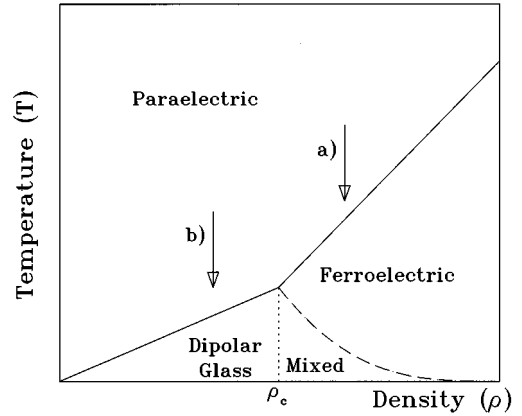


FIG. 1. A sketch of a possible phase diagram for spatially disordered dipolar systems. The various terms, symbols, and lines are referred to in the text.

[8,17], we expect that upon cooling within the ferroelectric phase, there will be a low-temperature “mixed” state ( $\rho_c < \rho < \rho_{\max}$ ), where strong irreversibilities and glassy behavior develops (i.e., the polarization in field-cooled and zero-field-cooled experiments differs below the long-dashed line in Fig. 1, which is commonly referred to as the Almeida-Thouless line in the mean-field theory of Ising spin glasses [8]). However, long-range ferroelectric dipolar order is not lost in the mixed phase, and there is likely no decrease of the polarization upon cooling from the ferroelectric state down into the mixed state [17]. For  $\rho < \rho_c$ , the random frustration leads to an unpolarized dipolar glass state characterized by an Edwards-Anderson order parameter [8]. Most naively, we expect that the intrinsic anisotropy of dipolar interactions stabilizes a dipolar glass phase at nonzero temperature in the three-dimensional Ising spin glass universality class [10] (with the proviso that recent numerical work suggests that the existence of a thermodynamic spin-glass transition in the three-dimensional Ising spin glass is *still* not completely settled [19]). In diluted magnetic systems with short-range frustrated interactions, such as diluted  $\text{Cd}_x\text{Mn}_{1-x}\text{Te}$  and  $\text{Eu}_x\text{Sr}_{1-x}\text{S}$ , one finds that the glass transition temperature vanishes for a nonzero density,  $\rho_-$ , which corresponds to a site percolation threshold [8]. For classical dipoles,  $\rho_-$  is zero due to the long-range nature of the interactions. However, for small nonclassical dipole moments, quantum effects will likely move  $\rho_-$  to a finite value due to the random-transverse fields acting on each spin in the frozen state [20].

Consider now the case of amorphous dipolar systems where there are little or no spatial correlations among the locations of the dipoles (i.e., the dipoles are not on lattice sites) [6]. Recently, Zhang and Widom [14,15] argued, using a mean-field model, that frozen amorphous dipolar systems could display spontaneous ferroelectric order for a packing density  $\rho > \rho_c(n)$  for  $n = 1$  (Ising model) and 3 ( $XYZ$  model) component dipoles [14,15]. It should be noted here that one clearly cannot make arbitrarily dense amorphous systems lacking *all* spatial correlations. However, the critical density for ferroelectric order in amorphous Ising and  $XYZ$  systems was found in Refs. [14,15] to be reasonably less than the close-packed value, and it should be possible to test the theoretical predictions for a range of densities. In other words,

varying the temperature for sufficiently large  $\rho$ , one should according to Zhang and Widom follow the trajectory (a) in Fig. 1, and find a ferroelectric phase below  $T_c(\rho, n)$ .

The main motivation of the present study was to investigate this possibility. Below, we report results from extensive computer simulations which show that for a high-density amorphous system, the Ising model does display a ferroelectric transition. In fact, for the density considered, the Ising system developed a polarization close to the full maximum value (i.e., the Ising system considered was at  $\rho \gg \rho_c$ ). However for the same and even larger densities, we found that the XY and XYZ models showed instead a dipolar glass transition, and no ferroelectric order was observed. Thus, these systems followed path (b) in the phase diagram sketched in Fig. 1.

### III. MODEL AND SIMULATION DETAILS

We consider systems of point dipoles embedded at the center of soft spheres. Soft spheres (ss) are defined by the pair potential

$$u_{ss}(12) = 4\varepsilon(\sigma/r)^{12}, \quad (1)$$

where the parameters  $\varepsilon$  and  $\sigma$  are the fundamental units of energy and length, and  $r$  is the distance between the particles. The dipole-dipole (DD) interaction is given by

$$u_{DD}(12) = -3(\boldsymbol{\mu}_1 \cdot \mathbf{r})(\boldsymbol{\mu}_2 \cdot \mathbf{r})/r^5 + \boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2/r^3, \quad (2)$$

where  $\boldsymbol{\mu}_i$  is the dipole of particle  $i$  and  $\mathbf{r}$  is the interparticle vector. As noted above, we consider Ising, XY, and XYZ models. In all three cases the potential is given by Eq. (2).

