How Reproducible Are Dynamic Heterogeneities in a Supercooled Liquid?

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The particle dynamics in a liquid exhibits a transient spatial distribution of dynamic heterogeneities. The relationship between this kinetic structure and the underlying particle configuration remains an outstanding problem. In this Letter, we present a general simulation technique for identifying the features of the dynamic heterogeneity which arise due to a specific configuration, as distinct from the random spatial variation due to the intermittent particle dynamics.

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Liquids do not become glasses homogeneously. Tammann [1] suggested as much as far back as 1933. With the accumulation of data from experiments and simulations of dynamic heterogeneities in supercooled liquids [2], we can now state the situation more explicitly. The transition to rigidity involves the appearance of slowly relaxing domains whose dimensions and lifetimes increase with supercooling. This phenomenological account of the glass transition neatly sidesteps the key question: what kind of structure is responsible for these slow domains? An answer to this question remains elusive. In a recent review, Ediger [2] observed, "At present, it is an article of faith that something in the structure is responsible for dynamics that can vary by orders of magnitude from one region of the sample to another at T_g."

While restricted in terms of time and length scales, molecular dynamics (MD) simulations represent the best opportunity currently available to unravel the relationship between structure and kinetics in glass-forming liquids. In this Letter, we demonstrate that, as supercooling increases, a given configuration increasingly constrains the *propensity* of particles to subsequently exhibit large displacements. We show that the particle displacements observed in any single trajectory offer just one sampling of this propensity, selected by the random contingency of momenta fluctuations. Our approach is based on the analysis of the correlations among the set of N-particle trajectories that pass through a specific particle configuration.

Over the last ten years, dynamic heterogeneity has become recognized as a general phenomenological feature of glass formation [2]. The existence of these long-lived kinetic fluctuations has been useful in rationalizing some puzzling aspects of kinetics in supercooled liquids. These include non-Fickian diffusion [3], deviations from classical crystal nucleation theory [4], and the breakdown of scaling between translational diffusion, on the one hand, and, on the other, rotational diffusion [5], shear viscosity [6], or structural relaxation [7]. Helpful as these developments are, they do not address the fundamental question of the relationship between structure and kinetics in the supercooled liquid. The spatial distribution of particle mobilities appears to offer a considerable amount of information on this very point. A number of papers have considered the local connection between dynamics and structure, the latter being characterized using topology [8], potential energy [9,10], and free volume [11]. While most have reported some correlation, none have established a correlation of sufficient strength to indicate a causal link, i.e., that the local kinetics was *determined* by the selected aspect of the local structure.

In this Letter, instead of trying to directly address the question "What aspect of the structure gives rise to the observed dynamic heterogeneity?", we shall answer the related question, "What aspect of the dynamic heterogeneity actually arises from the structure?" It is logically necessary to answer this question before attempting the first. As we shall show, it is also possible to answer the latter question without having to first solve the fundamental problem of identifying the correct measure of the particle structure relevant to determining the subsequent dynamics.

We shall consider a two-dimensional glass-forming liquid consisting of a binary mixture of particles interacting via purely repulsive potentials of the form

$$u_{ab}(r) = \epsilon\left[\frac{\sigma_{ab}}{r}\right]^{12}, \tag{1}$$

where $\sigma_{12} = 1.2 \times \sigma_{11}$ and $\sigma_{22} = 1.4 \times \sigma_{11}$. All units quoted will be reduced so that $\sigma_{11} = \epsilon = m = 1.0$ where m is the mass of both types of particle. Specifically, the reduced unit of time $\tau = \sigma_1\sqrt{m/\epsilon}$. A total of $N = 1024$ particles were enclosed in a square box with periodic boundary conditions. The molecular dynamics simulations were carried out at constant number of particles, pressure ($P = 13.5$), and using a Nosé-Poincaré-Andersen Hamiltonian developed by Laird and coworkers [12] which allows for the correct sampling from an isothermal-isobaric distribution. The equations of motion were integrated using a generalized leapfrog algorithm

[12]. The structure and dynamics of this model glass-forming liquid has been reported in detail elsewhere [8,13].

