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Orientational relaxation in a random dipolar lattice: Wave-number and frequency dependence

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In order to understand the role of translational modes in the orientational relaxation in dense dipolar liquids, we have carried out a computer ''experiment'' where a random dipolar lattice was generated by quenching only the translational motion of the molecules of an equilibrated dipolar liquid. The lattice so generated was orientationally disordered and positionally random. The detailed study of orientational relaxation in this random dipolar lattice revealed interesting differences from those of the corresponding dipolar liquid. In particular, we found that the relaxation of the collective orientational correlation functions at the intermediate wave numbers was markedly slower at the long times for the random lattice than that of the liquid. This verified the important role of the translational modes in this regime, as predicted recently by the molecular theories. The single-particle orientational correlation functions of the random lattice also decayed significantly slowly at long times, compared to those of the dipolar liquid. [S1063-651X(96)07810-5]

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I. INTRODUCTION

The objective of this work is to present the results of a computer ''experiment'' on orientational relaxation in a random dipolar lattice. This lattice was created by quenching the translational modes of the dipolar molecules from an equilibrated liquid configuration. A preliminary report of this work has been presented elsewhere, where the emphasis was on dielectric relaxation. Here we report the results of our molecular-dynamics calculations of the wave-vector-dependent collective orientational correlation functions (and also of the single-particle properties) for the random dipolar lattice. The main motivation of the present work is to understand the role of translational modes in orientational relaxation. We present a detailed comparison between the dynamics of a pure dipolar liquid and that of the random dipolar lattice. The results obtained here seem to confirm the important role of the translational modes predicted by the recent theoretical studies.

Madden and Kivelson [1] addressed the importance of the role of translation in the dielectric friction. These authors demonstrated that the translational modes can reduce the magnitude of dielectric friction significantly. Subsequently, several workers [2,3] have presented a more general approach based on an extended molecular hydrodynamic theory. This latter approach takes into account the effects of the local intermolecular correlations on the translational motion properly. This molecular theory also leads to the conclusion that the translational modes can reduce the dielectric friction drastically. The theory further predicts that while dielectric relaxation of a dipolar liquid can be strongly non-Debye in the absence of any translational motion of the dipolar molecules, it can be almost entirely Debye-like in the presence of a sizable translational contribution.

The reason for the predicted strong influence of the translational modes on orientational relaxation can be easily understood on simple physical grounds. In a dense dipolar liquid, the short-range local orientational correlations are significant. These correlations can give rise to a caging of the orientational degree of freedom that slows down the dynamics on molecular length scales. These correlations play an important role in determining the nature of the frequency dependence of dielectric friction. In the absence of the translational contribution, the decay of these local correlations is very slow in strongly polar dipolar liquids. This may give rise to a slowly decaying long-time tail in the torque-torque correlation function [4], which, in turn, can give rise to a subdiffusive slow long-time decay of the orientational correlation functions. However, in the presence of a significant translational contribution (as is normally available in liquids), the decay of local correlations is much faster, leading to a much smaller value of the friction at low frequency. As a result, the decay of orientational correlations is predicted to be highly nonexponential in the absence of translation but exponential-like in the presence of the same. These detailed predictions have been corroborated by other theoretical studies. In all the theoretical studies, the natural dynamic quantities are the wave-number- (k) and the frequency- (z) dependent orientational correlation functions that are predicted to show interesting dynamics at the intermediate wave numbers ($k=2\pi/\sigma$, where σ is the molecular diameter).

Direct experimental verification of the theoretical predictions, however, appear to be more difficult. Grochulski, Pszczolkowski, and Kempka [5] have studied the dielectric relaxation of a group of polar, near spherical molecules (1,1,1-trichloroethane, *t*-butyl chloride, and 2,2-dinitropropane). These molecules form plastic crystalline phases and hence on going from the liquid to the plastic-crystal phase it should be possible to observe experimentally the effect of freezing out translational degrees of freedom on the shape of the relaxational profile. Grochulski, Pszczolkowski, and Kempka found that for the whole class of small, rigid, and polar molecules the influence of rotational-translational coupling via dielectric friction was

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almost negligible. They concluded that the theory of Bagchi and Chandra [3] overestimated the effect of translational-rotational coupling on dielectric relaxation of liquids. Note, however, that as the systems studied in the experiments undergo a phase transition, the extent of orientational correlations in the new phase may differ considerably from that present in a dense liquid. In addition, the high symmetry of the plastic crystalline phase may hinder the formation of adequate local orientation correlation that would be present in a dense dipolar liquid and is predicted to be the reason for the strong influence of the translational modes. However, the experimental studies of Grochulski, Pszczolkowski, and Kempka raise several interesting questions. For example, what really controls the extent and the nature of the rotational and translational coupling in a dipolar liquid? Are they controlled entirely by the static correlations or do the dynamics also play an important role? The answers to these questions cannot be obtained easily by experiment because the role of rotational and translational motion change similarly with the change in the temperature and pressure. In such a case, the ideal choice would be to think of a simple model in which the effects of rotational and translational coupling can be controlled separately. The random dipolar lattice provides such a model system.

One should also mention here the recent computer simulation studies of orientational relaxation in Brownian dipolar lattices [6,7]. These studies clearly show the emergence of the non-Debye behavior as the polarity of the system is increased. Unfortunately, the scope of this study was somewhat limited because the maximum static dielectric constant of this lattice is only around 18 due to an impending ferroelectric phase transition. So, if one wants to study the dynamics of dense dipolar liquid then one should opt for a simple system with high dielectric constant (ϵ) where the above-mentioned effects are really significant. The simple models that one can think of are the dipolar soft-sphere and the Stockmayer liquid [8–12]. Therefore, we have performed detailed molecular-dynamics simulations of the soft-sphere dipolar liquid [8–11] and the Stockmayer liquid [11,12] and the corresponding random lattices. The statics and dynamics of these liquids have already been studied in considerable detail, which has helped us in checking our results. As already mentioned, the random lattices have been formed by quenching the translation motion and allowing only the rotational motion to exist.

There is an additional motivation to carrying out the present study. This motivation comes from the conjecture that the spatial density relaxation may be important in controlling the degree of nonexponentiality in supercooled liquids near the glass transition. It is known that molecular relaxation processes in general, and orientational dynamics in particular, exhibit marked nonexponentiality in supercooled liquids near the glass transition temperature. This nonexponentiality is so general that one often refers to it as ‘‘universal’’ to all supercooled liquids [13–16]. This nonexponentiality is sometimes explained by assuming that the liquid is heterogeneous in the time scale of the relaxation being probed; it is nearly exponential in a given environment, but the rates vary significantly among the environments. In an alternate picture, the liquid is imagined to be homogeneous while each molecule relaxes in an intrinsically nonexponential manner because of length-dependent intermolecular correlations present in a dense liquid. The latter model lies at the heart of many sophisticated theories such as mode coupling and other theories of glass transition [17–19]. Depending on the nature of the system studied, such as a simple molecular liquid or a networked liquid, one of the two extreme viewpoints may provide a more appropriate description. In fact, both Angell [16] and Ngai [20,21] have suggested that the degree of nonexponentiality may be correlated with the degree of fragility of the liquid. However, these concepts and pictures are yet to be incorporated in a quantitative description of orientational relaxation. Recently, several experiments [22–24] have been performed that measured selectively the orientational dynamics of a *subensemble* of relaxing vectors: the results were strikingly different from those which measure only the *average relaxation* of all the vectors. These experiments, performed not only on the simple liquids but also on the polymeric ones, reveal that this *few-particle* microscopic correlation time is 50–200 times larger than the *average* relaxation time. This naturally has led to the conclusion that the nonexponentiality observed in these liquids is at least partly due to spatially heterogeneous distribution of correlation times. Thus, while the system is still ergodic over a long-time scale, probes scattered over the whole system seem to probe different microenvironments of the system. Near the glass transition, these different microstates may have widely different relaxation dynamics, which in turn can lead to a marked nonexponentiality.

The above experimental results [22–24] also indicate that the *relaxation of these microdomains themselves may be slaved to the rate of density relaxation*, the latter being determined largely by the translational diffusion of the molecules [22,23]. Thus there may exist a different dynamic coupling between the translational and the rotational dynamics in the supercooled liquid and this again has two aspects. First, when the spatial density relaxation becomes slow, the orientational dynamics also becomes slow, not only because the viscosity is large but also because the translational motions may no longer be able to assist in the decay of the local orientational correlations. Second, these translational motions themselves can be even slower in these microdomains (which are often of higher density) leading to even slower orientational relaxation. The latter effect becomes significant near the glass transition. Clearly, these two effects are synergetic, which may explain the observed large (two orders of magnitude) increase of relaxation times in the slow domains.

The above results again raise the same questions we asked before, namely, how strong is the coupling of the translational motion in orientational relaxation? Another question that arises is the maximum realizable extent of nonexponentiality when the translational modes are totally absent. The latter may provide a quantitative measure of the nonexponentiality predicted by the homogeneous mechanism. It is also relevant in quantifying the heterogeneous picture of nonexponential relaxation. An earlier, theoretical calculation [2,3] predicted that the dielectric relaxation can be strongly non-Debye in the absence of the translational modes. However, this prediction was contested in an experimental study [5] of dielectric relaxation on dipolar liquids that raised doubts and also questions on the influence of the translational modes. Note that the answers to the questions raised above are also important in understanding the effects of dynamic disorder on the net translational diffusion coefficient of a supercooled liquid [25] and also the effects of such environmental fluctuations on chemical reactions [26].