All calculations were carried out employing periodic boundary conditions, and the long-range dipolar forces were taken into account using Ewald summation methods. The dielectric constant of the surrounding continuum  $\epsilon'$ , necessary in the Ewald method [1,21,22], was taken to be infinity (i.e., conducting boundary conditions). For the present dense strongly dipolar systems the dielectric constants are sufficiently large that conducting boundary conditions are an appropriate choice.

The existence of a ferroelectric phase can be detected by calculating the average polarization per particle,  $P$ , defined as

$$P = \frac{1}{N} \left\langle \sum_{i=1}^N \hat{\boldsymbol{\mu}}_i \cdot \hat{\mathbf{d}} \right\rangle, \quad (3)$$

where  $\hat{\mathbf{d}}$  is a unit vector in the direction of the total instantaneous moment,  $\mathbf{M} = \sum_{i=1}^N \boldsymbol{\mu}_i$ , and  $N$  is the number of particles in the system. In ferroelectric systems,  $P$  is nonzero, and tends to one as the ferroelectric order increases. In a disordered phase (either paraelectric or dipolar glass),  $P$  will be zero if the system is sufficiently large. However, in simulations  $P$  must be expected to exhibit significant system size dependence and, as demonstrated below, this must be carefully checked.

In the present work, we are also interested in the possibility that a system could orientationally ‘‘freeze’’ into an unpolarized state at low temperatures. Such an orientationally

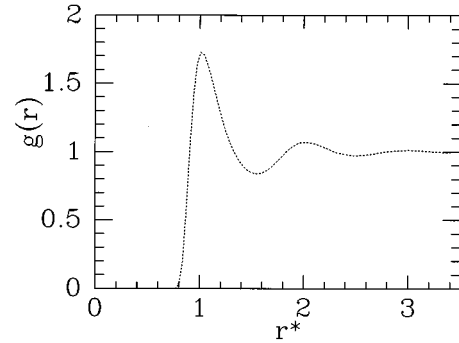


FIG. 2. The radial distribution function  $g(r)$ , for soft spheres at  $\rho = 0.8$  and  $T^* = 10.5$ .

frozen or dipolar glass phase can be detected by calculating the root-mean-square (rms) dipole length  $\langle S_{rms} \rangle$ , given by [23]

$$\langle S_{rms} \rangle = \frac{1}{N} \left[ \sum_i \langle (\mathbf{m}_i) \cdot \langle \mathbf{m}_i \rangle \rangle \right]^{1/2}, \quad (4)$$

where  $\langle \mathbf{m}_i \rangle = \tau^{-1} \sum_{\tau'=0}^{\tau} \hat{\boldsymbol{\mu}}_i(\tau')$ , and  $\tau$  is the number of MD time steps, or MC sweeps (i.e.,  $N$  attempted moves). Briefly, for ferroelectric systems both  $P$  and  $\langle S_{rms} \rangle$  will be nonzero. If  $P \approx 0$  but  $\langle S_{rms} \rangle$  is nonzero, the system is an orientationally frozen dipolar glass. If both  $P$  and  $\langle S_{rms} \rangle$  are near zero, the particles are freely rotating as in a plastic crystal or normal isotropic fluid.

Systems of dipolar soft spheres can be characterized by specifying the reduced density  $\rho^* = N\sigma^3/V$ , the reduced temperature  $T^* = kT/\varepsilon$ , where  $k$  is the Boltzmann constant, and the reduced dipole moment  $\mu^* = (\mu^2/\varepsilon\sigma^3)^{1/2}$ . In the present work, the reduced dipole moment and reduced density were constant at  $\mu^* = 4$  and  $\rho^* = 0.8$ . This density is well within the range where Zhang and Widom predict a ferroelectric phase. For example, the lowest density of the ferroelectric phase is predicted to be  $\rho^* = 0.31$  for the Ising system and  $\rho^* = 0.55$  for the XYZ model [14,15]. In the present case with  $\mu^* = 4$  and  $\rho^* = 0.8$ , the theory of Zhang and Widom predicts that the Ising model will be ferroelectric if  $T^* \leq 35.2$ , and the XYZ model if  $T^* \leq 4.8$  [24].

