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Structural and dynamical heterogeneity in a glass-forming liquid

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We use the "isoconfigurational ensemble" [Phys. Rev. Lett. **93**, 135701 (2004)] to analyze both dynamical and structural properties in simulations of a glass-forming molecular liquid. We show that spatially correlated clusters of low-potential-energy molecules are observable on the time scale of structural relaxation, despite the absence of spatial correlations of potential energy in the instantaneous structure of the system. We find that these structural heterogeneities correlate with dynamical heterogeneities in the form of clusters of low molecular mobility.

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Over the last decade, the identification and study of dynamic heterogeneity (DH), especially in computer simulations, has added a new dimension to our understanding of complex relaxation in glass-forming liquids [1,2]. DH refers to the emergence and growth of spatially correlated domains of mobile and immobile molecules as the temperature T approaches the glass transition temperature T_g. A question that dominates research on DH concerns its connection to the structure of the liquid: What local configurational properties influence whether a given molecule is mobile or immobile?

Recent work by Widmer-Cooper, Harrowell, and Fynewever [3] has shown conclusively that a structure-dynamics connection must exist at the molecular level. To do so, they use an "isoconfigurational (IC) ensemble" [3–5], a set of microcanonical molecular dynamics (MD) trajectories in which each run starts from the same initial equilibrium configuration, but with molecular momenta chosen randomly from a Maxwell-Boltzmann distribution. The result is a set of trajectories lying on the same energy surface and evolving away from their common initial point in configuration space. They then define the "dynamic propensity": the average, in the IC ensemble, of the squared displacement of a molecule at a time comparable to the structural relaxation time. DH is observed in this approach in the form of increasing spatial correlations of the dynamic propensities in a glass-forming liquid as $T \rightarrow T_g$. Since the influence of the initial momenta is averaged over, the observed spatial correlations must be configurational in origin.

The strength of Ref. [3] is that it exposed features of DH that are structural in origin, without needing to determine what structural properties are responsible. Other studies have worked towards explicitly identifying structural correlators to dynamics. A number of works have identified relationships between average structural properties (especially free volume and measures of symmetry in the local molecular environment) and bulk dynamics; see, e.g., Refs. [6–9]. More recently, several studies have sought a correlation at the microscopic level—e.g., between local free volume and local mobility—with more success in some systems [10,11] than in others [12]. A notable absence of correlation between the local volume and the local Debye-Waller factor has been reported recently [13]. Insights have also been realized using local measures of symmetry to elucidate local mobility [11,14,15]. Recently, the local Debye-Waller factor has been shown to correlate to the dynamic propensity [16], firmly establishing the connection between local dynamics at short and long times.

Notably absent from the list of structural quantities that correlate well to dynamics at the single-molecule level is the potential energy. It has been shown that a molecule with a low potential energy will be less mobile, *on average*, than one with a high potential energy [17]. However, the variance around this average trend is comparable to or larger than the trend itself, making it impossible to predict what a *given* molecule will do based on its potential energy. Careful time averaging [10] and the use of single-molecule energies from inherent structures (IS) has been shown to yield little gain in correlation [16]. This is both perplexing and disappointing. Perplexing since it is known that the total IS energy, including for quite small systems, correlates well to the total system relaxation [18,19] and because simulation evidence exists for a growing length scale of potential energy fluctuations as $T \rightarrow T_g$ [20,21] and disappointing because the potential energy is a natural observable to correlate to dynamics, given the wide interest in the analysis of glass-forming systems using the potential energy landscape [22].

Here, by expanding the application of the IC ensemble to structural quantities, we show that it is possible to identify heterogeneities of the potential energy that correlate well to dynamic heterogeneities in a liquid where no useful correlation is discernible from the instantaneous properties of the system.

Our results are based on MD simulations of $N=1728$ water molecules interacting via the ST2 pair potential [23]. Much is known about this simulation model, in terms of both thermodynamic and transport behavior, making it a good candidate for a detailed analysis of structure-dynamics relationships in a model three-dimensional (3D) molecular liquid [24–27]. We study three T (350, 290, and 270 K) all at density $\rho=0.83$ g/cm^3. At this ρ, the hydrogen bond network in this model is more prominent than at other ρ, suggesting that local energetics may have a particularly strong influence on dynamics. This ρ is also convenient because the isothermal compressibility K_T (which is related to the strength of static density fluctuations) is decreasing with T (Fig. 1). Thus any DH that emerges as T decreases will not be due to the growth of conventional density fluctuations. At the same time, the isochoric specific heat C_V (and hence the magnitude of fluctuations of the system energy) is increasing to a maximum, so spatial variations of potential energy may be occurring.