In Fig. 1, we present the plots of the particle displacement vectors following three different runs starting from the same configuration of an equilibrated liquid. The three runs differ only in the random assignment of particle momenta from the Maxwell-Boltzmann distribution at the appropriate temperature. Each run was carried out at a pressure $P = 13.5$ and a temperature $T = 0.4$, which is just below the onset temperature of β relaxation. The run times were all 1000τ, equal to roughly 1.5 times the structural relaxation time τ_e (τ_e is defined in terms of the intermediate incoherent scattering function $F(q, t)$ such that $F(q_o, \tau_e) = 1/e$ where q_o is the wave vector of the Bragg peak and $e = 2.7183$, the base of the natural logarithm). This run interval was chosen to maximize the observed dynamic heterogeneities. If one were to choose run times much shorter or longer, the dynamic heterogeneities would be unobservable since they represent the transient phenomenon associated with structural fluctuations.

Each plot in Fig. 1 exhibits the now familiar features of dynamics in deeply supercooled liquids: large variations in the particle displacements, clear clustering of the "slow" particles, and aggregation of the more mobile particles, sometimes in "stringlike" features. What is just as striking is that the spatial arrangement of particle displacements differs markedly from plot to plot. While some particles exhibit a mobility that is reproducible from run to run, the dynamics of other particles varies substantially. The trajectory plots in Fig. 1 illustrate the significant role that noise, here in the form of momenta fluctuations, plays in determining the spatial distribution of the particle displacements.

Let us consider the possibility that there is no correlation at all between an initial configuration and the subsequent particle dynamics. In this case, each particle's squared displacement, averaged over many trajectories with the same initial configuration, would be the same as that of every other particle of the same species. This conclusion arises from the fact that the only point of connection between the different trajectories is the common initial configuration. It follows, therefore, that the magnitude of variation between the trajectory-averaged squared displacements of different particles of the same species is sufficient to establish the degree to which the initial configuration determines dynamics.

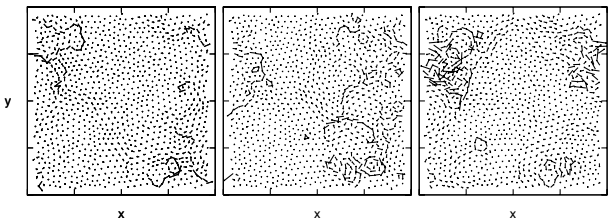

FIG. 1. The particle displacements, indicated as vectors joining the initial to final particle positions, resulting from three MD runs of 1000τ at $T = 0.4$. All runs made use of the same initial configuration and differed only in the assignment of initial momenta to particles.

To this end, we introduce the *isoconfigurational ensemble* consisting of N_{runs} separate simulation runs over a fixed time interval, all starting from the same particle configuration but with momenta randomly assigned from the Maxwell-Boltzmann distribution at the appropriate temperature. Let $f_i(\Delta r)$ be the ensemble distribution of the displacement of particle i over the fixed time interval. These distributions represent the ensemble characterization of each particle's capacity for movement from a specific initial configuration. (We note that these distributions are invariant to time reversal.) We shall refer to the second moment of $f_i(\Delta r)$, i.e, the ensemble mean of the squared displacement of particle i, $\langle \Delta r_i^2 \rangle_{ic}$, as the *propensity for motion* of particle i in the given initial configuration. (The expression $\langle \cdots \rangle_{ic}$ indicates an average over the isoconfigurational ensemble.) To compare the propensities from different temperatures T we set the time interval over which a given trajectory is run to be $1.5\tau_e(T)$.

In Fig. 2, we plot the distribution of propensities for the small particles for configurations at $T = 1.0$ and 0.4, averaging over 1000 runs at each temperature. Note the substantial increase in width of the distribution on cooling (the large-particle distribution shows a similar increase in width). As argued above, this increase in the differences in the ensemble mean squared displacements among particles on cooling can only be the result of the increasing degree to which particle configurations determine the subsequent dynamics. With this result, we can now replace the "act of faith" of Ref. [2] with the explicit demonstration of the heterogeneity of particle *propen-*

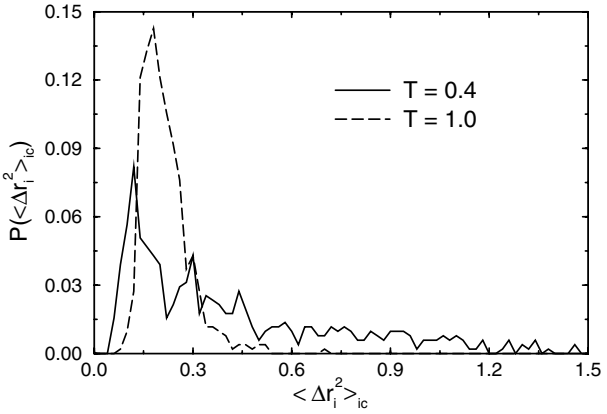

FIG. 2. The distribution of small-particle propensities calculated using 1000 runs for single configurations at $T = 0.4$ and 1.0. Note the increase in width with increasing supercooling.