### IV. RANDOMLY FROZEN SYSTEMS

In our simulations the ‘‘randomly’’ frozen spatial structure is taken to be a typical fluid configuration of soft spheres at  $T^* = 10.5$  and  $\rho^* = 0.8$ . Such configurations are readily generated by MD simulation of the soft-sphere fluid. Unfortunately, it is impossible to have a truly random and uncorrelated [i.e., the radial distribution function,  $g(r) = 1$  for  $r \geq \sigma$ ] spatial configuration at  $\rho^* = 0.8$ . The radial distribution function for a soft-sphere fluid at  $\rho^* = 0.8$  and  $T^* = 10.5$  is shown in Fig. 2. Clearly, the spatial correlations in this system are weak and very short ranged. The point dipoles are located at the centers of the soft spheres, initially with random orientations. Constant temperature MD simulations [25] were carried out for the XY and XYZ models. The reduced simulation time step  $\delta t^* = (\varepsilon/m\sigma^2)^{1/2} \delta t = 0.00125$ , where  $m$  is the particle mass, was used together with the

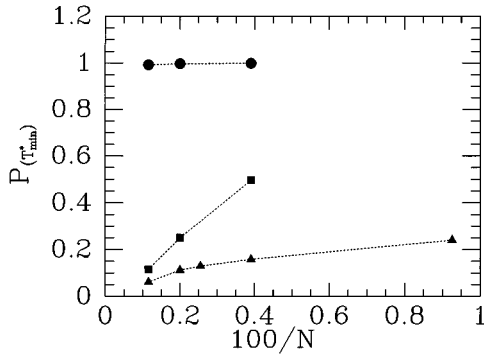


FIG. 3. The polarization  $P$  at  $T_{\min}^*$  vs  $100/N$  for the randomly frozen Ising (circles), XY (squares), and XYZ (triangles) models. Results are included for 108 (XYZ only), 256, 500, and 864 particles.

reduced moment of inertia  $I^* = I/m\sigma^2 = 0.025$ . Of course, these MD simulations involved only rotational motion since the particles remain spatially frozen. Monte Carlo simulations were performed for the Ising model. One Monte Carlo ‘‘sweep’’ consisted of  $N$  attempted random flips of the dipolar orientations. Typically, the results reported involved aging runs of 100 000 MD time steps or MC sweeps followed by production runs of the same length.

The average polarization as a function of  $1/N$  for the Ising, XY, and XYZ models is shown in Fig. 3. The systems considered ranged from 108 to 864 particles. The polarization values that are plotted were obtained at the lowest temperature where equilibrium could be achieved independent of the starting configuration. We call this temperature  $T_{\min}^*$ . The values of  $T_{\min}^*$  for the Ising, XY, and XYZ models are 10.0, 4.0, and 3.5, respectively. Below these temperatures, simulations that were started from perfectly aligned and random states did not converge to the same result, at least not in simulation runs of practical length. However, the values of  $T_{\min}^*$  attained are within the temperature range where Zhang and Widom predicted a ferroelectric phase. As discussed below, it appears that the Ising system develops ferroelectric order with  $P > 0$  in the thermodynamic limit. In this case,  $T_{\min}^*$  may qualitatively correspond to the long-dashed line in Fig. 1.

From Fig. 3 we see that the Ising model at  $T_{\min}^* = 10.0$  is almost completely polarized, and shows little or no system size dependence. A detailed  $P$  vs  $T^*$  plot for the frozen  $N = 256$  Ising system is given below (see Fig. 7). It can be seen that ferroelectric order develops spontaneously in this system at  $T^* \approx 25$ . This transition temperature is significantly lower than that (i.e.,  $T^* = 35.2$ ) predicted by the theory of Zhang and Widom. Returning to Fig. 3, we see that the XY and XYZ models at  $T_{\min}^*$  show significant polarization for the 108- and 256-particle systems. However, in both cases the polarization decreases monotonously with increasing system size, and appears to approach zero in the thermodynamic limit. The observed polarization of the XY model is strongly dependent on system size, decreasing from  $\sim 0.49$  for  $N = 256$  to  $\sim 0.10$  for  $N = 864$ . The polarization for the XYZ model shows a similar, although not as pronounced, system size dependence.

Further information about the behavior of the XYZ and

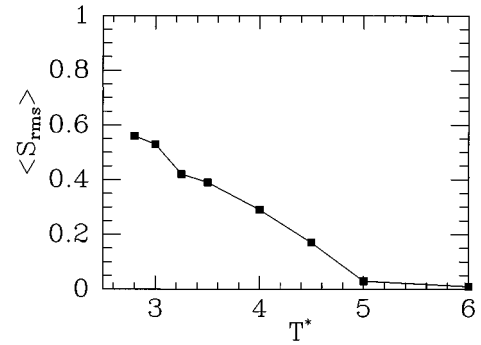


FIG. 4. The root-mean-square dipole length  $\langle S_{\text{rms}} \rangle$  for the frozen XYZ model with  $N = 256$ .

XY models can be obtained by examining the temperature dependence of  $\langle S_{\text{rms}} \rangle$ . Results for the XYZ model ( $N = 256$ ) are shown in Fig. 4. These results were obtained for samples initially begun with random dipolar orientations. We see that  $\langle S_{\text{rms}} \rangle$  is zero at high temperatures, as expected, but becomes nonzero and grows with decreasing  $T^*$  at lower temperatures. A similar behavior was observed for the XYZ system with 864 particles, and for the XY model. The growth of  $\langle S_{\text{rms}} \rangle$  at low temperatures without a corresponding development of polarization provides qualitative evidence that the XYZ and XY models freeze orientationally to form dipolar glasses.