The third motivation of the present work comes from recent studies [27,28] on ultrafast solvation dynamics. These studies have raised several interesting questions regarding the connection between the orientational relaxation and the solvation dynamics. An important ingredient of most molecular theories of solvation dynamics is the wave-vector- and frequency-dependent collective orientational memory (or dissipative) function [2]. Theoretical studies suggest that this memory function may depend strongly on the translational modes of the liquid, particularly at the intermediate wave vectors. Such predictions can be easily tested via computer simulations.

The organization of the rest of the paper is as follows. In the next section we explain the computational details. Section III contains the results of our molecular-dynamics simulations of dipolar liquids, while Sec. IV contains the same for the random dipolar lattice. Section V contains the results of the wave-vector- and frequency-dependent orientational correlation functions. Section VI concludes with a brief discussion of the results.

II. COMPUTATIONAL DETAILS

We model the dipolar liquid by two different potential forms: the dipolar soft-sphere [8] and the Stockmayer [12] potentials. The dipolar soft-sphere potential is given by

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

where

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

is the soft-sphere part and $u_{DD}(12)$ is the dipolar part.

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

In the above equation, μ_1 is the dipole moment of the particle **i** and $\mathbf{r}=\mathbf{r}_2-\mathbf{r}_1$. The Stockmayer liquid has the potential form

$$u(12)^{\mathrm{St}}=u_{\mathrm{LJ}}+u_{DD}(12), \tag{4}$$

with

$$u_{\mathrm{LJ}}=4\epsilon_{\mathrm{SS}}[(\sigma/r)^{12}-(\sigma/r)^6]. \tag{5}$$

Here ϵ_{SS} and σ are the parameters characterizing the energy and the diameter of the dipolar soft-sphere, Lennard-Jones (LJ) and the Stockmayer potentials.

The long-range nature of the dipole-dipole potential given by Eq. (3) requires that care must be taken in specifying the boundary conditions in these systems. It has also been found [8,12,29] that the boundary condition employed in a computer simulations of a polar liquid can have a large impact upon the dynamic behavior studied. These boundary conditions are an effort to mimic the true behavior of the infinite system. Two different approaches are now widely used: The reaction field method [31–33] and the Ewald summation method [31,33–36]. The reaction field method truncates the dipole-dipole interaction at a distance (r_c) from each particle and approximates the medium beyond this separation by dielectric continuum with a dielectric constant (ϵ_{RF}). A main drawback of this method is that it requires an initial guess of the dielectric constant of the medium. In addition, the energy in these simulations is not conserved in a microcanonical or constant-NVE molecular-dynamics simulation [31]. The Ewald summation method [8,31] considers a macroscopic spherical sample composed of a large number of periodic replicas of the basic simulation cell, which is again surrounded by a dielectric continuum characterized by ϵ_{RF}. This approach is commonly referred to as periodic boundary conditions (PBCs) [8]. In the present study we consider only the PBC where the dipole-dipole interactions have been estimated using the Ewald summation technique.

The potential form U_{DD} using Ewald summation can be given as follows. The potential at a single site is given by the expression

$$u_{DD}^{\mathrm{PBC},\epsilon_{\mathrm{RF}}}(12)=-(\boldsymbol{\mu}_1\cdot\boldsymbol{\nabla})(\boldsymbol{\mu}_2\cdot\boldsymbol{\nabla})\psi(r)+\frac{4\pi}{(2\epsilon_{\mathrm{RF}}+1)L^3}\,\boldsymbol{\mu}_1\cdot\boldsymbol{\mu}_2, \tag{6}$$

where $\psi(r)$ is given by [8]

$$\psi(\mathbf{r})=\frac{1}{L}\sum_{\mathbf{n}}\frac{\mathrm{erfc}(\alpha|\mathbf{r}/L+\mathbf{n}|)}{|\mathbf{r}/L+\mathbf{n}|}+\frac{1}{\pi L}\sum_{\mathbf{n}\neq\mathbf{0}}\frac{1}{n^2}\exp\left(\frac{-\pi^2n^2}{\alpha^2}+\frac{2\pi i}{L}\,\mathbf{n}\cdot\mathbf{r}\right), \tag{7}$$

where α is the convergence parameter. L is the cubic simulation box length. $\mathbf{n}=(l,m,n)$ is the lattice sum, and erfc is the complementary error function.

There are three different parameters that must be specified in the calculation of the Ewald summation techniques and each will influence the accuracy of the results [8]. These parameters are the truncation of the real-space and the Fourier space contributions and the value of the convergence parameter (α). The α is usually chosen to be large enough so that the only term that contributes to the sum in real space is that with $\mathbf{n}=(0,0,0)$ and so the first term in the equation for $u_{DD}^{\mathrm{PBC},\epsilon_{\mathrm{RF}}}(12)$ reduces to the normal minimum image convention. Next we consider the sum over reciprocal vectors **k**. The values of **k** are restricted to $\mathbf{k}=2\pi\mathbf{n}/L$ [31]. In a simulation, the aim is to choose a value of α and a sufficient number of **k** vectors so that the above equation with the real space truncated at $\mathbf{n}=\mathbf{0}$ gives the same energy for typical liquid configurations. The values for all the above-mentioned parameters have been taken from the paper of Kusalik [8], who has done an exhaustive study of the soft-sphere dipolar systems. The values of all the parameters used in simulations are tabulated in Table I.

TABLE I. Parameters employed in evaluating the Ewald summation for the dipolar soft-sphere liquid simulations. The values have been obtained from Ref. [8].

N	R	$n^2_{\max}$	α
256	2.56σ	38	5.75

The nondipolar part is handled using the potential truncation and the minimum image convention. For the soft-sphere dipolar and Stockmayer liquids the nondipolar part of the potential (i.e., the soft-sphere and the Lennard-Jones potentials) was truncated at 2.56σ.

All the molecular-dynamics simulations reported in this paper have been performed using 256 particles using conducting boundary conditions ($\epsilon_{RF}=\infty$) [8,31,37]. The reasons for choosing the conducting boundary conditions in our simulations is because the dipolar liquids we consider are highly dense isotropic liquids and their dielectric constants have been found to be larger [8]. Therefore, we would expect the usual Ewald-Kornfeld boundary conditions that correspond to $\epsilon_{RF}=\infty$ to give a good approximation to infinite-system behavior. The number dependence for the soft-sphere dipolar liquid have already been studied by Kusalik [8], who found that 256 dipolar soft spheres are sufficient to mimic the most of the macroscopic properties. This applies also for Stockmayer liquid model reported in this paper. The equations of motion are solved using leapfrog scheme suggested by Fincham [31,38,39]. It is convenient to characterize the dipolar soft-sphere and Stockmayer systems by the reduced density $\rho^*=\rho\sigma^3$, the reduced temperature $T^*=k_BT/\epsilon_{SS}$, and the reduced dipole moment $\mu^*=\sqrt{(\mu^2/\epsilon_{SS}\sigma^*)}$, where ρ is the number density, T is the absolute temperature, and k is the Boltzmann constant. Simulations have been performed for fixed values of ρ^* and T^*, given by $\rho^*=0.8$ and $T^*=1.35$. Three values of dipole moments were considered: $\mu^*=2.0$, 1.5, and 0.5. The reduced moment of inertia ($I^*=I/m\sigma^2$) was taken to be 0.025 and the reduced times step $\Delta t^*=\Delta t/\sqrt{m\sigma^2/\epsilon_{SS}}=0.0025$. Equilibrations have been done over 2×10^5 time steps and the averages have been mostly computed over 2.5×10^5 time steps. Error bars representing the statistical uncertainty in the dielectric constant were determined using block average as suggested by Allen and Tildesley [31] with each block of length 25×10^3 time steps each.

For each of the systems studied and at each polarity, we generated a quenched state, in which the translational motion of each molecule is removed and only the rotational motions are allowed. These quenched states have been prepared using the following procedure. Initial configurations for these simulations have been taken from well-equilibrated liquid simulation runs. These configurations are then quenched and equilibrated, for 1.2×10^5 time steps, and production runs were continued for another 1.5×10^5 time steps. Such a state will be positionally and orientationally disordered and hence we call it a random lattice. Three different random lattices have been formed for each system and for each polarity studied. The results obtained from each of the three different random lattices were nearly the same. The results given in this article correspond to one such random lattice.

