

Orientalional Relaxation in a Random Dipolar Lattice: Role of Spatial Density Fluctuations in Supercooled Liquids

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We have carried out a computer “experiment” of orientational relaxation in a spatially random and orientationaly disordered dipolar lattice (RDL), generated by quenching only the translational motion of a dense liquid. In the high polarity limit, the orientational relaxation of the RDL is dramatically different from that of the parent liquid, the former exhibits a very slow, nonexponential long time decay of the orientational correlation functions and markedly non-Debye dielectric relaxation. These results clearly demonstrate the importance of spatial density fluctuations in orientational relaxation.

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Molecular relaxation processes, in general, and orientational dynamics, in particular, exhibit marked nonexponential decay in supercooled liquids near the glass transition temperature. This nonexponential decay is so general that one often refers to it as “universal” to all supercooled liquids [1–4]. This nonexponential decay 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 the mode coupling and other theories of glass transition [5–7]. 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 [4] and Ngai [8] have suggested that the degree of nonexponential decay 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 novel experiments [9,10] have been performed that measured selectively the orientational dynamics of a *subensemble* of relaxing vectors—the results were strikingly different from those that 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 nonexponential decay 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 at different positions seem to experience different microenvironments. Near the glass transition, these different microstates may

have widely different correlation times, which may lead to a marked nonexponential decay. The above experimental results [9,10] 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 [9]. Thus, there may exist a novel *dynamic* coupling between the translational and rotational dynamics in the supercooled liquid. When the spatial density relaxation becomes slow, the orientational dynamics may become even slower because the translational motions may no longer assist in the decay of the local orientational correlations. This effect may be particularly important in those microdomains that are of higher density. The above two factors may combine to give the observed large (2 orders of magnitude) increase in the relaxation time.

The above results raise the following questions. What is the precise role of translational motion in orientational relaxation? How strongly are they coupled? More importantly, what is the maximum realizable extent of nonexponential decay when the translational modes are totally absent? An earlier theoretical calculation [11] predicted that the dielectric relaxation (DR) of a dipolar liquid can be strongly non-Debye in the absence of the translational modes. However, a later experimental study [12] of DR in dipolar solids raised doubts regarding the influence of the translational modes. Thus, this has remained a controversial subject. 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 [13] and the effects of environmental fluctuations on chemical reactions [14].

In this Letter we present results of a computer “experiment” to study the influence of the translational modes on orientational relaxation in a strongly correlated system. We have carried out detailed molecular dynamics (MD) simulations of orientational relaxation, first for a dense, strongly polar, dipolar liquid, and then for the corresponding random dipolar lattice (RDL). The latter has been formed by quenching only the translational motion

of the dipolar molecules, while keeping the rotational motions untouched. The RDL is the disordered analog of the simple dipolar cubic lattice model studied by Zwanzig [15] many years ago.

The results of the simulations are indeed surprising. The orientational time correlation functions of the RDL are found to be markedly different from that of the corresponding liquid. The first rank correlation function [$C_{\ell=1}(t)$] shows a very slow, highly nonexponential long time decay in RDL that is completely absent in the parent liquid. The Cole-Cole plot of the liquid is Debye-like, as expected, but that of the RDL is markedly non-Debye.

Computer simulations have been carried out for dipolar soft spheres and the Stockmayer liquid models, whose interaction potential can be written in a general form as follows:

$$U_{\lambda,\mu}(\mathbf{r}_{ij}, \mu_i, \mu_j) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \lambda \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + \frac{\mu^2}{r^3} \left[\mu_i \cdot \mu_j - \frac{3}{r^3} \times (\mu_i \cdot \mathbf{r}_{ij})(\mu_j \cdot \mathbf{r}_{ij}) \right], \quad (1)$$

where μ_i corresponds to the dipole moment of particle i , $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$, ϵ is the energy parameter, r is the magnitude of distance between the particles, and σ is the molecular diameter. λ is the parameter that controls the role of dispersive interactions. The above expression gives the soft-sphere dipolar potential when $\lambda = 0$; when $\lambda = 1$ it gives back the form for the usual Stockmayer potential.