To summarize, at  $\rho^* = 0.8$  we find no evidence of ferroelectric states in the thermodynamic limit for the randomly frozen XYZ and XY models. This clearly disagrees with the theory of Zhang and Widom, which predicted that the XYZ model should have a stable ferroelectric phase in the temperature range we consider. Additional MD calculations at  $\rho^* = 1.05$  were carried out for the XYZ model, but again no ferroelectric behavior was observed. The Ising model does have a ferroelectric phase; however, at  $\rho^* = 0.8$  spontaneous polarization was observed at  $T^* \approx 25$ , which is much lower than the transition temperature predicted by Zhang and Widom.

## V. DYNAMICALLY DISORDERED SYSTEMS

In the simulations described above, a configuration was selected from a MD simulation of soft spheres at  $\rho^* = 0.8$  and  $T^* = 10.5$ , and was then used as a ‘‘typical’’ randomly frozen system. Point dipoles were embedded at the centers of the soft spheres and rotational MD or MC simulations were performed. Ideally, as in spin glass models [8], many (i.e., 100–1000) randomly frozen configurations should be used to obtain accurate values of the ‘‘disorder-averaged’’ polarization. However, for the dipolar systems considered here this would be a very laborious procedure requiring many long simulations.

As an alternative approach to the study of orientational ordering in random media, we have used a MD simulation technique where the rotational and translational equations of motion are completely decoupled. That is, we consider dipoles embedded in a dynamic random ‘‘substrate’’ rather than in a frozen system. The underlying soft-sphere substrate is a simple fluid. It has no long-range positional correlations, and the short-range correlations are not influenced by the

dipolar interactions (i.e., the spatial correlations are identical to those of a soft-sphere model [Eq. (1)] at a given density and translational temperature). However, the “equilibrium” state of the dipoles will depend on the underlying motion of the substrate. This model is similar in spirit (but not equivalent to due to its lack of obvious energy currents) to those used in recent studies of nonequilibrium phase transitions in magnetic systems subject to Lévy flights [26]. It is fundamentally different from dipolar fluid simulations in that the spatial structure is not affected by dipole-dipole interactions, but it is also not an amorphous solid simulation since the particles move.

With this technique, we can gain a good deal of insight into the role of short-ranged spatial correlations on phase behavior. By controlling the rate that the substrate moves relative to the rate of dipolar reorientations, we can effectively “turn on” or “turn off” the specific details of the random spatial structure which the dipoles “see.” The implementation is straightforward. The force between two particles is simply given by

$$\mathbf{f}(12) = -\nabla_{\mathbf{r}} u_{ss}(12), \quad (5)$$

where  $u_{ss}(12)$  is the soft-sphere potential defined above. The torques are given by the dipole-dipole interactions. The spatial structure of the system is then determined only by the soft-sphere part of the pair potential. The translational and rotational temperatures are decoupled such that the structure and motion of the substrate is not affected by changes in the rotational temperature. The rate at which the substrate moves relative to the dipolar reorientations can be varied by changing the particle mass. Obviously, since it is a classical fluid, adjusting the particle mass will have no effect on the equilibrium structure of the soft-sphere substrate. For large masses, the substrate changes slowly relative to dipole reorientations. An extrapolation to the infinite mass case would give results of a randomly frozen system. For light masses, the substrate moves rapidly relative to dipole reorientations. The substrate motion may be so rapid that the dipoles cannot react to structural details, and a mean-field-like limit is reached [26]. Thus, from a dipole’s point of view, increasing the mass effectively “turns on” the specific structural details of its surrounding dipolar environment. The moving substrate is a means of simulating dipolar systems in a dynamically random medium that lacks any specific spatial correlations. Clearly, in these systems positional correlations which favor ferroelectric order are not present initially and, due to the decoupling, such correlations cannot develop as the system evolves. Contact with the randomly frozen systems can be made by examining the behavior at intermediate masses and then extrapolating to the infinite mass limit.

In the decoupled MD simulations, the underlying substrate is a soft-sphere fluid at  $\rho^* = 0.8$  and  $T^*(\text{translational}) = 10.5$ . All decoupled simulations were carried out using the reduced time step  $\delta t^* = (\varepsilon/m'\sigma^2)^{1/2} \delta t = 0.00125$ , and the reduced moment of inertia  $I^* = I/m'\sigma^2 = 0.025$ . The equations of motion of the soft-sphere substrate were written in terms of the reduced mass,  $m^* = m/m'$ , which could be varied to change the rate of translational motion of the substrate. Note that  $I^*$  and the rotational equations of motion which govern the dipoles have no dependence on  $m^*$ .