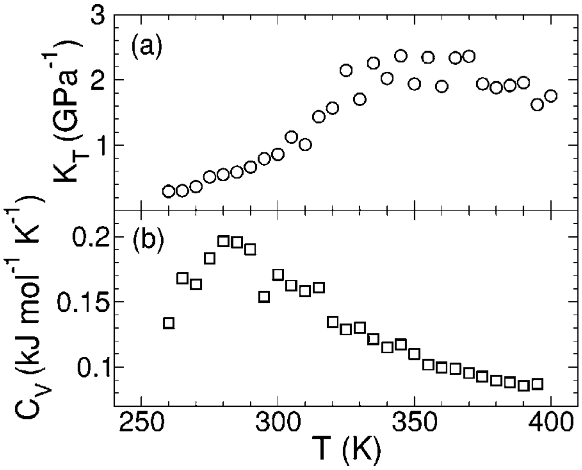

FIG. 1. (a) K_T and (b) C_V as a function of T along the ρ=0.83 g/cm^3 isochore. Data are derived from the simulations described in Ref. [26].

The ST2 model therefore provides a promising context for studying energy-dynamics correlations in a generic structured molecular liquid. We note that it is not our goal to elucidate the specific behavior of water, which would better be studied using one of the several more realistic water models currently available.

All simulations have constant N and volume V, a 1-fs time step, and use the reaction field method with direct intermolecular interactions cut off at 0.78 nm. At each T, we first conduct a standard T-controlled MD run. To ensure equilibration, these runs last for twice the time required for the mean-squared displacement to reach 1 nm^2. We then use the configuration at the end of these runs to initialize M=1000 runs of an IC ensemble. Each run is carried out in the microcanonical ensemble for a time t=308 ps (350 and 290 K) or 937 ps (270 K).

Let $r^2(i,k,t)$ be the squared displacement of the O atom of molecule i at time t in run k of an IC ensemble. The system-averaged and IC-ensemble-averaged mean-squared displacement $\langle r^2\rangle=(NM)^{-1}\Sigma_{i=1}^{N}\Sigma_{k=1}^{M}r^2(i,k,t)$ and non-Gaussian parameter $\alpha=[(3\langle r^4\rangle)/(5\langle r^2\rangle^2)]-1$ are shown in Fig. 2. Both show the characteristic pattern of a glass-forming liquid in which DH occurs. $\langle r^2\rangle$ develops a plateau at low T, indicating the onset of molecular caging, and α displays an increasingly prominent maximum as T decreases.

The dynamic propensity of each molecule is the value of $\langle r_i^2\rangle_{\rm ic}=M^{-1}\Sigma_{k=1}^{M}r^2(i,k,t)$ when t is on the order of the structural relaxation time [3]. It measures the propensity for molecule i to undergo a given displacement, given its starting point in the initial configuration, rather than indicating what the molecule will do in any particular run. Here, we extend the use of the IC ensemble to study structural properties as well as dynamics. We focus on $u(i,k,t)$, the contribution of molecule i to the instantaneous potential energy of the system at time t in run k of an IC ensemble. Specifically, $u_i=\Sigma_{j=1}^{N}\phi_{ij}$, where ϕ_{ij} is the pair potential energy of molecules i and j. Analogous to $\langle r_i^2\rangle_{\rm ic}$ we define $\langle u_i\rangle_{\rm ic}=M^{-1}\Sigma_{k=1}^{M}u(i,k,t)$. At a fixed t, $\langle u_i\rangle_{\rm ic}$ measures the propensity of molecule i to have a given value of the potential energy, given its starting point in the initial configuration.