Our MD calculations were performed using the leap-frog algorithm [16] for 256 particles, and we verified our simulation code by reproducing the results of Kusalik [17]. For both potentials, two values of the reduced dipole moment ($\mu^* = \mu^2/\epsilon\sigma^3 = 2.0$ and 0.5) have been considered to simulate systems of widely different polarities. The reduced density ($\rho^* = \rho\sigma^3$) and the reduced temperature ($T^* = k_B T/\epsilon$) have been kept fixed at 0.8 and 1.35 . These are essentially the same systems simulated by Kusalik [17]. The long-range dipolar interactions are handled with the Ewald summation technique using “tin-foil” boundaries [18]. Following Kusalik, the reduced time step $\Delta t^* (= \Delta t/\sqrt{m\sigma^2/\epsilon}) = 0.0025$ (where m is the mass of a particle) has been used in all the simulations. For each liquid simulation run, equilibrations have been performed over 2×10^5 time steps, and averages have been collected over 2.5×10^5 time steps. The RDL was generated by the following method. We started with an equilibrated liquid configuration and instantly froze the translational motions of all the molecules. This translationally quenched state was then equilibrated for another 4×10^5 time steps by allowing the dipolar rotation. Both the torque-torque and the angular velocity-velocity autocorrelation functions of the equilibrated RDL were

approximately the same as those of the parent liquid. This suggests that the generated RDL was in a spatially homogeneous and orientationally disordered state. For the RDL, at least three different runs have been carried out to check the ergodic nature of the results; the different runs for the RDL gave almost the same results. In the liquid state, the simulated values of kinetic and potential energies, radial distribution functions, dielectric constant, etc., are all in close agreement with the results of Kusalik [17]. The value of the dielectric constant of the random lattice was found to be slightly smaller than that of the liquid. For example, the dielectric constant (ϵ_0) for $\mu^* = 2.0$ was 88 ± 2 for the liquid and 86 ± 3 for the corresponding random lattice.

We have also checked for the formation of any orientationally ordered phase in our systems by computing the average orientational order parameters $\langle P_1 \rangle$ and $\langle P_2 \rangle$ [19]. While $\langle P_1 \rangle$ has been calculated directly from the average total moment, $\langle P_2 \rangle$ was calculated from the largest eigenvalue of the ordering matrix \mathbf{Q} with elements given by [19]

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

where μ_{α}^i is the α component of the unit vector ($\hat{\mu}_i$). We find that for both the liquid and all the RDLs, the values ($\langle P_1 \rangle$ and $\langle P_2 \rangle$) are close to zero, indicating the absence of the formation of any macroscopic orientational order in the systems studied. We have also checked for the system size dependence by simulating a system of 108 dipolar soft spheres. The single particle orientational correlation functions showed almost no size dependence. The magnitudes of the collective functions (such as the value of the static dielectric constant) did show, as expected, some size dependence, which was, however, negligible for the normalized time correlation functions.

The single particle, rank (ℓ) dependent, orientational correlation function, $C_{\ell}(t)$, is defined by

$$C_{\ell}(t) = \frac{4\pi}{2\ell + 1} \sum_{m=-\ell}^{\ell} \langle Y_{\ell m}^*(\Omega(0)) Y_{\ell m}(\Omega(t)) \rangle, \quad (3)$$

where $Y_{\ell m}(\Omega)$'s are the usual spherical harmonics. We have also computed the collective, total moment-moment time correlation function, $C_M(t)$, defined by

$$C_M(t) = \langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle / \langle [\mathbf{M}(0)]^2 \rangle, \quad (4)$$

where $\mathbf{M}(t) = \sum_{i=1}^N \mu_i(t)$. While $C_M(t)$ for the liquid could be fitted by an exponential, the same for the RDL could be fitted only by a stretched exponential, $C_M(t) \approx \exp[-(t/\tau)^{\beta}]$, with $\beta \approx 0.9$. From $C_M(t)$ the frequency dependent dielectric function has been computed using the known procedure [17]. Again, the liquid phase values of this quantity were in perfect agreement with the results of Kusalik [17].