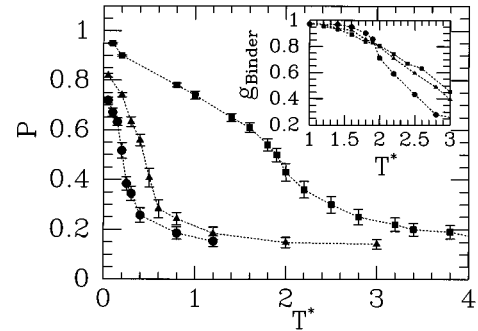


FIG. 5.  $P$  vs  $T^*$  (rotational) for dynamically random XYZ systems. The squares, triangles, and circles are for  $m^* = 1, 5,$  and  $10$ , respectively. The error bars represent one estimated standard deviation.  $g_{\text{Binder}}$  vs  $T^*$  (rotational) is shown in the inset for  $N = 64$  (squares),  $108$  (triangles), and  $256$  (circles) particles.

$P$  versus  $T^*$  (rotational) for the XYZ model is plotted in Fig. 5. Systems with particle masses  $m^* = 1, 5,$  and  $10$  are included. Clearly, spontaneous polarization develops for all systems, and the temperature at which  $P$  begins to rise decreases with increasing mass. For  $m^* = 5$ , the transition occurs at  $T^* \approx 0.55$ , and for  $m^* = 10$ , at  $T^* \approx 0.25$ . For  $m^* = 1$ , we have also calculated the Binder ratio  $g_{\text{Binder}}$ , defined as [8]

$$g_{\text{Binder}} = \frac{5}{2} - \frac{3}{2} \frac{\langle |\mathbf{M}|^4 \rangle}{\langle |\mathbf{M}|^2 \rangle^2}, \quad (6)$$

for systems with  $64, 108,$  and  $256$  particles. A plot of  $g_{\text{Binder}}$  vs  $T^*$  is included as an inset in Fig. 5. A clear crossing, and hence a thermodynamic transition, at  $T^* \approx 1.9$  is evident.

XYZ systems with larger masses (up to  $m^* = 20$ ) were investigated, but all were disordered above  $T^* = 0.1$ . Below  $T^* = 0.1$ , calculations for very large masses converged too slowly to be useful. Similar results were obtained with  $N = 108-$ ,  $256-$ , and  $500$ -particle systems, and the polarization showed no significant dependence on system size. The results shown in Fig. 5 strongly suggest that for any finite mass the XYZ model will spontaneously polarize at some rotational temperature, but as the mass becomes very large the transition temperature will approach zero. As shown in Fig. 6, the dynamically decoupled XY model behaves much as the XYZ system. It can be seen that systems

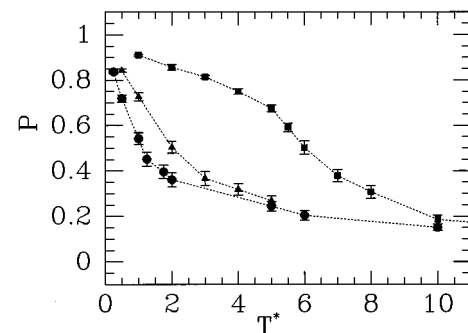


FIG. 6.  $P$  vs  $T^*$  (rotational) for dynamically random XY systems. The squares, triangles, and circles are for  $m^* = 1, 5,$  and  $10$ , respectively. The error bars represent one estimated standard deviation.

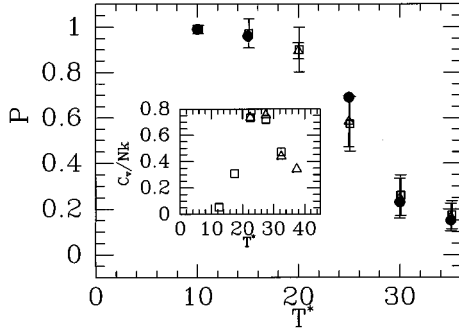


FIG. 7.  $P$  vs  $T^*$  (rotational) for the Ising model. Results are shown for dynamically random systems with  $m^* = 1$  (squares) and 5 (triangles) and for the randomly frozen case (solid circles). The reduced heat capacities per particle,  $C_V/Nk$ , are plotted vs  $T^*$  (rotational) in the inset.

with  $m^* = 1, 5$ , and 10 spontaneously polarize at  $T^*$  (rotational)  $\approx 6, 2$ , and 1.8. Again, the transition temperature decreases with increasing mass.

In the Ising model the potential does not vary as a continuous function of orientation, and hence this model is not well suited to MD simulations. Therefore, a MC scheme was devised that allowed the substrate to move independently of the Ising dipoles. This involved combining a soft-sphere MD simulation with a MC Ising dipole simulation. The soft-sphere substrate evolved as in the XY and XYZ decoupled calculations, however, after each MD time step,  $N$  attempted dipole flips (one MC sweep) were performed using the usual Metropolis Monte Carlo method [25]. In Fig. 7,  $P$  vs  $T^*$  (rotational) results are plotted for  $m^* = 1$  and 5 and the randomly frozen system (i.e.,  $m^* = \infty$ ). We see that the ordering behavior of the Ising model is essentially independent of mass [27] and that the results for the dynamically disordered systems lie very close to those for the randomly frozen case. Reduced constant volume heat capacities per particle,  $C_V/Nk$ , obtained by numerically differentiating the average dipolar energy with respect to the rotational temperature, are also shown in Fig. 7 (see inset) [28]. The randomly frozen and  $m^* = 5$  results are very similar, and indicate a phase transition at  $T^* \approx 25$ .