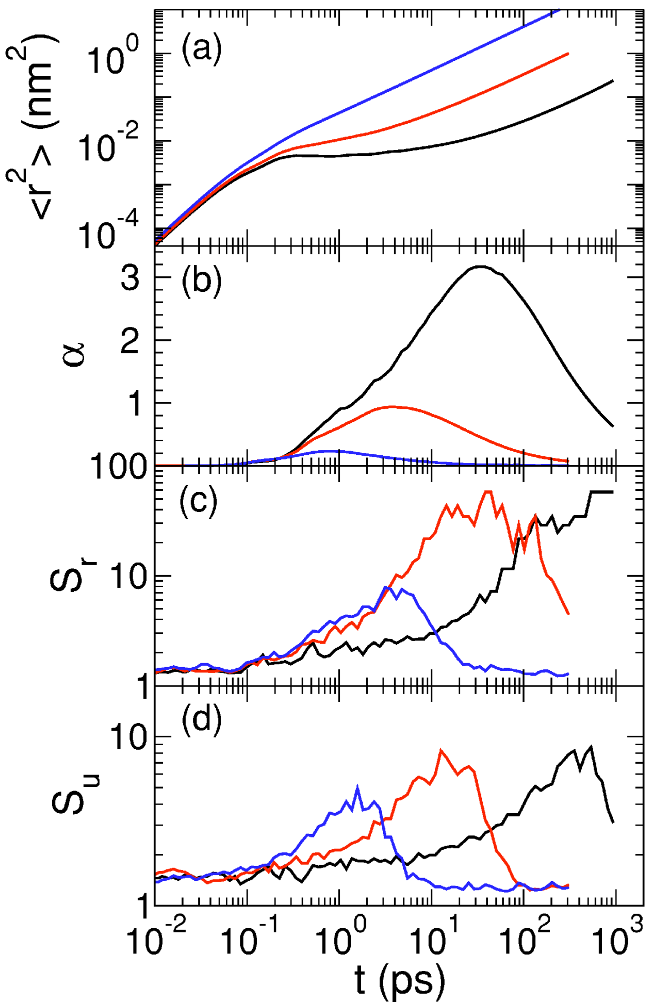

FIG. 2. (Color online) (a) Mean-squared displacement $\langle r^2\rangle$, (b) non-Gaussian parameter α, (c) mean cluster size for least mobile molecules, S_r, and (d) mean cluster size for tightly bound molecules, S_u, all as a function of t. From left to right in (a), the curves are for T=350, 290, and 270 K. In (b)–(d), the curve with the leftmost maximum is T=350 K, the middle maximum is 290 K, and the rightmost is 270 K.

First we test for the occurrence of DH, by evaluating $\langle r_i^2\rangle_{\rm ic}$ for each molecule as a function of t and examining the spatial arrangement of this quantity via a cluster analysis [28]. For reasons that will become clear below, we focus on the least mobile molecules, specifically the subset having the lowest 10% of $\langle r_i^2\rangle_{\rm ic}$ values. Clusters are defined by the rule that two molecules of this subset that are also within 0.35 nm of one another (the position of the first minimum of the O-O radial distribution function) in the initial configuration must be assigned to the same cluster. The number-averaged mean cluster size S_r is then found from $(1/N_c)\Sigma_n nC(n)$, where $C(n)$ is the number of clusters of size n and N_c is the total number of clusters. Figure 2(c) shows the t dependence of S_r at each T. At small t, S_r has a value consistent with a random choice of 10% of the molecules, approximately S_r=1.27, indicating no spatial correlations in $\langle r_i^2\rangle_{\rm ic}$. However, at intermediate times corresponding to the onset of structural relax-