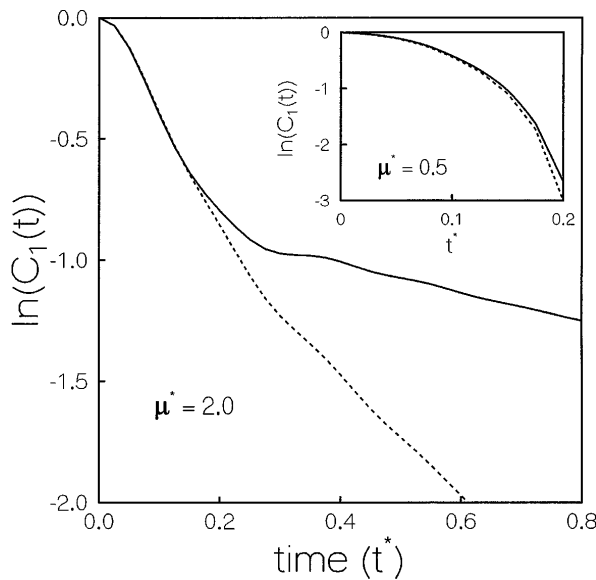


FIG. 1. The single particle orientational correlation function $C_\ell(t)$, for $\ell = 1$, is plotted against reduced time on a semilogarithmic plot for liquid and the random lattice, for $\mu^* = 2.0$, $\rho^* = 0.8$, and $T^* = 1.35$. The dotted lines represent the liquid state, and the solid lines are for 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.

In Fig. 1 the relaxation of the single particle correlation function, $C_1(t)$, for both the liquid and random lattice systems is shown for a system of dipolar soft spheres at the high polarity ($\mu^* = 2.0$). Note the nearly identical decay at the short time *but the widely different time scales of relaxation at the long time*. In the RDL, the slow decay is subdiffusive, with $C_1(t) \approx (t)^{-\alpha}$, with $\alpha \approx 0.75$. Thus, $C_1(t)$ and $C_M(t)$ behave rather differently in the RDL. In the inset of the same figure we show

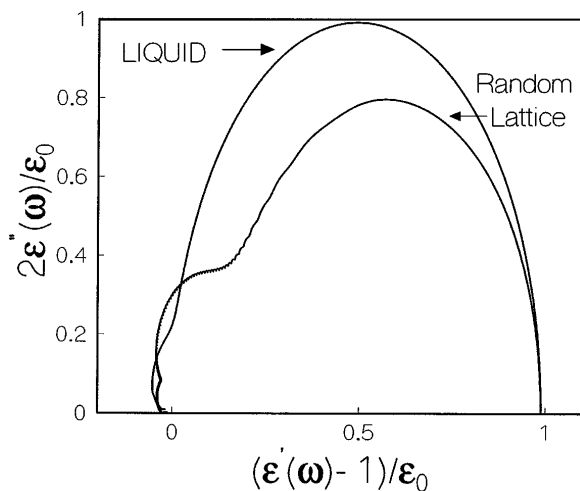


FIG. 2. The Cole-Cole plot for the liquid and the random lattice at $\mu^* = 2.0$. Here the imaginary part $[\epsilon''(\omega)]$ has been plotted against the real part $[\epsilon'(\omega)]$. ϵ_0 is the static dielectric constant.

the decay of the same correlation function at the *lower* polarity, $\mu^* = 0.5$. Here the decay is nearly identical for both the liquid and the random lattice over the whole dynamic range for this weakly polar system. A similar behavior has been observed for the Stockmayer liquid and the corresponding random lattice.