The dependence of the ferroelectric transition temperature  $T_F^*$  (rotational) on particle mass  $m^*$  for the XY and XYZ models is shown in Fig. 8. The transition temperatures were estimated from heat capacities (see Fig. 8, inset) obtained from numerical differentiation of the dipolar energy per particle. Results for the Ising system are not plotted because the transition temperature is essentially independent of the mass [27]. As the mass increases, the transition temperature drops for both the XY and XYZ models. As noted earlier, for large masses and low rotational temperatures, convergence becomes prohibitively slow, but it seems reasonable to assume that the graph would simply continue with the transition temperature approaching zero in the infinite mass limit. This is clearly consistent with the fact that we did not find a ferroelectric phase for randomly frozen systems at finite temperatures.

## VI. MEAN-FIELD THEORY: ISOLATING THE EFFECT OF LONG-RANGE INTERACTIONS

In order to understand the simulation results discussed above better, it is useful to consider a simple mean-field

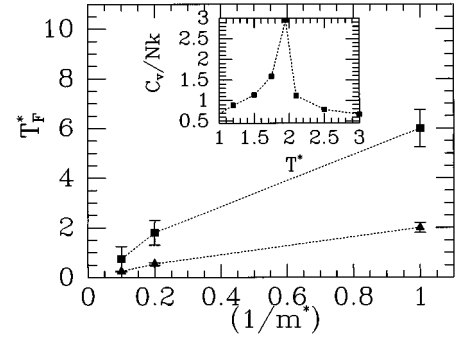


FIG. 8. The mass dependence of the disordered-to-ferroelectric transition temperature  $T_F^*$  (rotational). The squares and triangles are results for the XY and XYZ models, respectively. The values of  $T_F^*$  were obtained from plots of the heat capacity,  $C_V/Nk$ , vs  $T^*$  (rotational), and a typical example is shown in the inset. The error bars represent estimated uncertainties in the peak position.

theory for a system where only long-range reaction field interactions are included. The properties of such a system are completely independent of spatial structure, and it is instructive to compare its behavior with the simulation results for the various models.

We consider  $N$  particles in a spherical cavity of radius  $r_c$ , surrounded by a continuum of dielectric constant  $\epsilon'$ . The reaction field  $\mathbf{R}$  within the cavity arises from the polarization of the surroundings by the dipoles in the sphere, and is given by [25,29]

$$\mathbf{R} = f(\epsilon') \mathbf{M} / r_c^3, \quad (7a)$$

where

$$\mathbf{M} = \sum_{i=1}^N \boldsymbol{\mu}_i, \quad (7b)$$

is the total dipole moment of the sphere and  $f(\epsilon') = 2(\epsilon' - 1)/(2\epsilon' + 1)$ . If, as in the simulations,  $\epsilon' = \infty$ , then  $f(\epsilon') = 1$ , and we shall write all further expressions for this specific case. It is also obvious from the definition of  $f(\epsilon')$  that, as  $\epsilon'$  increases,  $f(\epsilon')$  rapidly approaches 1 and becomes effectively independent of the exact value of  $\epsilon'$ . This is the justification mentioned above for using  $\epsilon' = \infty$  in simulations of dipolar systems with large dielectric constants.

The total instantaneous energy of the system,  $U$ , can be written in the form

$$U = -\frac{1}{2} \sum_{i=1}^N \boldsymbol{\mu}_i \cdot \mathbf{R}, \quad (8)$$

where the factor  $\frac{1}{2}$  arises when one calculates the energy of a point dipole in a reaction field [25,29,30]. It takes account of the work required to polarize the surrounding continuum. Clearly, the low-energy state is when the dipoles are aligned with the reaction field. Using Eqs (7),  $U$  can be expressed in the form

$$U = -\frac{2\pi}{3} \rho \mu^2 \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N \hat{\boldsymbol{\mu}}_i \cdot \hat{\boldsymbol{\mu}}_j, \quad (9)$$

where we have also used  $N=4\pi r_c^3\rho/3$  and  $\rho=N/V$ .

