Rotational correlation and dynamic heterogeneity in a kinetically constrained lattice gas

Albert C. Pan
Department of Chemistry, University of California, Berkeley, California 94720-1460

(Received 29 June 2005; accepted 24 August 2005; published online 21 October 2005)

We study the dynamical heterogeneity and glassy dynamics in a kinetically constrained lattice-gas model which has both translational and rotational degrees of freedom. We find that the rotational relaxation time tracks the structural relaxation time as density is increased whereas the translational diffusion constant exhibits a strong decoupling. We investigate distributions of exchange and persistence times for both the rotational and translational degrees of freedom and compare our results on the distributions of rotational exchange times to recent single molecule studies.

I. INTRODUCTION

Glassformers are dynamically heterogeneous. Neighboring regions, nanometers in size, can have local relaxation times which differ by several orders of magnitude. The presence of heterogeneous dynamics is often measured experimentally by probing rotational degrees of freedom such as molecular dipoles. For example, Deschenes and Vanden Bout and colleagues have recently measured the rotation of single probe molecules in polymer films near the glass transition. These experiments found spatially heterogeneous dynamics on long-time scales characterized by fast local exchange of dynamical environments and a broad distribution of times between exchange events. We would like to capture the essential physics of these experiments with a simple microscopic model.

A popular class of models for studying glassy dynamics are the kinetically constrained lattice-gas models (for a review, see Ref. 4). They are simple caricatures of glassformers that consist of a noninteracting lattice gas with local constraints on particle motion. Despite their simplicity, these models exhibit surprisingly many of the hallmarks of glassy behavior that have been the focus of recent experimental and theoretical efforts. Here, we investigate a kinetically constrained lattice-gas model with translational and rotational degrees of freedom which captures many of the features seen in experiments such as stretched exponential decay of rotational autocorrelation functions and heterogeneous distributions of exchange times.

In Sec. II, we present the model and the computational methods used. Section III demonstrates the existence of heterogeneous dynamics. We also present ensemble measurements which display a precipitous dynamical slowdown and breakdown of mean-field dynamical relations. Section IV measures distributions of persistence and exchange times. Finally, Sec. V compares these distributions to those observed recently in single molecule studies.

II. MODELS AND COMPUTATIONAL DETAILS

The model consists of hard-core particles on a triangular lattice with no static interactions other than those that prohibit multiple occupancy of a single site. To each particle is associated a vector which can point along the six directions bisecting the triangular lattice. In other words, the vectors point toward the interstitial sites of the lattice.

Translation of particles obeys the kinetic constraints of the two vacancy assisted triangular lattice gas or the \(2\)-TLG: a particle at site \(r\) is allowed to move to a nearest-neighbor site \(r'\) if (1) \(r'\) is not occupied and (2) the two mutual nearest-neighbor sites of \(r\) and \(r'\) are also empty. These rules coincide with a physical interpretation of steric constraints on the movement of hard-core particles in a dense fluid.

Rotation of particles obeys a similarly physically motivated kinetic constraint if one imagines that the particles have small hard protrusions along the direction of their orientation vector; a particle \(i\) with a unit vector \(p_i\) can rotate either \(60^\circ\) clockwise or counterclockwise provided the two neighboring lattice sites along the direction between the initial and final orientations of \(p_i\) are empty. Translations preserve the direction of \(p_i\). We refer to this model as the rotational TLG. Due to the absence of nontrivial static interactions, there are no static correlations between particles. However, constraints on the kinetics allow nontrivial dynamic correlations to emerge in trajectory space.