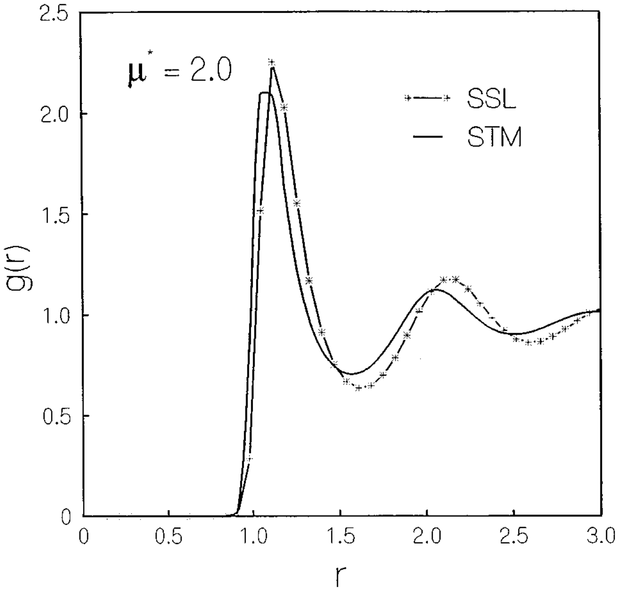

FIG. 1. Comparison of the radial distribution for the dipolar soft-sphere liquid (markers with a solid line) and the Stockmayer liquid (solid line) at $\mu^*=2.0$, $\rho^*=0.8$, and $T^*=1.35$. Note that r is expressed in reduced units.

III. COMPUTATIONAL RESULTS ON LIQUID

A. Static properties

In Fig. 1, we plot the radial distribution function for both the soft-sphere dipolar liquid and the Stockmayer liquid, at $\mu^*=2.0$. As expected for the liquid phase, the $g(r)$ tends to 1 as $r\rightarrow\infty$. These calculations are reported to show that our simulation results agree closely with those of Kusalik [8]. As one can see, the $g(r)$ for dipolar soft-sphere and Stockmayer fluids differ at least in two ways. Not only is the $g(r)$ more structured for the dipolar soft-sphere liquid but the whole function is also shifted by a constant factor to large separa-

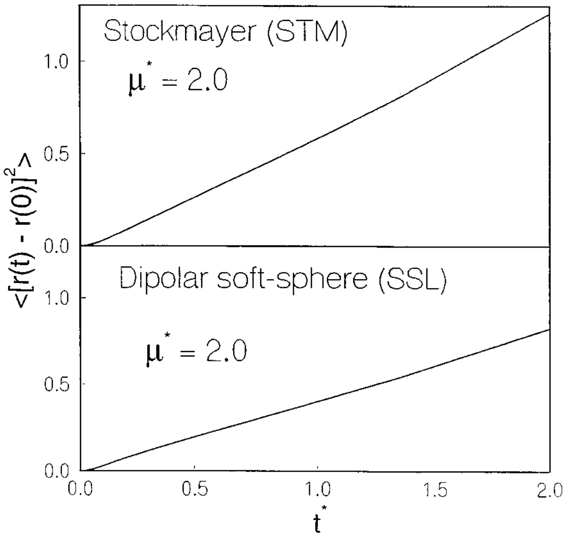

FIG. 2. Mean-square displacement as a function of the reduced time for the soft-sphere dipolar liquid (SSL) and the Stockmayer liquid (STM) for $\mu^*=2.0$, $\rho^*=0.8$, and $T^*=1.35$.

tions. This can be understood because the dipolar soft-sphere liquid without the attractive part of the Lennard-Jones have a large ''effective radius'' that makes the $g(r)$ shift by a constant factor.

In order to confirm the liquid phase, we calculated the mean-square displacement $\langle|\mathbf{r}_i(t)-\mathbf{r}_i(0)|\rangle$, where $\mathbf{r}_i(t)$ is the position vector of molecule i at time t. For fluids the mean-square displacement (MSD) continually increases with time varying linearly at long times according to the Einstein relationship [31]

$$\langle|\mathbf{r}_i(\mathbf{t})-\mathbf{r}_i(\mathbf{0})|^2\rangle=6Dt, \tag{8}$$

where D is the translational diffusion coefficient. Figure 2 shows the respective MSD for the soft-sphere dipolar liquid and the Stockmayer liquid at $\mu^*=2$. As expected, the MSD plots for the two models (soft-sphere dipolar and Stockmayer) in their liquid phase shows a linear dependence with time. The Stockmayer liquid shows slightly faster diffusion. This can be interpreted in terms of Fig. 1. Since the soft-sphere liquid is more structured at molecular length scales, a tagged particle experiences more frictional force in this liquid. The latter follows from the recent mode-coupling expression of the friction in terms of the density modes [40].

The static dielectric constant ϵ is a fundamental property of polar liquids [41] and thus remains a major focus of research interest. Unfortunately, the determination of this quantity by computer simulation is known to give both conceptual [12,29,30] and computational difficulties [8]. In order to obtain reliable estimates of the ϵ the simulations should be long enough to yield $\langle M\rangle^2/\langle M^2\rangle\approx 0$. In practice, for a strongly interacting polar liquids, such as the ones considered in this work, the ratio may not be exactly zero. But, in our simulations we get a ratio $\langle M\rangle^2/\langle M^2\rangle\approx 0.1$ [9]. Dielectric constants (ϵ) reported in this work were obtained from the mean-square fluctuations $\langle\mathbf{M}^2\rangle$ of the total dipole moment of the system [31]. In general the relative permittivity ϵ of the system is not the same as that of the surrounding medium ϵ_{RF}. The expression for calculating ϵ from the simulation can be written as [31]

$$\frac{1}{\epsilon-1}=\frac{1}{3yg(\epsilon_{\mathrm{RF}})}-\frac{1}{(2\epsilon_{\mathrm{RF}}+1)}. \tag{9}$$

where $g(\epsilon_{\mathrm{RF}})$ is related to the fluctuations in the total dipole moment of the simulation box

$$g=g(\epsilon_{\mathrm{RF}})=\frac{\left\langle\left|\sum_{i=1}^{N}\mu_i\right|^2\right\rangle-\left\langle\left|\sum_{i=1}^{N}\mu_i\right|\right\rangle^2}{N\mu^2}. \tag{10}$$

The calculated value of g factor depends upon ϵ_{RF} through the simulation Hamiltonian. When $\epsilon_{\mathrm{RF}}=\infty$, the above equation reduces to the Clausius-Mosotti result [31]

$$\epsilon=1+3yg(\infty). \tag{11}$$

where $y=4\pi\rho\mu^2/9k_BT$.

TABLE II. Results for dipolar soft sphere fluids at $\rho^*=0.8$ and $T^*=1.35$. Note that the $U_{DD}/N\epsilon_{\mathrm{SS}}$ is the reduced dipole-dipole energy per particle and $U/N\epsilon_{\mathrm{SS}}$ is the reduced total energy per particle. The values for ϵ given in parentheses are estimates of the uncertainties.

μ^*	$U_{DD}/N\epsilon_{\mathrm{SS}}$	$\langle U\rangle/N\epsilon_{\mathrm{SS}}$	ϵ
1.5	−2.783	2.397	19.35(±3.0)
2.0	−6.061	−0.69	88.0(±2.0)

Molecular-dynamics results for the average dipole-dipole energy $\langle U_{DD}\rangle/N\epsilon_{\mathrm{SS}}$, total configurational energy $\langle U\rangle/N\epsilon_{\mathrm{SS}}$, total moment squared $\langle M^2\rangle$, and the static dielectric constant for the two systems, the soft-sphere dipolar liquid and the Stockmayer liquid, have been presented in Table II. In fact, such a comparative study had been presented earlier by Kusalik [11]. His results were similar to the ones reported here except for a dipole moment of $\mu^*=1.65$. The value of the dielectric constants of the random lattices were found to be slightly smaller than that of the corresponding liquids. For example, the dielectric constant (ϵ) of the dipolar soft-sphere liquid for $\mu^*=2.0$ was 88±2 for the liquid and 88±3 for the corresponding random lattice.

The possible existence of orientationally ordered phases was monitored for both liquids and random lattices (for both soft-sphere dipolar and Stockmayer) by calculating the equilibrium first- and second-rank orientational order parameters $\langle P_1\rangle$ and $\langle P_2\rangle$, respectively. The instantaneous second-rank order parameter P_2 was taken to be the largest eigenvalue of the ordering matrix $\mathbf{Q}$ with elements by [9,10]

$$Q_{\alpha\beta}=\frac{1}{N}\sum_{i=1}^{N}\tfrac{1}{2}(3\mu_\alpha^i\mu_\beta^i-\delta_{\alpha\beta}), \tag{12}$$

where N is the number of particles in the simulation box and μ_α^i is the α component of the unit vector $\hat{\mu}_i$. The corresponding eigenvector is the instantaneous director $\hat{\mathbf{d}}$. The instantaneous first-rank order parameter P_1 is defined by [9,10]

$$P_1=\frac{1}{N}\left|\sum_{i=1}^{N}\hat{\boldsymbol{\mu}}_i\cdot\hat{\mathbf{d}}\right|. \tag{13}$$

The equilibrium order parameters are the ensemble averages of P_1 and P_2. The equilibrium order parameters for both the models in both the phases (liquid and random lattice) have been computed and found to be close to zero, suggesting the inexistence of macroscopic order in the liquid and the random dipolar lattice (RDL).