In the canonical ensemble, the average polarization can be obtained by evaluating

$$P = \frac{\int P_{\text{ins}} e^{-\beta U} d\mathbf{\Omega}^N}{\int e^{-\beta U} d\mathbf{\Omega}^N}, \quad (10)$$

where  $P_{\text{ins}} = (1/N) \sum_{i=1}^N \hat{\boldsymbol{\mu}}_i \cdot \hat{\mathbf{d}}$  is the instantaneous polarization, and  $d\mathbf{\Omega}^N$  represents integration over the angular coordinates of the  $N$  particles (here  $\hat{\mathbf{d}}$  defines the  $z$  axis of the coordinate system). If we make the mean-field approximation [31]

$$(\hat{\boldsymbol{\mu}}_i - P\hat{\mathbf{d}}) \cdot (\hat{\boldsymbol{\mu}}_j - P\hat{\mathbf{d}}) = 0, \quad (11)$$

then Eq. (9) simplifies to

$$U \approx -\frac{4\pi}{3} \rho \mu^2 P \sum_{i=1}^N \hat{\boldsymbol{\mu}}_i \cdot \hat{\mathbf{d}} + \frac{2\pi}{3} \mu^2 N P^2, \quad (12)$$

and Eq. (10) can be easily solved for  $P$ . Actually, here we dealing with an effective infinite-range system where each dipole is coupled with every other dipole with the coupling constant  $2\pi\rho\mu^2/3N$  [see Eq. (9)]. In this infinite-range case, the mean-field solution is equivalent to the Hubbard-Stratonovich solution and is essentially exact [32]. For the  $XYZ$ ,  $XY$ , and Ising models, respectively, one obtains

$$P = \coth(x) - 1/x, \quad (13a)$$

$$P = \frac{I_1(x)}{I_0(x)}, \quad (13b)$$

$$P = \tanh(x), \quad (13c)$$

where  $x = 4\pi\rho\beta\mu^2 P/3$  and  $I_n(x)$  is the modified Bessel function of order  $n$ . The average energy per particle is given by

$$\langle U \rangle / N = -2\pi\rho\mu^2 P^2/3, \quad (14)$$

and the constant volume heat capacity can be obtained by taking the derivative with respect to temperature.

The mean-field theory predicts ferroelectric transitions for all three models. By expanding Eqs. (13) about  $x=0$ , one finds that the mean-field ferroelectric transition temperatures are given by

$$T_F^* = 4\pi\rho^* \mu^{*2}/3n, \quad (15)$$

where  $n$  is the number of dipole components. For the Ising and  $XYZ$  models, Eq. (15) agrees with the ‘‘conventional mean field’’ results given by Zhang and Widom [15]. For the present parameters ( $\mu^* = 4$ ,  $\rho^* = 0.8$ ) the transition temperatures obtained are 17.9, 26.8, and 53.6 for the  $XYZ$ ,  $XY$ , and Ising models, respectively. We emphasize that the driving force for the transition in this simple theory is just the reaction field due to the self-consistent polarization of the surrounding continuum.

It is clear from the above discussion that the reaction field interactions favor ferroelectric order for all three models. However, as described in Secs. IV and V, computer simula-

tions of randomly frozen or dynamically decoupled systems indicate the existence of ferroelectric order only for the Ising model. Ferroelectric phases were not observed for the  $XY$  and  $XYZ$  models, and the MD evidence strongly suggests that these systems are unpolarized at all finite temperatures. This behavior can be explained if we consider that the reaction field  $\mathbf{R}$  is only one contribution to the total local field  $\mathbf{E}_{\text{local}}$  experienced by a particle. The local field can be written as

$$\mathbf{E}_{\text{local}} = \mathbf{R} + \mathbf{E}, \quad (16)$$

where the remaining contribution  $\mathbf{E}$  is dependent on positional correlations, and may or may not favor ferroelectric order. If  $\mathbf{R}$  dominates, ferroelectric phases are to be expected. However, if the local field is largely determined by  $\mathbf{E}$ , then the existence, or nonexistence of ferroelectric phases will depend on the details of the spatial correlations (e.g., as in Bravais lattices).

From this point of view, it is useful to divide the average energy obtained in the simulations into reaction field (RF) and structurally dependent (SD) parts such that

$$\langle U \rangle = \langle U_{\text{RF}} \rangle + \langle U_{\text{SD}} \rangle. \quad (17)$$

Of course,  $\langle U_{\text{RF}} \rangle$  depends only on particle orientation with respect to  $\mathbf{R}$ , whereas  $\langle U_{\text{SD}} \rangle$  will be sensitive to details of the local spatial structure experienced by a particle. The total energy and both contributions obtained in dynamically decoupled simulations of all three models are shown as functions of  $T^*$  (rotational) in Fig. 9. Results for different values of the reduced mass are included. For all three models we see that  $\langle U_{\text{RF}} \rangle$  dominates in the ferroelectric state, and that  $\langle U_{\text{SD}} \rangle$  dominates in the paraelectric phase. In fact, in all cases, as the system becomes ferroelectric  $\langle U_{\text{SD}} \rangle$  increases (i.e., becomes less negative), indicating that the structurally dependent interactions do not favor ferroelectric order.