In the computer simulations, we investigated particle densities \(\rho\) between 0.10 and 0.81 on a lattice with edge length \(L=128\) (\(L=256\) for \(\rho=0.81\)). The density \(\rho=1\) corresponds to the completely full lattice. At densities up to and including 0.77, over 60 independent trajectories of lengths 10–100 times \(\tau_n\), where \(\tau_n\) is the time for the self-intermediate scattering function at \(q=(\pi,0)\) Ref. 14 to reach \(1/e\) of its initial value (see below), were run. At densities 0.79, 0.80, and 0.81, 4–16 trajectories were run. These trajectories were stored logarithmically for later analysis (i.e., configurations were saved after 1, 2, 4, 8, 16, 32, etc., sweeps). Time was measured in Monte Carlo sweeps. During each sweep, particles were chosen randomly and transla-
tional and orientational moves were attempted with equal probability. For the higher density runs, a continuous time algorithm was used for greater efficiency. This algorithm involved making and updating a list of only those particles which have the possibility of either moving or rotating and choosing from among those exclusively during every move. The time was then incremented as one over the number of possible moves. Due to the lack of static correlations, initial configurations could be generated by random occupation of empty lattice sites by particles with random orientations until the desired density was reached.

III. HETEROGENEOUS DYNAMICS AND ROTATIONAL RELAXATION TIMES

Despite the lack of static correlations between rotational and translational degrees of freedom, dynamic coupling exists via the kinetic constraints. A particle which cannot rotate because it is sterically blocked by neighboring particles must wait for those particles to translate away before it is allowed to rotate again. In this sense, we expect rotational dynamics to be a good indicator of local structural relaxation in this model, as they are in experiment.

Figure 1 shows rotational trajectories of six particles at low and high densities. The particles at low density [Fig. 1(a)] rotate freely, performing a random walk through all angles. At higher densities, the particles perform random walks punctuated by periods of little to no rotation. In contrast to the trajectories at low density, dynamics at high density are clearly heterogeneous: at any given time, some particles are rotating quickly while others are essentially frozen. Similar behavior has been observed for translational motion of a probe molecule immersed in spin-facilitated models and in polymer films.

A useful ensemble measure of slow dynamics is the rotational autocorrelation function, \( C_\alpha(t) = \langle \mathbf{p}(0) \cdot \mathbf{p}(t) \rangle \), which indicates the time it takes for a particle to lose memory of its initial spin orientation. Here, the angled brackets denote an average over all particles and times \( t \). A plot of \( C_\alpha(t) \) is shown in Fig. 2(a). At low densities, relaxation shows a simple exponential profile. As density increases, the curves become more and more stretched exponential indicative of averaging over multiple relaxation time scales. This stretched exponential decay is what one would expect qualitatively from rotational trajectories such as those depicted in Fig. 1(b). An important quantity that can be extracted from \( C_\alpha(t) \) is the rotational relaxation time \( \tau_\alpha \), which is defined as \( C_\alpha(\tau_\alpha) = 1/e \).

Translational relaxation is often studied via the self-intermediate scattering function, \( F_\alpha(q,t) = \langle e^{i\mathbf{q} \cdot (\mathbf{r}_i(t) - \mathbf{r}_i(0))} \rangle \). Here, \( \mathbf{r}_i(t) \) denotes the position of particle \( i \) at time \( t \). The decay of the scattering function to \( 1/e \) at wave vector \( \mathbf{q} = (\tau, 0) \) is typically defined to be a structural relaxation time \( \tau_s \) as it gives a sense of how density fluctuations relax at relatively short length scales. Dynamic behavior at large length scales is studied via the self-diffusion constant \( D_s \) extracted from the mean-squared displacement, \( \langle |\Delta \mathbf{r}_i(t)|^2 \rangle = \langle \mathbf{r}_i(t) - \mathbf{r}_i(0) \rangle^2 \). The self-diffusion coefficient \( D_s \) is defined as \( D_s = \lim_{t \to \infty} \langle |\Delta \mathbf{r}_i(t)|^2 \rangle / 4t \). We omit further discussion of these quantities as they have been presented at length elsewhere for this and other models.