B. Dynamic properties of dipolar liquids

The normalized autocorrelation function $[C_A(t)]$ of a microscopic quantity $A_i(t)$ associated with the ith molecule is computed in the molecular-dynamics simulations using the expression

$$C_A(t)=\lim_{T\to\infty}\frac{1}{T}\int_0^T ds\, A(s)A(t+s)\bigg/\lim_{T\to\infty}\frac{1}{T}\int_0^T ds\, A(s)A(s). \tag{14}$$

In this expression the dynamic quantity can be force, torque, position, or angular velocity of the particles present in the system. Correspondingly, we get the respective time autocorrelation functions [31]. In Fig. 3 the torque autocorrelation function $[C_T(t)]$ and its power spectrum have been shown for dipolar-soft spheres at $\mu^*=2$. The Fourier transforms consist of a well-developed, although not a very broad, peak with a short high-frequency tail.

Of particular importance for the interpretation of light-scattering experiments and dielectric relaxation experiments are the orientational time correlations [42]. In Fig. 4 we present the semilogarithmic plot of normalized time correlation functions for the collective moment $[C_M(t)]$ for both the dipolar soft-sphere and the Stockmayer liquid models at $\mu^*=1.5$.

$$C_M(t)=\langle \mathbf{M}(t)\cdot\mathbf{M}(0)\rangle/\langle M^2\rangle, \tag{15}$$

where $\mathbf{M}(t)=\Sigma_i^N\boldsymbol{\mu}_i(\mathbf{t})$. Figure 5 shows the time dependence of the single-dipole autocorrelation function $C_1(t)$ for both systems (soft-sphere liquid and Stockmayer),

$$C_1(t)=\langle \boldsymbol{\mu}(t)\cdot\boldsymbol{\mu}(0)\rangle/\mu^2. \tag{16}$$

It can be seen from Figs. 4 and 5 that the relaxation time for the dipolar soft-sphere systems is slightly shorter than that for the Stockmayer fluid [11]. This is opposite the behavior observed for the translational diffusion. This may be due to the attractive part of the Lennard-Jones potential, which makes the particles to come closer in the Stockmayer liquid (as evident from Fig. 1). When the particles are closer the dipole-dipole interactions are larger, which gives rise to greater friction and this makes the decay slower. This is, of course, a tentative explanation: a detailed theoretical study is required to fully understand the differences between the two liquids.

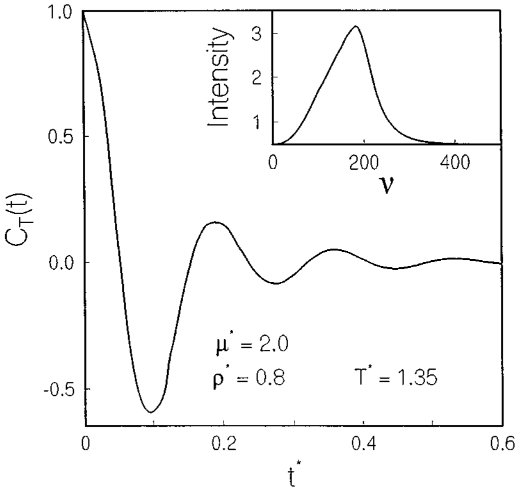

FIG. 3. Decay of the normalized torque autocorrelation function with reduced time for the dipolar soft-sphere liquid. The inset shows the power spectra of the corresponding time correlation function.

In Fig. 6 we compare the decay of the single-particle orientational correlation function with that of the total moment correlation function for the highest μ^* considered in this study. The decay of $C_1(t)$ is faster than that of the $C_M(t)$. The usual interpretation for this behavior is the following. Since the total-moment time correlation function is a collective quantity, it is affected by the long-wavelength orientational correlations present in a strongly correlated system. These correlations are responsible for the decay being much slower for the collective moment than for the single-particle case. Note that a similar observation has already been made earlier by others [8,11], although a detailed comparison of the simulation results with the detailed microscopic theories is yet to be done.

The relaxation of the single-particle orientational correlation function $C_1(t)$ is really interesting. After a short-time inertial decay, the decay is nearly exponential at the intermediate times. The relaxation again becomes nonexponential. A distinct bend appears at $t\approx 0.3$. Again, this kind of shoulder has already been reported in the earlier simulations of dipolar fluids [8]. Again, a detailed theoretical explanation of such behavior is missing. Unlike the single-particle correlation function, the total-moment time correlation function rapidly becomes exponential after an initial nonexponential Gaussian decay [8]. We have shown in a separate study on orientational relaxation in a simple cubic dipolar lattice that the memory function for the single-particle correlation function is much larger than that for the collective moment correlation function. This can explain the nearly exponential decay of the collective moment. The slower decay of the collective moment is due to the long-wavelength static correlations that

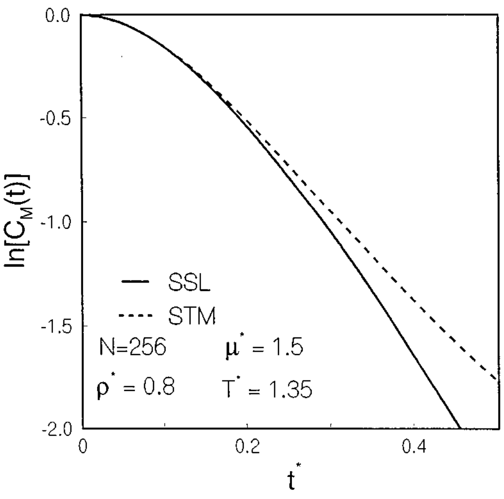

FIG. 4. Comparison of the total-dipole-moment time correlation for SSL (solid line) and STM (dashed line) at $\rho^*=0.8$, $T^*=1.35$, and $\mu^*=1.5$.

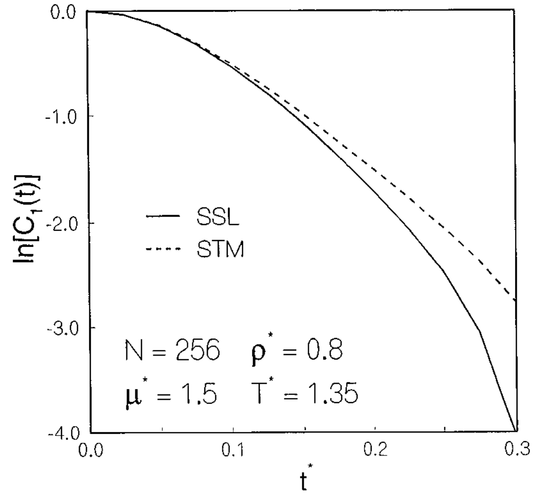

FIG. 5. Normalized single-dipole orientational time correlation function for SSL and STM at $\rho^*=0.8$, $T^*=1.35$, and $\mu^*=1.5$.

affect the total moment but not the single-particle correlation function.

For quantitative purposes, it is useful to define the following average collective correlation times associated with $C_1(t)$ and $C_M(t)$:

$$\tau_s=\int_0^\infty C_1(t)dt \tag{17}$$

and

$$\tau=\int_0^\infty C_M(t)dt. \tag{18}$$

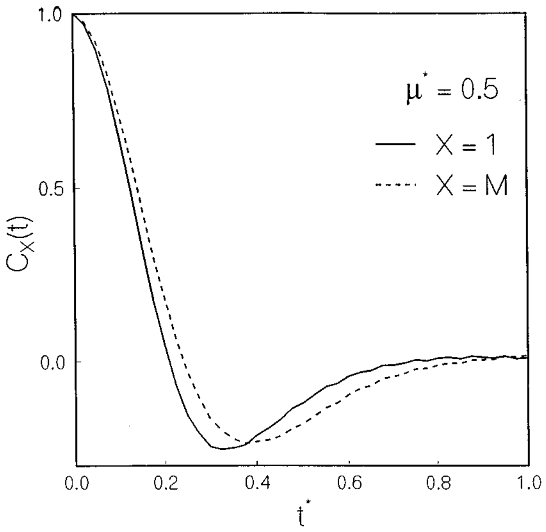

FIG. 7. Comparison of the single-dipole $(X=1)$ and total-dipole $(X=M)$ orientational time correlation functions for the dipolar soft-sphere liquid at $\rho^*=0.8$, $T^*=1.35$, and $\mu^*=0.5$.

The values of $C_1(t)$ were calculated for sufficiently long times with more than adequate precision to allow the straightforward numerical integration of Eq. (17). However, in the evaluation of Eq. (18) [as well as in the evaluation of the frequency dependent dielectric constant $\epsilon(\omega)$] it was necessary to extrapolate the simulated $C_M(t)$ to obtain the long-time behavior. This was done by assuming that for $t>0.3$, $C_M(t)$ is given by the simple exponential form

$$C_M(t)=Ae^{-t/\tau_{\mathrm{slope}}}, \tag{19}$$

where τ_{slope} is the asymptotic slope obtained from the semilogarithmic plots of Fig. 4, where $\ln[C_M(t)]$ is plotted against time. The same procedure was also used by Kusalik [8]. The study of Stockmayer liquids has a long history and the trends for the Stockmayer liquid show similar nature and are not shown here.