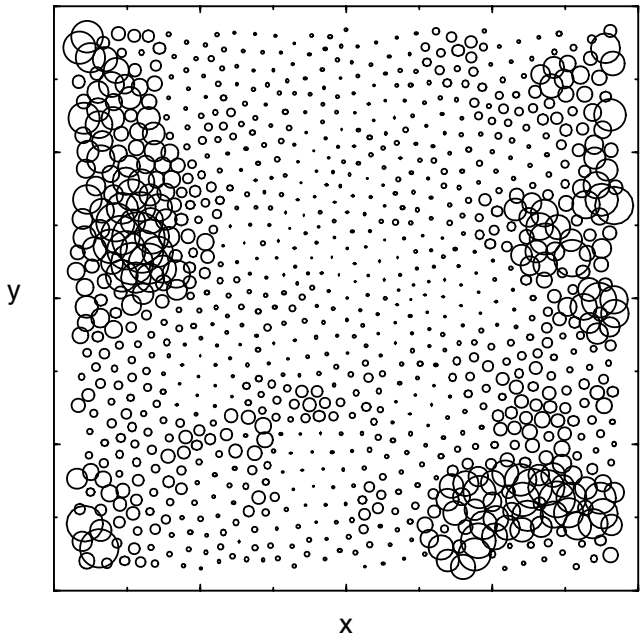

FIG. 3. The spatial distribution of propensities at $T = 0.4$ calculated using 1000 runs. A circle of radius $\langle \Delta r_i^2 \rangle_{ic}$ has been drawn about the initial position of each particle i.

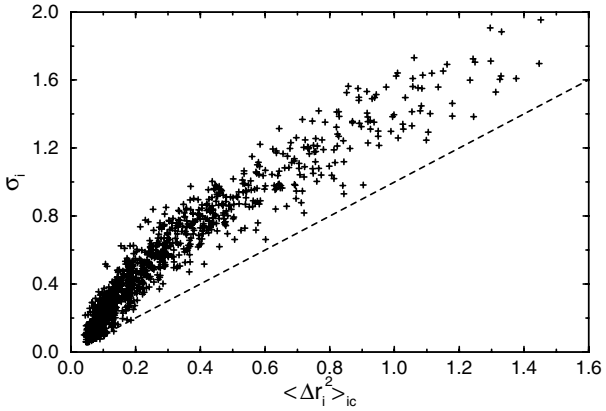

FIG. 4. A scatter plot of the standard deviation σ_i (calculated over 1000 runs at $T = 0.4$) of the squared displacement of each particle plotted against its propensity. The dashed line is the expected relation for a 2D random walk where each point along the line can be interpreted as arising from a different value of the diffusion constant.

sities, a feature which, by construction, is completely determined by the initial configuration.

The spatial distribution of the propensities for the same $T = 0.4$ configuration used in Fig. 1 is mapped in Fig. 3. The radius of the circle about a particle's position in the initial configuration is equal to that particle's propensity. On comparison of the propensity map in Fig. 3 with the individual trajectory maps in Fig. 1 from the same initial configuration, we find that the domains of high propensity are generally more compact than the often stringlike clusters of large displacements observed in individual trajectories.

The significant variation in the ith particle's mobility between different runs, as illustrated in Fig. 1, can be quantified using the standard deviation, σ_i, of the propensity, where $\sigma_i^2 = \langle \Delta r_i^4 \rangle_{ic} - \langle \Delta r_i^2 \rangle_{ic}^2$. As shown in Fig. 4, σ_i at $T = 0.4$ is significantly larger relative to the propensity $\langle \Delta r_i^2 \rangle_{ic}$ than one would have expected from a continuum random walk in 2D. The size of this deviation underscores the reason for the introduction of the isoconfigurational ensemble. It also determines the minimum value of N_{runs} required to ensure that the standard error of quantities like the propensity are small enough so that their spatial variation is statistically significant. (The average relative standard error of the propensities plotted in Fig. 3 is roughly 6.5% and considerably smaller than much of the observed spatial variation in the propensities.)