For the  $XYZ$  [Fig. 9(a)] and  $XY$  [Fig. 9(b)] models, the different contributions to the energy are strongly mass dependent. As the mass increases, and the particles move more and more slowly,  $\langle U_{\text{SD}} \rangle$  dominates at lower and lower rotational temperatures. Thus, if we begin at a fixed rotational temperature in the ferroelectric phase and increase the mass, the dipoles eventually respond to the details of the random local structure,  $\langle U_{\text{SD}} \rangle$  dominates, and the ferroelectric phase disorders. The Ising model does not exhibit this behavior. In the Ising case both contributions to the energy are largely independent of mass [Fig. 9(c)], and a stable, mass-independent, ferroelectric phase is observed. The difference in behavior of the Ising model must arise from the fact that, with only two dipolar directions available, its response to local structure is much more limited than that possible for the  $XY$  and  $XYZ$  systems.

## VII. SUMMARY AND CONCLUSIONS

In this paper, we used computer simulation methods to explore the phase behavior of spatially disordered dipolar systems. Both randomly frozen and dynamically disordered models were considered. It was found that the behavior observed depended upon the number of components included in the dipoles. Ferroelectric phases were not observed for the

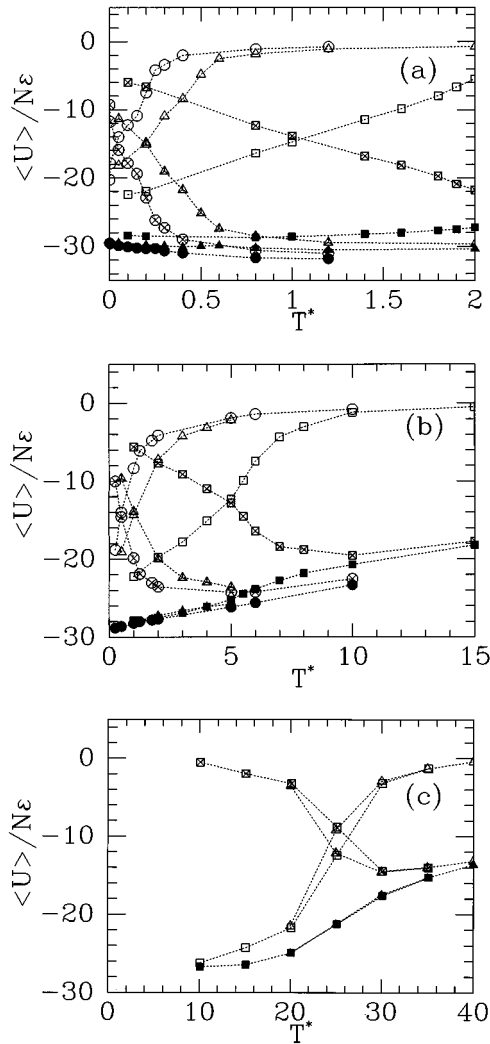


FIG. 9. The contributions to the average energy for the XYZ (a), XY (b), and Ising (c) models.  $T^*$  is the rotational temperature. The solid, crossed, and open symbols denote  $\langle U \rangle$ ,  $\langle U_{SD} \rangle$ , and  $\langle U_{RF} \rangle$ , respectively. The squares, triangles and circles indicate  $m^* = 1, 5$ , and 10, respectively.

randomly frozen XY and XYZ models. Rather, these systems appear to freeze orientationally into dipolar glasses as the temperature is lowered. The behavior of the randomly frozen Ising model was significantly different. This model does have a stable ferroelectric phase at sufficiently low temperatures.

We also considered dynamically disordered systems simulated such that the translational motion of the particles was independent of the dipolar forces. The rate of translational motion was adjusted by varying the particle mass. Interacting dipoles embedded in this moving substrate can respond to the short-range spatial structure only if the motion is sufficiently slow. For small masses (rapid translational motion), ferroelectric phases were observed for all three models. However, as the mass is increased and the dipoles become “aware” of the short-range random structure, the ferroelectric order is destroyed in the XY and XYZ models. In the infinite mass limit both the XY and XYZ models appear to be paraelectric at all temperatures. This is consistent with our observations for randomly frozen systems. In contrast, the Ising model exhibits a paraelectric-to-ferroelectric transition at a temperature which is essentially independent of mass, and agrees with the result for the randomly frozen case.

In order to understand our observations, it is useful to divide the total local field experienced by a dipole into two parts. These are a reaction field contribution which has no dependence on the local spatial structure, and a structure-dependent part which includes everything else. Clearly, the average total energy can be divided into corresponding reaction field and structure-dependent contributions. Both contributions to the total energy were evaluated in our simulations. In all systems where ferroelectric order exists, it was shown to be stabilized by the reaction field interactions. In spatially random systems, the structure-dependent contribution never favors ferroelectric order. In the XY and XYZ models, the structure-dependent part dominates, and paraelectric dipolar glasses rather than ferroelectric phases are observed. For the Ising model, the reaction field contribution dominates, and ferroelectric order is observed. In all likelihood, the Ising model differs from the XY and XYZ systems simply because with a one-component dipole the opportunities for strong local interactions are severely limited.

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