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Dynamics of Chain Molecules in Disordered Materials

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The dynamic behavior of hard chains in disordered materials composed of fixed hard spheres is studied using discontinuous molecular dynamics simulations. The matrix induces entanglements in the chain fluid, i.e., for high matrix densities the diffusion coefficient D scales with the chain length N as $D \sim N^{-2}$. At high matrix densities the rotational relaxation time becomes very large but the translational diffusion is not affected significantly; i.e., the chains display a dynamic heterogeneity reminiscent of probe diffusion in supercooled liquids and glasses. We show that this is because some chains are trapped, and move via a hopping mechanism. There are no signatures of this dynamic heterogeneity in the matrix static structure, however, which is identical to that of a hard-sphere liquid.

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A central question in soft matter is how complex fluids move in complex environments. Practical examples are the diffusion of macromolecules in crowded living cells [1,2], gels [3,4], or glasses [5]. Often on the time scale of interest for solute transport the matrix is essentially static, and it is of considerable importance to be able to relate the structure of the matrix to the dynamic properties of the solutes. While this is an area of active experimental research, what has been lacking is a set of dynamical models with structural complexity that could play the same role that Ising and lattice models did for critical phenomena. In this Letter we present molecular dynamics simulations of a simple model, namely, hard chains in a matrix of fixed hard spheres, and show that this simple model has very interesting dynamics and captures much of the phenomenology seen in the dynamics of probes in structural glasses [6].

The heterogeneous nature of the dynamics of probes in glasses is a topic of continuing interest. NMR [7] and dynamic hole burning [8] experiments on the rotational dynamics of probes in glasses and supercooled liquids have shown that a subset of probe molecules have rotational relaxation times that are orders of magnitude greater than the average. More recently, single molecule experiments [9] have demonstrated that the rotational dynamics of probes in supercooled liquids is strikingly heterogeneous, i.e., different probes rotate at very different rates, with single probes switching from “fast” to “slow” or vice versa almost instantaneously. The molecular origin of these spatially heterogeneous dynamics remains an open question of considerable current interest [6].

Computer simulations have played an important role in our understanding of supercooled liquids. In fact, spatial heterogeneity is observed in simulations of binary (noncrystallizable) mixtures of Lennard-Jones particles [10,11], although this occurs at temperatures much above the glass transition. As the liquid is cooled, however, the relaxation times become prohibitively large, preventing the simulation of the glass transition itself.

In this work, we take a different approach to the problem and focus on the dynamics of probes in glasses *by construction* rather than trying to create a structural glass by cooling. We model the matrix as a collection of spheres fixed in space and investigate the dynamics of chainlike probe molecules in these matrices. We find that the dynamic behavior can be very interesting and can reproduce much of the phenomenology observed in experiment. There is no signature of this in the average static structure factor of the matrix, however, which is (by construction) identical to that of a hard-sphere liquid.

The main challenge in the computational study of disordered materials is that the positions of the matrix particles are quenched. An average over realizations of the matrix is necessary, which make the simulations computationally intensive. Consequently, although there have been a number of computational studies of lattice and/or two dimensional models or single chains [12–16], to our knowledge there have been no studies of the dynamics of solutions of macromolecules in random media except for solutions of chains [17] and rods [18] in two dimensions. We overcome the problems associated with simulations by employing a model with only impulsive forces that allows us to use the efficient discontinuous molecular dynamics (DMD) algorithm [19]. Monte Carlo (MC) simulations [13–16] provide useful insight into chain behavior, but there is a worry that the dynamics might be influenced by the MC moves used to propagate the system, and MD simulations are therefore important.

The solute molecules are modeled as chains of N hard spheres of diameter σ, where N is the number of monomers (or sites) in a chain. The bond length between adjacent beads is allowed to vary freely between $(1 - \delta_B)\sigma$ and $(1 + \delta_B)\sigma$, with $\delta_B = 0.05$ [20]. The static properties of this model are identical to the tangent hard-sphere chain model [21]. The disordered matrix is a set of immobile hard spheres with diameter σ. We define our length, energy, and mass scales by setting $\sigma = 1$, $k_B T = 1$, and $m = 1$ where k_B is Boltzmann's constant, T is the temperature, and m is the mass of each monomer. The time t is reported in units of $\sigma\sqrt{m/k_B T}$. The simulation cell is a cube of side length L which contains N_p chains, with $N_p \geq 16$. L is chosen so that it is larger than the root mean-square end-to-end distance of the chains and contains a large enough number of chains and matrix particles for good statistics. In most cases $L = 11.026\sigma$ and for $N_m = 16$ and high matrix volume fractions $L = 13.892\sigma$. We investigate chain lengths ranging from $N = 1$ to 16. These chain lengths are relatively short compared to previous MC studies [13–16] but the qualitative behavior is similar to longer chains. Realizations of the matrix are obtained from statistically independent configurations of a hard-sphere liquid. The chain molecules are then inserted at randomly chosen positions. At high densities this is done using a growth and equilibration technique. We investigate chain volume fractions, ϕ_c ($\equiv N N_p \pi\sigma^3/6L^3$) ranging from 0.05 to 0.3, and matrix volume fractions, ϕ_m ($\equiv N_m \pi\sigma^3/6L^3$ where N_m is the number of matrix spheres) ranging from 0 to 0.2. Note that $\phi_m = 0.2$ corresponds to a very *dense* matrix. In fact, in the infinite dilution limit, a hard-sphere fluid in a hard-sphere matrix is predicted by mode coupling theory to undergo a *glass transition* for $\phi_m \approx 0.175$ [22]. At higher matrix concentrations ($\phi_m > 0.2$) chains are virtually trapped and do not diffuse normally.