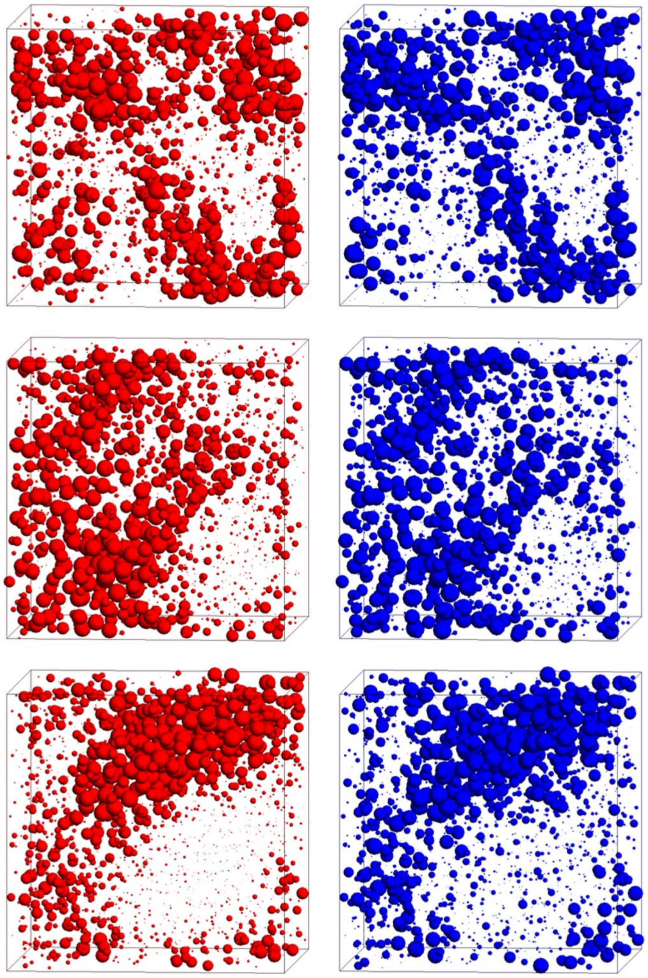

FIG. 3. (Color online) Dynamical heterogeneity (left panels) and structural heterogeneity (right panels) in the initial configuration at $T=350$ K (top panels), 290 K (middle panels), and 270 K (bottom panels). To make each panel, the values of $\langle r_i^2\rangle_{\rm ic}$ (or $\langle u_i\rangle_{\rm ic}$), evaluated at the time of the maximum of S_u, are assigned to each molecule in the initial configuration. These values are sorted and assigned an integer rank R_i from 1 to N, from smallest to largest. Each O atom is then plotted as a sphere of radius $R_{\rm min}\exp\{[(R_i-N)/(1-N)]\log(R_{\rm max}/R_{\rm min})\}$, where $R_{\rm max}=0.14$ nm and $R_{\rm min}=0.004$ nm. The result represents the rank of $\langle r_i^2\rangle_{\rm ic}$ or $\langle u_i\rangle_{\rm ic}$ on an exponential scale, such that the largest spheres on the left represent the least mobile molecules and the largest on the right the most tightly bound. Note that hydrogen atoms are not shown.

ation, a maximum occurs, indicating significant clustering of the least mobile molecules. At large t, S_r begins its return to the uncorrelated value, and the DH dissolves. The morphology of the DH observed near the maxima in Fig. 2(c) is illustrated in the left panels of Fig. 3. The correlated domains of larger spheres in Fig. 3 indicate the locations of the large clusters that generate the maxima in Fig. 2(c).

We then carry out exactly the same analysis, but using the lowest 10% of $\langle u_i\rangle_{\rm ic}$ values; this selects the subset of molecules with the greatest propensity to be "tightly bound." The mean cluster size for this subset, S_u, shows a similar behavior to S_r [Fig. 2(d)]. Note that in the limit $t\rightarrow 0$, we have $\langle u_i\rangle_{\rm ic}\rightarrow u_i^0$, where u_i^0 is the instantaneous potential energy of each molecule in the initial configuration. The behavior of S_u at small t confirms that u_i^0 shows essentially no spatial correlation at any T. And yet, on the same time scale as the signature of DH is observed in S_r, a maximum also occurs in S_u. The spatial correlations of molecular potential energies (i.e., *structural* heterogeneities) that generate the maxima in S_u are illustrated in Fig. 3. The morphology of the two types of heterogeneity shown in Fig. 3 is strikingly similar: there is a clear correlation between regions with a propensity to be the least mobile and a propensity to be tightly bound. It is worth bearing in mind that these two types of heterogeneity are defined independently. Neither the time scale on which the structural heterogeneity occurs nor the definition of the structural clusters depends on dynamical information.