The increasing importance of collective effects as μ^* is increased at a given density and temperature is demonstrated in Figs. 7–9 by comparing the autocorrelation of the total

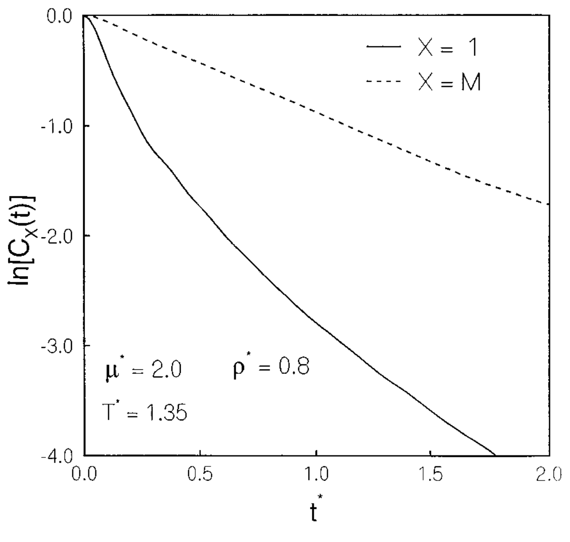

FIG. 6. Comparison of the total-dipole time correlation function with the single-dipole time-correlation function for the dipolar soft-sphere liquid at $\rho^*=0.8$, $T^*=1.35$, and $\mu^*=2.0$.

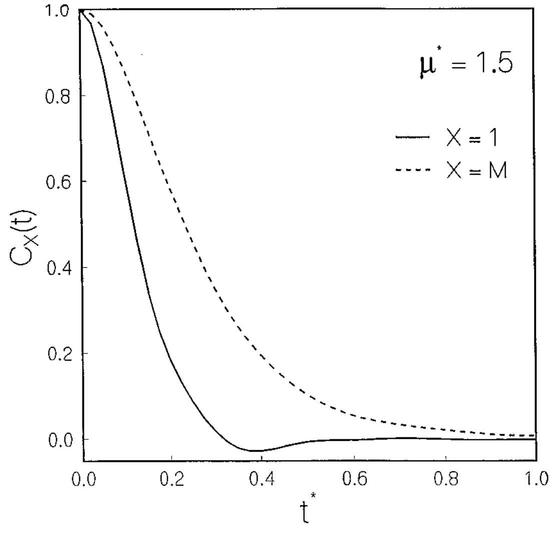

FIG. 8. Comparison of the single-dipole $(X=1)$ and total-dipole $(X=M)$ orientational time correlation functions for the dipolar soft-sphere liquid at $\rho^*=0.8$, $T^*=1.35$, and $\mu^*=1.5$.

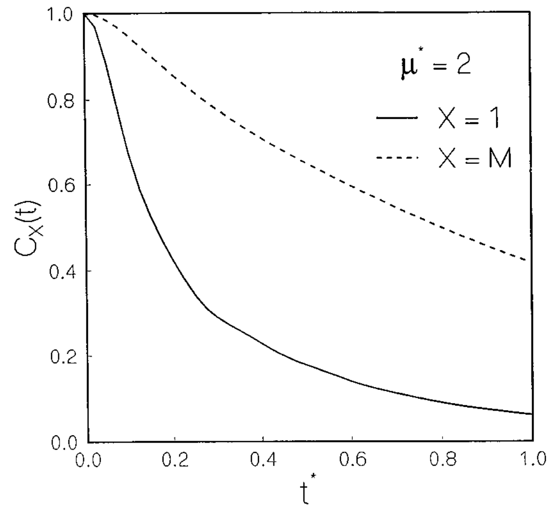

FIG. 9. Comparison of the single-dipole ($X=1$) and total-dipole ($X=M$) orientational time correlation functions for the dipolar soft-sphere liquid at $\rho^*=0.8$, $T^*=1.35$, and $\mu^*=2.0$.

moment $C_M(t)$, with the single-particle dipole reorientational correlation function $C_1(t)$. At $\mu^*=0.5$, the dipolar interaction energy is weak compared to the rotational kinetic energy. The similarity of the single dipole and the total-moment correlation function indicates only weak cooperative effects. At higher values of μ^*, the two correlation functions have, as before, the same quadratic short-time decay, corresponding to the free rotors, but at larger times collective effects dominate the decay of the total polarization and lead to a nearly exponential decay [8,11]. A similar study for Stockmayer liquid already exists and the same kind of trend has been reported [43].

IV. ORIENTATIONAL DYNAMICS OF RANDOM DIPOLAR LATTICES

Having studied the liquid-state properties in detail, we now concentrate on the dynamic properties of the random dipolar lattice. The random dipolar lattice was, as mentioned before, formed from a fully equilibrated dipolar liquid by totally quenching the translational motion of every dipolar molecule. The study of the orientational order parameters and the radial distribution function indicates that the random dipolar lattice so formed were orientationally random and positionally disordered. Below we discuss the results obtained for various time correlation functions calculated for the random lattice. A few of the results mentioned here were reported previously [44].

In Fig. 10 the torque-torque correlation function $[C_T(t)]$ of the liquid and random lattice for the dipolar soft-sphere liquid are plotted. The plot shows that the decay nature of the correlation functions is almost similar. The same kind of observation has been observed for the angular velocity also and it is not shown here.

As mentioned in Sec. III, the long-time part of the collective moment correlation function for a soft-sphere dipolar liquid could be fitted to an exponential [see Eq. (19)]. However, the same for the corresponding RDL could be fitted only to a stretched exponential $C_M(t) \simeq \exp-(t/\tau)^\beta$, with $\beta \simeq 0.9$.

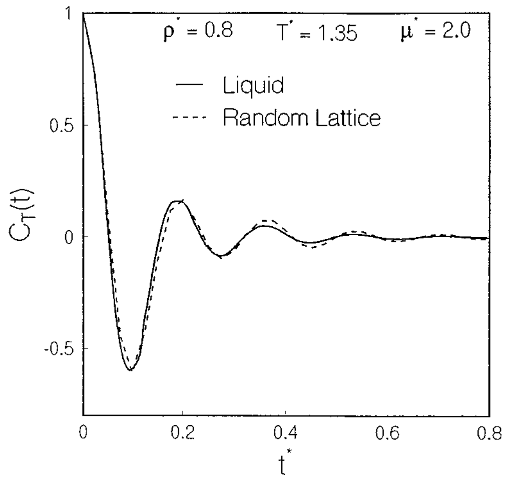

FIG. 10. Comparison of the torque-torque autocorrelation functions $C_T(t)$ for the dipolar soft-sphere liquid (solid line) and the corresponding random lattice (dotted line) at $\rho^*=0.8$, $T^*=1.35$, and $\mu^*=2.0$.

In Fig. 11 the relaxation of the single-particle correlation function $C_1(t)$ for both the liquid and the random lattice systems is shown for a system of dipolar soft spheres at the high polarity ($\mu^*=2.0$). Note that the nearly identical decay at the short time, *but the widely different time scales of relaxation at the long times*. For the liquid the long time of the single-particle correlation function is found to have a stretched exponential nature with $C_1(t) \simeq e^{-(kt)^\beta}$, with $\beta \simeq 0.9$. In the corresponding RDL, the slow decay is subdiffusive, with $C_1(t) \simeq (t)^{-\alpha}$, with $\alpha \simeq 0.75$. In the inset of Fig. 11 we show the decay of the same correlation function at the

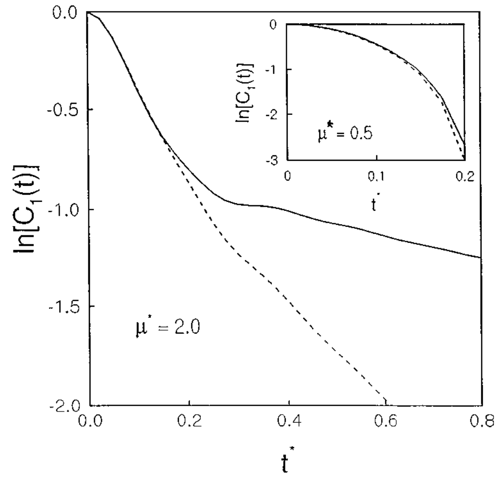

FIG. 11. Single-particle orientational correlation function $C_1(t)$ plotted against reduced time on a semilogarithmic plot for liquid and the random lattice, for $\mu^*=2.0$, $\rho^*=0.8$, and $T^*=1.35$. The dashed lines represent the liquid state and the solid lines are for the random lattice. The inset shows a graph of the same function against time for the smaller dipole-moment ($\mu^*=0.5$) system studied, as discussed in the text.

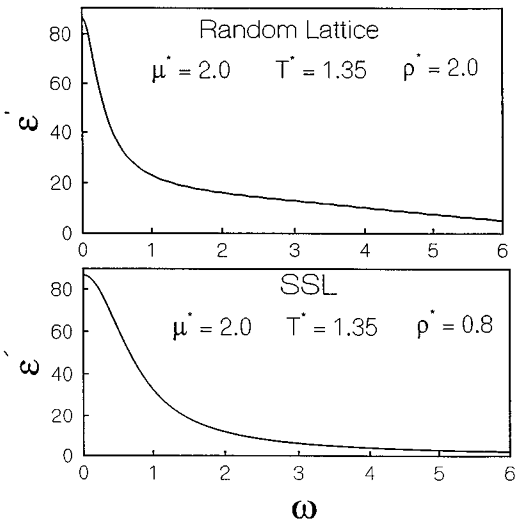

FIG. 12. Real component of the frequency-dependent dielectric constant for the dipolar soft-sphere liquid and the corresponding random lattice at $\rho^*=0.8$, $T^*=1.35$, and $\mu^*=2.0$.

lower polarity $\mu^*=0.5$. Here the decay is nearly identical for the both the liquid and the random lattice over the whole dynamic range for this weakly polar system. Note that $C_1(t)$ and $C_M(t)$ behave rather differently in the random lattice. The same trend is observed in the Stockmayer system also.