Simulations are performed using DMD [19] where trajectories are evolved as a sequence of collisions. First it is determined which pair of spheres will be the next to collide, then all spheres are moved with constant velocities for the time it takes for the colliding spheres to come into contact, and finally the velocities of the colliding spheres are reset according to the dynamics of an elastic collision. Properties are time averaged over many collisions. Details regarding the simulation method can be found elsewhere [23,24]. The DMD method has the advantage that one can replay trajectories if the identity of colliding pairs (at each collision) is stored.

The simulations require a time average for each realization of the matrix and then an ensemble average over different realizations of the matrix. For each realization of the matrix, properties are averaged over 1000 trajectories, with the final configuration of one trajectory used as the initial configuration of the next. The length of the simulation depends on the matrix density and the chain length. For $\phi_c = 0.05$ and $\phi_m = 0.2$, the total duration of the simulation is 10^4, 10^5, 3×10^5, and 10^6 for $N_m = 2$, 4, 8, and 16, respectively. Properties are then averaged over 8–16 different realizations of the matrix, depending on the matrix volume fraction. Error bars in this Letter correspond to 1 standard deviation about the mean of the matrix average.

For the chain lengths studied, the scaling of the translational diffusion coefficient D and rotational relaxation time τ_R with N is consistent with entangled behavior. D is obtained from the mean-square displacement of the chain center of mass, and τ_R is obtained by fitting the initial decay of the end-to-end vector rotational autocorrelation function, $U(t)$ (defined below), to an exponential function. $U(t)$ is defined as $U(t) \equiv \langle \mathbf{R}(t) \cdot \mathbf{R}(0)\rangle / \langle \mathbf{R}(0) \cdot \mathbf{R}(0)\rangle$ where $\mathbf{R}(t)$ is the end-to-end vector of a chain at time t. $U(t)$ is first calculated for each chain, with an average over initial times, and the result is averaged over the ensemble of chains. In the absence of the matrix $D \sim R_g^{-1}$ in dilute solutions and $D \sim N^{-1}$ in semidilute solutions, consistent with a crossover from Zimm to Rouse behavior. The exponent is markedly different in the presence of the matrix. For $\phi_m = 0.1$ and 0.2, D is well fit by a power law for $N \geq 4$, i.e., $D \sim N^{-\alpha}$, with $\alpha = 1.5 \pm 0.01$ and 2.06 ± 0.06, and the latter is consistent with the scaling expected for entangled chains. Similarly, in the absence of the matrix, $\tau_R \sim N^{\beta}$ with β varying from approximately 1.2 to 2 as ϕ_c is increased, which corresponds to a transition from Zimm to Rouse dynamics. As the matrix volume fraction is increased, the value of β increases as well, and for $\phi_m = 0.2$, $\beta = 3 \pm 0.2$, corresponding to entangled chains. This increase of the dynamic scaling exponent with increasing matrix concentration is consistent with Monte Carlo simulations [13,14,16]. In fact, the exponent can be even larger (in magnitude) than observed here [13,14] and the value of the exponent depends on the model as well as the matrix density [16]. Our results are consistent with the picture that the chains diffuse in channels inside the matrix, which act as tubes, thus resulting in reptationlike dynamics for the chains.