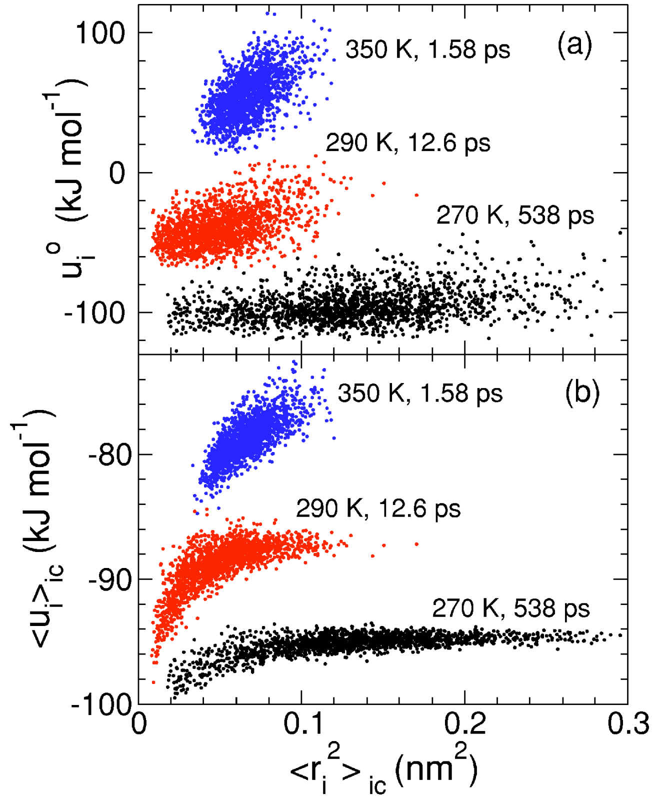

FIG. 4. (Color online) (a) u_i^0 and (b) $\langle u_i\rangle_{\rm ic}$, both versus $\langle r_i^2\rangle_{\rm ic}$, at each T. The times indicated, at which $\langle u_i\rangle_{\rm ic}$ and $\langle r_i^2\rangle_{\rm ic}$ are evaluated, correspond to the maxima of S_u. To ease comparison, in (a) the cloud for 290 K has been shifted upward by 50 kJ/mol and that for 350 K by 130 kJ/mol; in (b), the cloud for 350 K has been shifted down by 4 kJ/mol.

The absence of a useful correlation between u_i^0 and the dynamic propensity is demonstrated by a scatter plot of u_i^0 against $\langle r_i^2\rangle_{\rm ic}$, evaluated at the time of the maximum of S_u at each T [Fig. 4(a)]. The best correlation is found at high T, but even here some molecules in the lowest 10% of u_i^0 have values of $\langle r_i^2\rangle_{\rm ic}$ comparable or even larger than the mean of $\langle r_i^2\rangle_{\rm ic}$. At lower T the correlation only gets worse: molecules with the lowest values of u_i^0 are found across the entire spectrum of $\langle r_i^2\rangle_{\rm ic}$ values.

Figure 4(b) shows a scatter plot of $\langle u_i\rangle_{\rm ic}$ versus $\langle r_i^2\rangle_{\rm ic}$ at the time of the maximum of S_u at each T. Here we see the reason why we focus on the least mobile and most tightly bound molecules: it is at the lower end of these scatter plots that the points are most easily distinguished from the overall population. In contrast, the correlation between the most mobile and least tightly bound molecules is little improved over that in Fig. 4(a). We have also examined the clusters formed by the 10% most mobile and least tightly bound subsets. The most mobile molecules also form clusters at intermediate times, although the strength of the effect is weaker than for the least mobile molecules. Interestingly, the least tightly bound subset shows a *decreasing* tendency to cluster as T decreases, with the maximum in S_u becoming difficult to discern at the lowest T. Whether this is a generic behavior or a feature of this particular network-forming liquid requires further study.

We have tested if the poor correlation between $\langle r_i^2 \rangle_{\mathrm{ic}}$ and u_i^0 [Fig. 4(a)] improves if we replace u_i^0 with its value in the IS of the initial configuration, but as in Ref. [16] it does not. Since the evaluation of both the IS and IC ensembles removes the influence of molecular momenta (respectively, by quenching and by averaging), it is instructive that the former reveals no correlation to single-molecule mobility [16], while the latter does. This difference shows that the IC ensemble not only averages out the "noise" imposed by molecular momenta, but also captures additional information not available from the IS of the initial configuration. For example, an IC ensemble samples local transition states (i.e., saddle points of the potential energy field experienced by a molecule), information that is not captured in a single IS.

In summary, we demonstrate that the emergence and growth of heterogeneity in a glass-forming liquid is not solely a dynamical phenomena, but also structural, and that both types of heterogeneity can be analyzed using the IC ensemble. In contrast to previous studies, but in line with expectations, our work shows that the potential energy of a single molecule does indeed have a relationship to its mobility. We also note that the IC ensemble can be used to relate any molecular quantity (e.g., local volume, local symmetry) to mobility, which will permit the structural origins of DH to be sought in a broad range of cases, including those where potential energy itself may not correlate to mobility (e.g., hard sphere systems). We note that a clear deficiency of the IC ensemble is that it does not immediately generate observables that can be measured in current experiments, although there is some promise that this issue might be resolved by adapting the approach of Refs. [21,29]. Despite this, the IC ensemble offers a crucial and unique insight: it exposes in real space the morphology of the structural heterogeneity present in a *single* instantaneous configuration, information that is lost if the conventional average over initial configurations is also taken.

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