The large variation in an individual particle's movement from run to run represents an important piece of kinetic information, distinct from the propensities and their spatial distribution. This variability in the mobility of a particle from run to run arises from the *intermittent* nature of particle motion in supercooled liquids. The large variances of the individual particles are typically associated with highly asymmetric $f_i(\Delta r)$'s, with a peak at a low value of Δr and a long tail extending to large displacements. This asymmetry can be quantified as a deviation from a Gaussian form through the use of a non-Gaussian parameter α_i for particle i given by

$$\alpha_i = \frac{\langle \Delta r_i^4 \rangle_{ic}}{2\langle \Delta r_i^2 \rangle_{ic}^2} - 1. \tag{2}$$

The quantity α_i equals zero for a Gaussian distribution. The distributions of α_i for configurations at $T = 1.0$ and 0.4 are plotted in Fig. 5. While at high temperatures we

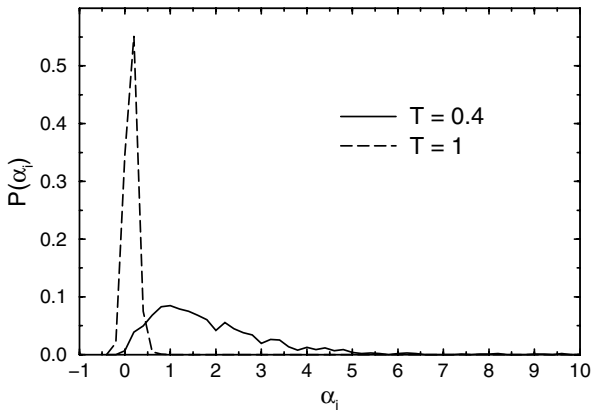

FIG. 5. The distribution of non-Gaussian parameters α_i for individual particles [see Eq. (2)] for configurations at $T = 0.4$ and 1.0 (calculated using 1000 runs).

find that all the individual $f_i(\Delta r)$'s are close to Gaussian, the supercooled sample exhibits a broad distribution of α's with most particles exhibiting a significantly non-Gaussian distribution of displacements. Note that this non-Gaussian parameter is quite distinct from that discussed previously in the context of supercooled liquids [14]. The α_i introduced here refers to the variety of displacements achieved by a *single* particle over the ensemble of trajectories, as opposed to the variety of displacements achieved by *different particles* in a single trajectory. In the language of the jump model of particle motion [15], the propensity characterizes the average waiting time and jump length, while the non-Gaussian character of the $f_i(\Delta r)$'s is a result of either displacement correlations between successive jumps and/or non-Poisson statistics for the number of jumps within the observation time.

As the glass transition is defined by its dynamics, the task of establishing its structural origin, therefore, requires us to begin with the dynamics and deduce what structures are responsible. This is an inversion of the usual problem in condensed matter and presents us with a new quandary: how trustworthy are the structural clues provided by the observed particle dynamics? In this Letter, we have demonstrated that there is considerable variation in the dynamical evolution of a specific particle configuration. We conclude that some aspects of the particle dynamics are not significantly correlated with the initial configuration and therefore cannot be "explained" by reference to that configuration. Through the introduction of the isoconfigurational ensemble, we have established that it is the spatial variation in the propensity for particle motion, rather than the motion itself, that is completely determined by the initial configuration. Because of the intermittency of particle motion, the failure to observe motion of a particle in a single run actually provides little information about the particle's *propensity* to move.

A number of recent papers have characterized the transition in particle dynamics on supercooling as a transition from hydrodynamically-governed dynamics to landscape-dominated dynamics [16]. The "landscape" here refers to the potential energy surface over the configuration space. We have arrived in this Letter at an alternative description of this fundamental temperature dependent change, i.e., a transition, on cooling, from structure-independent (hence, liquidlike) propensities for motion to structurally-determined propensities. One advantage of this new account over the landscape picture is that it refers directly to the behavior of the liquid in real space rather than the abstract configuration space.

The assignment of propensities to particles represents the major result of this Letter. This result provides a rigorous method for establishing the link between a given configuration and the subsequent dynamics. The remaining problem is to uncover the causal link between specific structural features of a configuration and the resulting propensities. A detailed account of the correlation between propensity and structure in the 2D mixture is currently in preparation.

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