The rotational dynamics of the chains display two regimes, with a rapid relaxation at short times followed by (in some cases) a slow relaxation at long times. A long tail in $U(t)$ is prominent for high matrix volume fractions. This can be seen in Fig. 1, which depicts $U(t)$ as a function of t/N^3 for $\phi_m = 0.2$, $\phi_c = 0.05$, and various chain lengths. At long times $U(t)$ levels off at a nonzero value for all chain lengths, even $N = 2$. Interestingly, there is no signature of this slow dynamic behavior in the translational diffusion. In fact, the mean-square center-of-mass displacement, $W(t)$, is linear with time at long times in all cases (although anomalous diffusion is observed at intermediate times). Although it is true that the translational diffusion should eventually lead to rotational relaxation, we do not observe a complete relaxation even though the chains appear to diffuse freely, on average. Therefore at high matrix volume fractions ($\phi_m = 0.20$) the chain dynamics are similar to those of entangled polymer melts ($\tau_R \sim N^3$ and $D \sim N^{-2}$), except that there is a long-time component similar to what is observed in experiments for the dynamics of probes in glassy materials.

The difference in the rotational and translational dynamics can be explained if some chains are assumed to be trapped. For normal diffusion, $W(t)$ increases linearly with time and $U(t)$ decays rapidly to zero. Consider the case, however, that a small number of chains are immobile. The

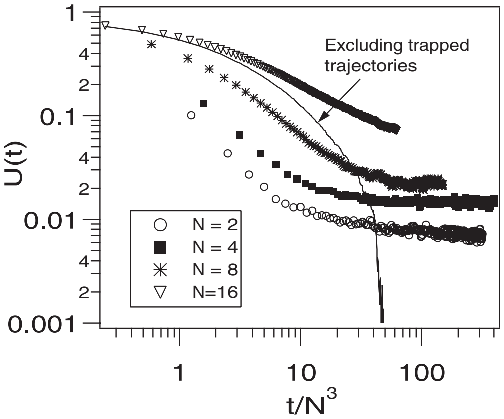

FIG. 1. End-to-end vector autocorrelation function, $U(t)$, for various chain lengths as a function of t/N^3 for $\phi_c = 0.05$ and $\phi_m = 0.20$, plotted on a logarithmic scale.

contribution of these trapped chains to $W(t)$ is a constant at long times and the average $W(t)$ is dominated by the mobile chains. If the number of trapped chains is small, the translational diffusion will show no signature of trapping. The contribution of these trapped chains to $U(t)$, however, is more significant because at long times the contribution of mobile chains is zero, and that of trapped chains is finite. As a consequence, at long times, the average rotational relaxation is dominated by the trapped chains while the average translational relaxation is dominated by mobile chains.

If the contribution from the trapped chains is removed from $U(t)$, then this function decays rapidly to zero in all cases. Figure 2 shows the probability distribution of finding a chain with a value of $U(\tau)$ as a function of $U(\tau)$, for $\tau = 2.55 \times 10^5$, and for $N = 16$, $\phi_c = 0.05$, and $\phi_m = 0.20$. The distribution has a strong peak at $\tau \approx 0$, and a fraction of chains have $U(\tau = 2.55 \times 10^5) > 0.2$ that clearly do not belong to the primary peak. We define these chains as trapped over the course of the simulation. Although the fraction of the trapped chains is small, these trajectories dominate the long-time behavior of the rotational relaxation. The solid line in Fig. 1 is $U(t)$ averaged over the subset of untrapped chains and shows normal relaxation. Note, however, that the short-time rotational relaxation is less sensitive to the trapped trajectories, and the relaxation time τ_R discussed earlier does not change significantly when the contribution of the trapped chains is removed.

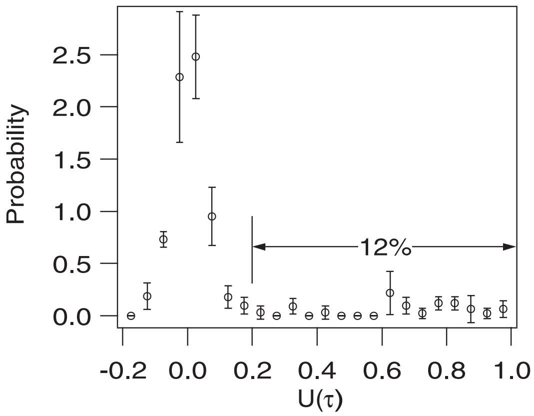

FIG. 2. Probability distribution of $U(\tau = 2.55 \times 10^5)$ of 16-bead chains for $\phi_c = 0.05$ and $\phi_m = 0.20$. About 12% of 256 chains give values greater than 0.2.

An examination of the trajectories of individual chains provides molecular information consistent with the above physical picture. This analysis shows that the molecules can be divided into two categories, at the highest matrix fraction. A small fraction of chains are trapped over the entire duration of the simulation and do not translate or rotate. The other chains do diffuse on long time scales but do so via a hopping mechanism. Figure 3 shows a sample trajectory for a $N = 16$ chain that shows how the center of mass displacement fluctuates about a constant value for long periods of time and then shows sudden changes which we attribute to hopping. An analysis of the hopping process shows that the probability distribution of trapping times is roughly exponential and not power law as might be expected if the process was a continuous time random walk.