The frequency-dependent dielectric constant $\epsilon(\omega)=\epsilon''(\omega)-i\epsilon'(\omega)$ was determined using the general expression [8]

$$\mathcal{L}_{i\omega}[-\dot{C}_M(t)]=1-i\omega\mathcal{L}_{i\omega}[C_M(t)]=\frac{\epsilon(\omega)-1}{\epsilon-1}\,\frac{2\epsilon_{\mathrm{RF}}+\epsilon}{2\epsilon_{\mathrm{RF}}+\epsilon(\omega)}, \tag{20}$$

in which $\mathcal{L}_{i\omega}[\ ]$ denotes the usual Fourier-Laplace transform. In Figs. 12 and 13 we show the real and imaginary components of the frequency-dependent dielectric constant for the soft-sphere dipolar liquid and the corresponding random lattice, respectively, at $\mu^*=2.0$. In Fig. 14 we show the Cole-Cole plot of the dielectric relaxation of the soft-sphere dipolar liquid and the corresponding random lattice for the highly polar system. Note the markedly non-Debye behavior of the random lattice, in contrast to the nearly Debye behavior of the liquid. Note also the increased role of inertia at high frequency for the random lattice. In Fig. 15 we show the second-rank orientational correlation function $C_2(t)$. Here again the decay in the corresponding random lattice is markedly slower than that in the liquid. As already mentioned, no signature of macroscopic orientational ordering has been observed either in the liquid or in the random lattice systems. Essentially the same results have been obtained for the Stockmayer liquid.

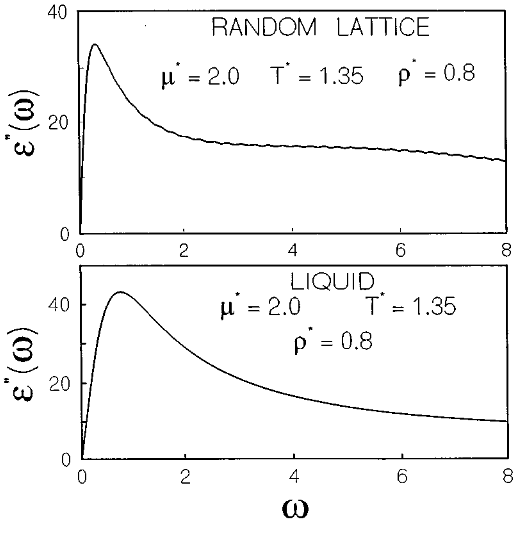

FIG. 13. Imaginary component of the frequency-dependent dielectric constant for the dipolar soft-sphere liquid and the corresponding random lattice at $\rho^*=0.8$, $T^*=1.35$, and $\mu^*=2.0$.

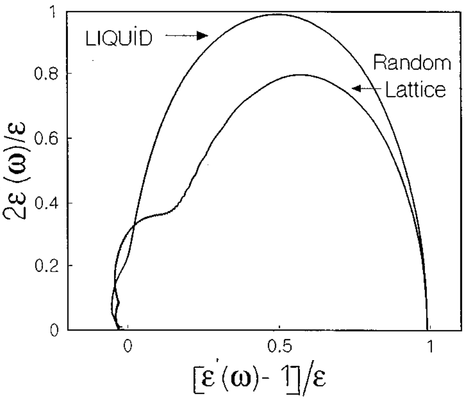

FIG. 14. Cole-Cole plot for the liquid and the corresponding random lattice at $\mu^*=2.0$. Here the imaginary part $[\epsilon''(\omega)]$ has been plotted against the real part $[\epsilon'(\omega)]$. ϵ is the static dielectric constant.

How should the dramatic slowing down of relaxation in the random dipolar lattice be interpreted? It is well known

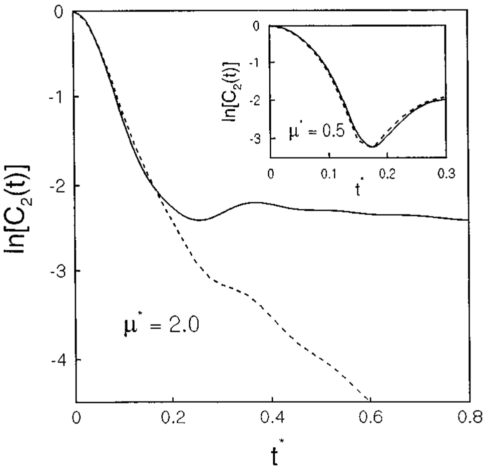

FIG. 15. Second-rank single-particle orientational correlation function $C_2(t)$ plotted against the reduced time on a semilogarithmic plot. The dashed lines represent the liquid state and the solid lines are for the random lattice. The inset shows the dependence of the same function against reduced time for a smaller dipole moment ($\mu^*=0.5$).

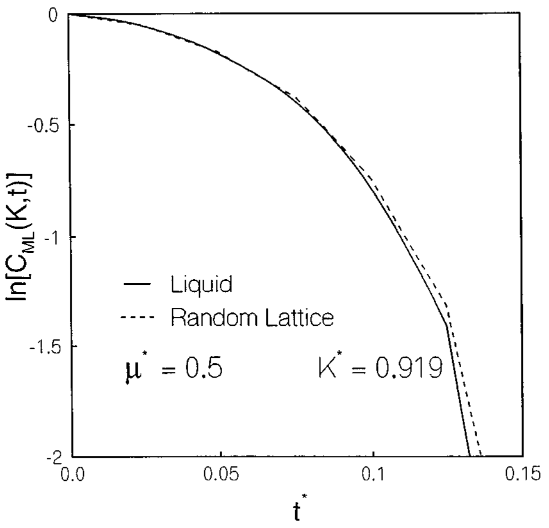

FIG. 16. Normalized longitudinal part of the total moment-moment time correlation function for the dipolar soft-sphere liquid (solid line) and the corresponding random lattice (dashed line) at $\rho^*=0.8$, $T^*=1.35$, $\mu^*=0.5$, and $K^*=0.919$.

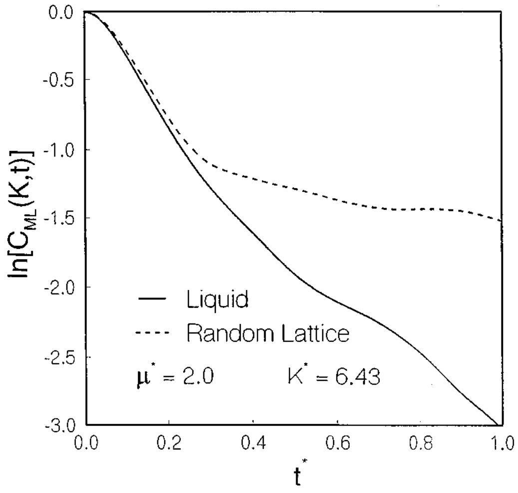

FIG. 18. Normalized longitudinal part of the total moment-moment time correlation function for dipolar soft-sphere liquid (solid line) and the corresponding random lattice (dashed line) at $\rho^*=0.8$, $T^*=1.35$, $\mu^*=2.0$, and $K^*=6.43$.

that the translational modes are most effective in accelerating the decay of intermolecular correlations at the intermediate to large wave vectors, that is, at short times [2,3,45]. The nearly identical decay observed for the liquid and the random lattice at low polarity indicates that here the translational modes are not important and this is because the local orientational order is small at low polarity. The anomaly observed at higher polarity must then be attributed to the much higher degree of local orientational correlations present in the latter. When the translational modes are totally absent, then these local correlations cause the orientational relaxation to proceed at a much slower rate. This is similar to the situation common in atomic liquids where this slowing down of density relaxation at molecular length scales is known as de Gennes's narrowing [45]. We quantify these concepts below.

For dipolar liquids, the single-particle friction $\zeta(z)$ is usually separated into a short-range part, denoted by ζ_0, and a long-range dipolar part (termed the dielectric friction) $\zeta_{\mathrm{DF}}(z)$. The bare friction ζ_0 may include the friction from all the angle-dependent but nondipolar interactions. In the present case, $\zeta_0=0$; therefore, the whole effect comes from ζ_{DF} only. The calculation of the dielectric friction evidently requires the calculation of the torque-torque correlation function. From molecular hydrodynamic theory one can obtain a microscopic expression for the torque acting on a particle at

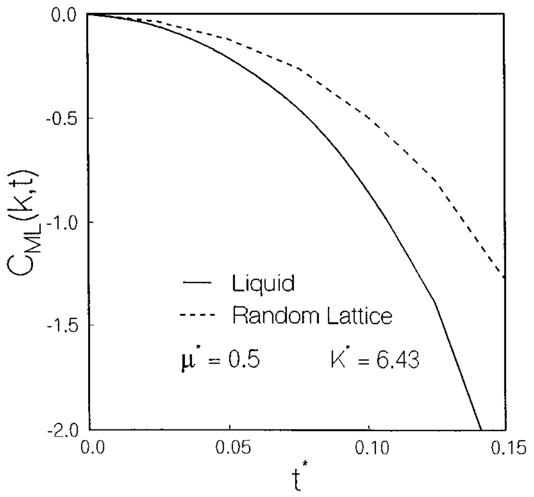

FIG. 17. Normalized longitudinal part of the total moment-moment time correlation function for the dipolar soft-sphere liquid (solid line) and the corresponding random lattice (dashed line) at $\rho^*=0.8$, $T^*=1.35$, $\mu^*=0.5$, and $K^*=6.43$.