An important ramification of heterogeneous dynamics is the breakdown of mean-field dynamical relations such as the much studied Stokes-Einstein (SE) relation. In a system with homogeneous dynamics such as a normal liquid, we expect the relaxation behavior to be similar at all but the smallest length scales. In a glass, the presence of dynamic heterogeneity implies that such mean-field relations can be
has been seen in experiment. The scaling of

That is, the ability to rotate is intimately tied to local structure.

be rationalized qualitatively from the idea mentioned above
does not. That is, relaxation tracks structural relaxation whereas self-diffusion
the translational structural relaxation time
states. For example, the distribution of rotational persistence
tion. Exchange times measure the duration of particular
first instance of a change in state given an initial configura-

FIG. 3. Distributions of translational (a) exchange and (b) persistence times at (from left to right) \( \rho = 0.50, 0.60, 0.65, 0.70, \) and 0.75. The inset to (a) shows the exchange time distributions as a function of linear time \( t \) as opposed to logarithmic time to emphasize the emergence of broader long-
time tails as density is increased. The two distributions are related via

\[ P_{x,\text{trans}}(t) = P_{x,\text{trans}}(\ln(t)) \ln(10). \]

The solid lines in (b) are the distributions of persistence times calculated from the distributions of exchange times via Eq. (1) and the open circles are results of direct calculations. Time is in units of Monte Carlo sweeps.

FIG. 4. Same as Fig. 3, except for rotational times.

violated. In Fig. 2(b), we plot the inverse of the rotational relaxation time \( \tau_r^{-1} \) and the self-diffusion constant \( D_s \) versus the translational structural relaxation time \( \tau_o \). Rotational relaxation tracks structural relaxation whereas self-diffusion does not. That is, \( \tau_r^{-1} \sim \tau_o^{0.6} \) whereas \( D_s \sim \tau_o^{-0.6} \). The same trend has been seen in experiment. The scaling of \( \tau_r \) with \( \tau_o \) can be rationalized qualitatively from the idea mentioned above that the ability to rotate is intimately tied to local structure.

IV. DISTRIBUTIONS OF EXCHANGE AND PERSISTENCE TIMES

Direct measures of heterogeneous dynamics in glassy systems are distribution functions of persistence \( P_p(t) \) and exchange \( P_e(t) \) times. Persistence times measure the first instance of a change in state given an initial configuration. Exchange times measure the duration of particular states. For example, the distribution of rotational persistence times \( P_{\rho,\text{rot}}(t) \) in this model is the distribution of times, given an initial configuration, when a particle changes its rotational state for the first time. The distribution of rotational exchange times \( P_{\rho,\text{rot}}(t) \) is the length of time a particle remains in a particular rotational state. These distributions are multipoint functions because they depend not only on two points in time, but on all intervening points as well. Figures 3(a) and 4(a) show the distribution of exchange times for translational and rotational motions, respectively. Distributions of exchange times are important for understanding the origin of dynamical decoupling phenomenon [see Fig. 2(b)].

The distribution of exchange times for translations and rotations are very similar. There is very little change in short-time structure as \( \rho \) increases. Evidence of broadly distributed dynamics occurs in the long-time tails. The distributions of persistence times for translation and rotation are also qualitatively similar and display the same features noted in previous studies. Differences in structure between rotational and translational persistence can be attributed to the differing kinetic constraints. A particle can have the ability to rotate while being constrained translationally and vice versa.

Recently, it has been shown that the distributions of exchange and persistence times are related via the equation:

\[ P_p(t) \sim P_e(t') dt'. \]

(1)

The constant of proportionality is fixed by normalization. This should be a general relation independent of the model or observable studied. It has only been verified numerically, however, in spin facilitated Ising models. The solid lines in Figs. 3(b) and 4(b) show the distribution of persistence times calculated via Eq. (1). The open circles are the results of direct calculations at intermediate densities. We see that Eq. (1) is well satisfied.