In Fig. 2, we show the Cole-Cole plot for the DR of the liquid and the random lattice for the highly polar system. Note that 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. We shall discuss its origin later. In Fig. 3, we show the decay of the second rank orientational correlation function $C_2(t)$. Here again the decay in the RDL 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 system. And essentially the same results have been obtained for the Stockmayer liquid.

How does one understand the dramatic slowing down of relaxation in the random dipolar lattice? It is well known 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 distances [11,20]. 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*

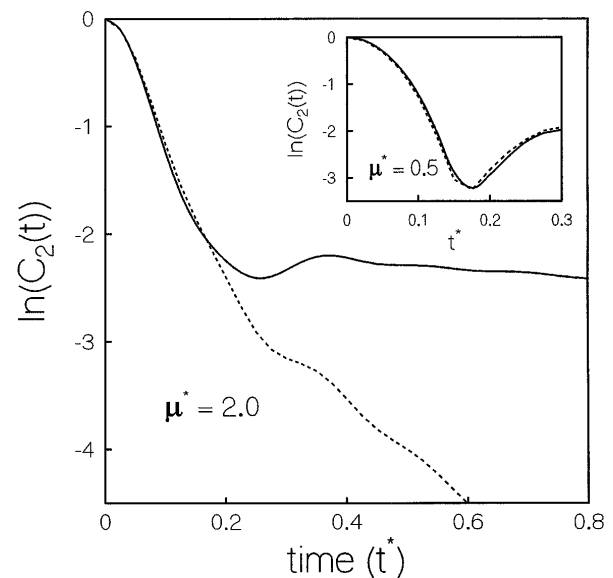


FIG. 3. The second rank single particle orientational correlation function, $C_2(t)$, is plotted against the reduced time on a semilogarithmic plot. The dotted lines represent the liquid state and the solid lines are for the random lattice. The inset shows the dependence of the same function against reduced time for a smaller dipole moment ($\mu^* = 0.5$).

correlations present in the latter. When the translational modes are totally absent, 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' narrowing [20].

The important role of the translational modes found in this simulation appears to be at variance with the experimental findings of Grochulski, Psczolkowski, and Kempka [12]. However, there are several rather involved issues that need to be considered before a fruitful comparison between the two can be carried out. First, our simulations suggest that the dielectric relaxation remains Debye-like for systems at low polarity. This feature seems to remain unchanged even in the crystalline solids as revealed by recent Brownian dynamics simulations of a dipolar lattice (BDL) [21]. For both the RDL considered here and the BDL, this Debye-like behavior persists until the value of the static dielectric constant (ϵ_0) reaches about 12–15. Noticeable non-Debye behavior emerges only when $\epsilon_0 > 20$. Moreover, when a molecular dynamics simulation of the dipolar simple cubic lattice was carried out, much less non-Debye behavior was observed even around $\epsilon_0 = 20$ (which is the largest ϵ_0 that could be studied because of an impending phase transition in this system) [22]. Thus, the polarity of the experimental systems (which were plastic crystals) perhaps was not sufficiently high to give a marked non-Debye behavior. The second point is that the generalized hydrodynamic model also assumed an overdamped dynamics [11]. For the spherical molecules considered here, this can lead to a significant overestimation of the dielectric friction, hence of the non-Debye behavior. Thus, there may not exist any serious discrepancy among theory, experiments, and simulations after all. Clearly, more studies are required to understand the issues involved.

What is the reason for the increased dispersion at the high frequency limit observed in the random lattice? This is because 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.

We believe that the results shown here are sufficiently general to be valid for any angle dependent interaction potential, although they need to be verified explicitly. This study also provides an indirect support of the heterogenous picture. In the microdomains where the translational diffusion is slow, the orientational relaxation of a dipolar molecule can be even slower. In order to address the heterogenous picture quantitatively, one needs to consider the probability distribution of the microdomains and consider the differing dynamics in each of them. In fact, the methods of treating such environmental fluctuations are already being developed [12].

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