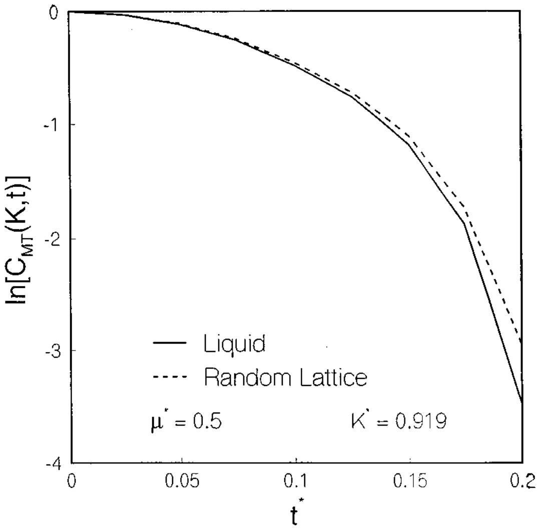

FIG. 19. Normalized transverse part of the total moment-moment time correlation function for the dipolar soft sphere liquid (solid line) and the corresponding random lattice (dashed line) at $\rho^*=0.8$, $T^*=1.35$, $\mu^*=0.5$, and $K^*=0.919$.

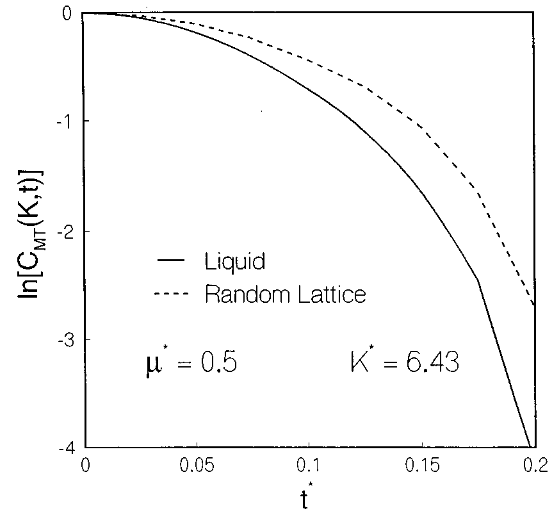

FIG. 20. Normalized transverse part of the total moment-moment time correlation function for the dipolar soft-sphere liquid (solid line) and the corresponding random lattice (dashed line) at $\rho^*=0.8$, $T^*=1.35$, $\mu^*=0.5$, and $K^*=6.43$.

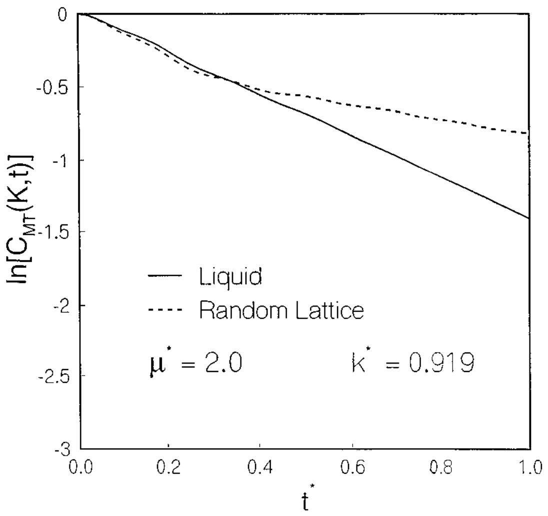

FIG. 21. Normalized transverse part of the total moment-moment time correlation function for the dipolar soft-sphere liquid (solid line) and the corresponding random lattice (dashed line) at $\rho^*=0.8$, $T^*=1.35$, $\mu^*=2.0$, and $K^*=0.919$.

position (r) and orientation (Ω) at time (t) [40]

$$\mathbf{N}(\mathbf{r},\mathbf{\Omega},t)=-\rho_s(\mathbf{r},\mathbf{\Omega},t)\nabla_R\int d\mathbf{r}'d\mathbf{\Omega}'c_{s0}(\mathbf{r},\mathbf{r}',\mathbf{\Omega},\mathbf{\Omega}')\times\delta\rho_0(\mathbf{r}',\mathbf{\Omega}',t), \tag{21}$$

where $\rho_s(\mathbf{r},\mathbf{\Omega},t)$ is the position-, orientation-, and time-dependent number density of the tagged particle and ∇_R is the angular momenta operator. $\delta\rho_0(\mathbf{r},\mathbf{\Omega},t)=\rho_0(\mathbf{r},\mathbf{\Omega},t)-\rho_0/4\pi$ is the fluctuation in the position- and orientation-dependent number density $\rho_0(\mathbf{r},\mathbf{\Omega},t)$ of the solvent molecules and ρ_0 is the corresponding average number density, while $c_{s0}(\mathbf{r},\mathbf{r}',\mathbf{\Omega},\mathbf{\Omega}')$ represents the two-particle direct correlation function of the tagged particle and a solvent molecule [40].

From this torque we can calculate the friction by using the well-known Kirkwood formula [46]. But this leads to a complex four-dimensional integration over the torque-torque autocorrelation function. Traditionally, it has been assumed that the tagged particle is immobile. This leads, after some tedious algebra, to the expression for the dielectric friction

$$\beta\zeta_{\mathrm{DF}}(z)=\frac{\rho_0}{2(2\pi)^4}\int_0^\infty dk\,k^2\times\left[\frac{c_{s0}^2(110;k)[1+(\rho_0/4\pi)h(110;k)]}{z+\Sigma_{10}(k,z)}+2\,\frac{c_{s0}^2(111;k)[1-(\rho_0/4\pi)h(111;k)]}{z+\Sigma_{11}(k,z)}\right], \tag{22}$$

where $c(llm{:}k)$ and $h(llm{:}k)$ are the (llm) components of the two particle direct correlation function and the pair correlation function of the liquid in the intermolecular frame with $\mathbf{k}$ parallel to the z axis [2]. $c_{s0}(110;k)$ is the (llm) component of the direct correlation function between the solute dipole and the solvent molecules and $\Sigma_{lm}(\mathbf{k},z)$ is the generalized rate of density relaxation and is given by [47]

$$\Sigma_{lm}(\mathbf{k},z)=\frac{l(l+1)k_BTf(llm;k)}{I\Gamma_R(\mathbf{k},z)}+\frac{k^2k_BTf(llm;k)}{M\Gamma_T(\mathbf{k},z)}, \tag{23}$$

where M and I are the mass and the average moment of inertia of a solvent molecule. $\Gamma_R(\mathbf{k},z)$ and $\Gamma_T(\mathbf{k},z)$ are the memory function for the single particle and the collective angular momentum relaxation, respectively. $f(llm;\mathbf{k})$ is related to the orientational pair correlation function and k_BT is the Boltzmann constant times the absolute temperature.

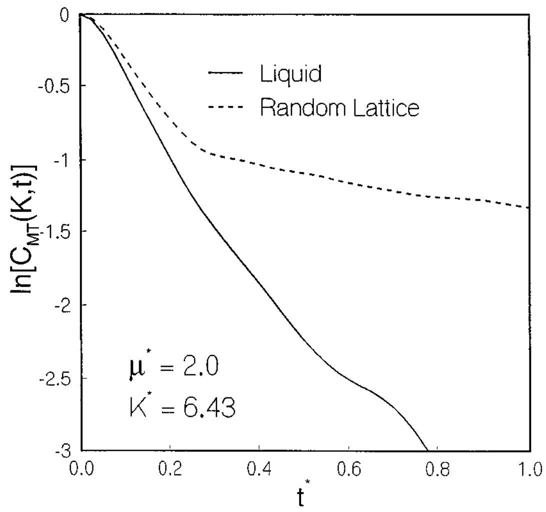

FIG. 22. Normalized transverse part of the total moment-moment time correlation function for the dipolar soft-sphere liquid (solid line) and the corresponding random lattice (dashed line) at $\rho^*=0.8$, $T^*=1.35$, $\mu^*=2.0$, and $K^*=6.43$.

In deriving the above expression, one assumes that the intermolecular correlations are given by a linear theory (such as mean spherical approximation or linearized hypernetted chain) [48,49], so that the only nonvanishing components of the direct correlation function are $c(000;k)$, $c(110;k)$, and $c(111;k)$. A microscopic expression for the dielectric friction was derived earlier [50] using a Markovian approximation for the dissipative kernels of the solvent. Here the generalization of this treatment to non-Markovian regime of solvent relaxation has been used.