The decoupling of translational and rotational relaxation and the presence of the hopping mechanism are signatures of dynamic heterogeneity. We refer to regions where the chains are trapped as *slow* regions and regions where the chains are mobile as *fast* regions. What determines if a region is fast? We find that the first peak in the pair correlation function, $g_{mc}(r)$, between the matrix and chain sites is higher for trapped chains than for mobile chains, and the distribution function of local matrix volume fraction (defined shortly), $P(\phi_l)$, is shifted to slightly higher volume fractions, although these differences are not statistically significant. [$P(\phi_l)$ is obtained by dividing the simulation box into cubic cells of side length Δ, with ϕ_l defined as the matrix volume fraction of the cell where the chain center of mass is located. $P(\phi_l)$ is the un-normalized distribution of ϕ_l] This can be seen in Figs. 4(a) and 4(b) which compare $g_{mc}(r)$ and $P(\phi_l)$, respectively, for mobile and trapped chains for $N = 16$, $\phi_c = 0.05$, and

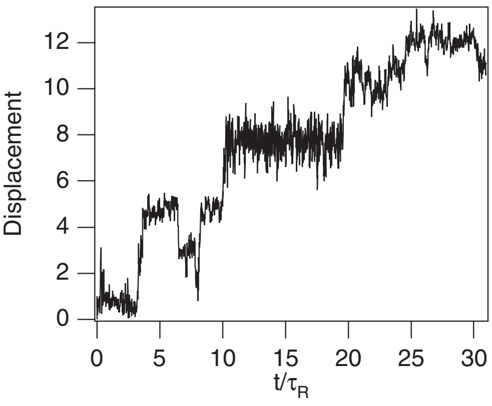

FIG. 3. Sample trajectory of the center of mass of a 16-bead chain for $\phi_c = 0.05$ and $\phi_m = 0.20$.

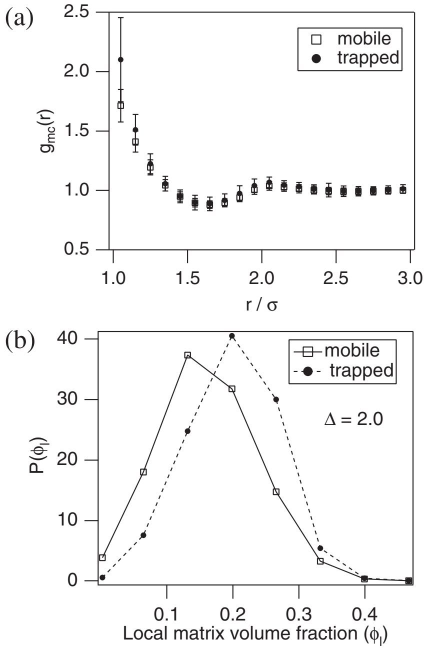

FIG. 4. (a) Pair correlation functions between the matrix and chain sites, $g_{mc}(r)$, and (b) distribution of local matrix volume fraction, $P(\phi_l)$, for $N = 16$, $\phi_c = 0.05$, and $\phi_m = 0.20$.

$\phi_m = 0.20$. Consistent with intuition, slower regions correspond to higher local matrix volume fractions as well as a higher probability of finding a matrix particle near a given monomer. The effect is not statistically significant, however, which suggests that factors other than matrix density must play a significant role in the chain dynamics. For example, the distribution of void spaces and their *connectivity* might be more important in determining solute dynamics.

In summary, we present MD simulations of hard chains in matrices of immobile hard spheres. Entanglement scaling is observed for the translational diffusion and initial decay of the rotational relaxation for high matrix densities. We observe that a fraction of chains are trapped at high matrix densities and this results in signatures of dynamic heterogeneity, i.e., the average end-to-end vector autocorrelation function does not decay even though the translational diffusion is normal. Under these conditions the mobile chains move via a hopping mechanism and can be trapped for several rotational relaxation times. The local matrix density near trapped chains is higher than that near mobile chains, but the effect is not statistically significant and probably not sufficient to explain the difference in dynamics. An important conclusion is that structural changes are not necessary for heterogeneity in the dynamics: The average structure of the random matrices in this work is identical to a hard-sphere liquid.

Extensions of this model can be used to study the melting of a glass and hence the glass transition. In this work the mass of the matrix spheres is infinite. By decreasing the mass of the spheres one can smoothly transition between a glass and a liquid, thus shedding light on the change in solute dynamics as the glass transition is approached. These are interesting directions that are promising avenues for understanding the nature of dynamics near a glass transition.

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