V. COMPARISON WITH EXPERIMENTS

Recent single molecule experiments determined the distributions of rotational exchange times by following the dipole of embedded dye molecules. Near the glass transition temperature, the absolute value of the rate of angular change, \( |\Delta \theta/\Delta t| \), showed abrupt changes between different dynamical environments. We can anticipate from Fig. 1(b) that the same quantity in the rotational TLG will show similar behavior. From this quantity, Deschene and Van den Bout extracted a distribution of exchange times using a standard deviation criterion. Here, we examine to what extent the distribution of times measured in this way corresponds to the distribution of rotational exchange times defined in Sec. IV.
In Fig. 5(a), we plot $|\Delta \theta/\Delta t|$ where $\Delta \theta = \theta(t+\Delta t) - \theta(t)$ for the rotational TLG at high density. Deschenes and Vanden Bout assigned an exchange event whenever the average angle jump changed by more than two standard deviations from the previous average angle jump. Due to the coarse-grained nature of the rotational TLG, $|\Delta \theta/\Delta t|$ changes by discrete jumps. Therefore, exchange events can be unambiguously assigned whenever such a jump occurs. Figure 5(a) plots $|\Delta \theta/\Delta t|$ in increments of ten sweeps during a portion of a single molecule trajectory. The fastest exchange event measurable at this time resolution is ten sweeps. With infinite time resolution, however, we see that the definition of exchange times used in Sec. IV would correspond precisely with the Deschenes-Vanden Bout procedure.

We verify this in Fig. 5(b). Here, the distribution of rotational exchange times obtained via the Deschenes-Vanden Bout procedure outlined above (open circles) are compared to the distribution of rotational exchange times calculated in Sec. IV (solid line). The comparison is very good for about ten orders of magnitude. This method overestimates the distribution at early times for the reasons of time resolution mentioned in the previous paragraph. The data for the open circles in Fig. 5(b) was obtained by sampling in several overlapping time windows each spanning three orders of magnitude in time. These windows were then stitched together by matching their values in the overlapping regions to create the distribution shown in Fig. 5(b). These data are not normalized and have been shifted vertically by a constant to facilitate comparison with the exact distribution of exchange times.

The inset of Fig. 5(b) shows a comparison of the distribution of rotational persistence times. The open circles in the inset are obtained from the open circles in the main panel of Fig. 5(b) via Eq. (1). Once again, the agreement is very good. In particular, the data obtained via the procedure of Deschenes and Vanden Bout captures the structure and location of the main peak.

Single molecule experiments also measured the mean rotational exchange time $\tau_{x,\text{rot}}$ (i.e., the first moment of $P_{x,\text{rot}}(t)$, Fig. 4(a), inset) as a function of temperature. The data are shown in panel (a) of Fig. 5(b) and directly (solid line, see Fig. 4(a), inset). The inset shows a comparison of the distribution of rotational persistence times. The values for the open circles in the inset are obtained by applying Eq. (1) to the data in the main part of panel (b). Time is in units of Monte Carlo sweeps.

**ACKNOWLEDGMENTS**

The author would like to acknowledge David Chandler, Juan Garrahan, and Younjoon Jung for valuable discussions and the U.S. National Science Foundation and Department of Energy (Grant no. DE-FE-FG03-87ER13793) for funding. The author was an NSF graduate research fellow for part of this work.

The wave vector dependent quantity $F_\omega(q,t)$ was conveniently calculated on the square lattice because a correspondence can be made between the reciprocal lattice vectors of the square and triangular lattices as in Ref. 9.

Strictly speaking, the time step should be a stochastic variable drawn from a Poisson distribution with a mean of one over the number of mobile particles [see A. B. Bortz, M. H. Kalos, and J. L. Lebowitz, J. Comput. Phys. 17, 10 (1975)]. We have found, however, that the results obtained here for quantities of interest like the self-intermediate scattering function and the rotational autocorrelation function using an algorithm which lacks these time step fluctuations are indistinguishable from those obtained using conventional Monte Carlo when compared at intermediate densities.