Equation (23) has an interesting structure. It shows that the dielectric friction is sensitive to the local orientational correlations. Moreover, both the longitudinal and the transverse modes contribute to the dielectric friction. Note that by the transverse mode, we mean here the (111) component in the coordinate frame when **k** is along the z axis: these are *not* the transverse electromagnetic modes. As already mentioned for a RDL, the friction entirely comes from the dielectric part as ζ_0 is identically zero. The structure of Eq. (23) helps us in understanding the strong effect of local intermolecular orientational correlations in the absence of translations. When translation is absent, $\Sigma_{lm}(\mathbf{k},z)$ is small at intermediate wave vectors, where $f_{110}(\mathbf{k})$ shows a softening. Thus the contribution of the intermediate wave vectors becomes very large for the random lattice. This, in turn, leads to the subdiffusive slow decay. The quantitative calculations are yet to be carried out.

What is the reason for the increased dispersion at the high-frequency limit observed in the random lattice? This is because of the same translational modes that reduce the low-frequency friction lead to an increased value of the friction at the high-frequency end. Thus the magnitude of friction decreases at the short times when the translational modes are removed, as in the random lattice case. This part deserves further study.

V. WAVE-VECTOR- AND FREQUENCY-DEPENDENT DIELECTRIC RESPONSE OF THE RANDOM DIPOLAR LATTICE

An important ingredient of several molecular theories of solvation dynamics is the wave-vector- and frequency-dependent collective orientational correlation functions. In fact, a few studies of the frequency-dependent dielectric response have already been reported [2,51–53].

The wave-vector-dependent permittivity of a particular system may be related to susceptibility $\chi(\mathbf{k},\omega)$ that determines the polarization due to the external field $\mathbf{E}(\mathbf{k},\omega)$.

$$\mathbf{P}(\mathbf{k},\omega)=\epsilon_0\chi(\mathbf{k},\omega)\mathbf{E}(\mathbf{k},\omega). \tag{24}$$

where ϵ_0 is the vacuum permittivity. For an infinite system of cubic or spherical symmetry it is readily shown that [51–54]

$$\chi_L(\mathbf{k},\omega)=\frac{\epsilon_L(\mathbf{k},\omega)-\epsilon(\infty)}{\epsilon_L(\mathbf{k},\omega)\epsilon(\infty)} \tag{25}$$

and

$$\chi_T(\mathbf{k},\omega)/2=\epsilon_T(\mathbf{k},\omega)-\epsilon(\infty), \tag{26}$$

where χ and the dielectric permittivity tensor $\epsilon(\mathbf{k},\omega)$ have been decomposed into longitudinal (L, parallel to **k**) and transverse (T, perpendicular to **k**) components. The $\epsilon(\infty)$ is the dielectric constant at the optical frequency [$\epsilon(\infty)=1$ for a system of rigid nonpolarizable molecules].

The susceptibility $\chi(\mathbf{k},\omega)$ can easily be expressed in terms of molecular correlation functions. The main interest in this work is to calculate these molecular correlation functions and check the predictions of the molecular theories. For rigid and nonpolarizable molecules with dipole moments of magnitude μ, linear response theory gives the expression for $\chi(\mathbf{k},\omega)$ [51–54],

$$\chi(\mathbf{k},\omega)=\frac{\rho}{k_BTN\epsilon_0}\left(\langle|\mathbf{M}(\mathbf{k})|^2\rangle+i\omega\int_0^\infty dt\,\exp(i\omega t)\times\langle\mathbf{M}(\mathbf{k},t)\cdot\mathbf{M}(-\mathbf{k},0)\rangle\right), \tag{27}$$

where ρ is the number density and N is the number of dipoles in the system. The quantity $\mathbf{M}(\mathbf{k},t)$ is the spatial Fourier transform of the dipole density

$$\mathbf{M}(\mathbf{k},t)=\sum_j \mu_j(t)\exp[i\mathbf{k}\cdot\mathbf{r}_j(t)],$$

where μ_{j} is the dipole moment of the jth molecule and $\mathbf{r}_j$ is the position of its center of mass with respect to the laboratory frame. Due to the periodic boundary conditions used in our simulations, the allowed wave vectors are of the form $\mathbf{k}=(l,m,n)2\pi/L$, where L is the length of the cubic simulation box and l,m,n are integers.

On decomposing $M(\mathbf{k},t)$ into longitudinal and transverse components, one gets

$$\begin{aligned}\mathbf{M}(\mathbf{k},t)&=\mathbf{M}_L(\mathbf{k},t)+\mathbf{M}_T(\mathbf{k},t)\\&=\mathbf{M}(\mathbf{k},t)\cdot\hat{\mathbf{k}}\hat{\mathbf{k}}+\mathbf{M}(\mathbf{k},t)\cdot(1-\hat{\mathbf{k}}\hat{\mathbf{k}}).\end{aligned}$$

The orientational correlation functions one is interested are

$$C_{ML}(\mathbf{k},t)=\langle\mathbf{M}_L(\mathbf{k},t)\cdot\mathbf{M}_L(-\mathbf{k},0)\rangle \tag{28}$$

and

$$C_{MT}(\mathbf{k},t)=\langle\mathbf{M}_T(\mathbf{k},t)\cdot\mathbf{M}_T(-\mathbf{k},0)\rangle. \tag{29}$$

An interesting prediction of the molecular theory is that at intermediate wave vectors ($\mathbf{k}=2\pi/\sigma$, with σ the molecular diameter), the orientation relaxation depends strongly on the translational diffusion of the solvent molecules. In fact, the theory makes even a stronger prediction that in the absence of the translational modes the orientation modes will be significantly slower and more nonexponential than in the presence of these modes. This is due to the strong local orientational correlations present in a strongly polar dipolar liquid that tend to ‘‘cage’’ the orientational motion. In fact, the simulations presented in Sec. IV are in complete agreement with these predictions. What now remains to be demonstrated is the strong dependence of orientational relaxation at intermediate **k** vectors on translation. This is done below.

In Figs. 16 and 17 the time dependence of the normalized $C_{ML}(\mathbf{k},t)$ is shown for a dipolar soft-sphere liquid and the corresponding random lattice at $\mu^*=0.5$ at the wave vectors $\mathbf{k}\sigma=0.919$ and 6.43, respectively. These figures clearly show that the translational modes, while not important at low wave vectors, dominate the long-time orientational relaxation at the intermediate wave vectors. This behavior is in complete agreement with molecular hydrodynamic theory. In Fig. 18 the time dependence of the normalized $C_{ML}(\mathbf{k},t)$ at $\mathbf{k}\sigma=6.43$ is shown for $\mu^*=2.0$. At this high polarity the orientational correlations between neighboring molecules are significant. The molecular hydrodynamic theory therefore predicts that the translational modes can be extremely important in this regime. Figure 18 clearly verifies this prediction. In Figs. 19 and 20 we show the time dependence of the transverse component $C_{MT}(\mathbf{k},t)$ for two wave vectors $\mathbf{k}\sigma=0.919$ and 6.43 for $\mu^*=0.5$. One again sees the importance of translational modes in the intermediate wave vectors. The dependence of $C_{MT}(\mathbf{k},t)$ on the translational modes at intermediate wave vectors increases at $\mu^*=2.0$. This behavior is similar to the one shown in the previous figures and is shown in Figs. 21 and 22.

The same kind of behavior has been observed for Stockmayer liquids. This amply verifies that the important role of translational modes at the intermediate wave vectors is independent of the detailed short-range interaction.

VI. CONCLUSION

Several different results have been reported in this work. They clearly demonstrate the coupling between rotation and the translation and their significant role in the orientational relaxation in the supercooled liquid. However, these results are for model systems and one should be cautious about their relative importance in real systems. The decay nature of the orientational relaxation of the single particle and the collective moment in these systems show a rather different behavior. The collective moment relaxation of the system becomes much slower as one goes to the higher polar systems. This clearly confirms the importance of collective effects in such systems. The importance of translational and rotational coupling can be understood by the following argument. In the microdomains where the translational diffusion is slow, the orientational relaxation of a dipolar molecule can be even slower. In the experiments where a subensemble of particles is selectively studied, it is the slow relaxation that is dominant. The dramatic slowing down of the orientational relaxation in the random lattice can be understood in two ways. First, the slow orientational relaxation of the random lattice can be easily explainable because of the many relaxation channels that are available for the liquid and not for the random lattice. Second, the heterogenous mechanism explained in the Introduction can be used to understand the dramatic slowing down of the orientational relaxation. Since there is no macroscopic order observed in the systems studied it may be concluded that the orientational slowing down can be partly due to the local ordering developed in the system. The results of the orientational correlation functions of the random lattice seem to show a subdiffusive behavior at long times. The strong dependence of orientational relaxation at intermediate wave vectors on translational diffusion is also confirmed by the simulation studies. Moreover, the results obtained here appear to be in good agreement with the computer simulation results of Skaf, Fonseca, and Ladanyi [54] for orientational relaxation in methanol. One particularly nice result obtained by them was the greater sensitivity of the relaxation of the transverse part of the collective moment to the translation than the longitudinal part. The same result has been obtained here.

ACKNOWLEDGMENTS

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