Correlation of Local Order with Particle Mobility in Supercooled Liquids Is Highly System Dependent

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We investigate the connection between local structure and dynamical heterogeneity in supercooled liquids. Through the study of four different models, we show that the correlation between a particle's mobility and the degree of local order in nearby regions is highly system dependent. Our results suggest that the correlation between local structure and dynamics is weak or absent in systems that conform well to the mean-field picture of glassy dynamics and strong in those that deviate from this paradigm. Finally, we investigate the role of order-agnostic point-to-set correlations and reveal that they provide similar information content to local structure measures, at least in the system where local order is most pronounced.

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Supercooled liquids display markedly heterogeneous dynamics, despite possessing structural properties that appear nearly unchanged from those of normal liquids from which they are prepared [1]. While there has been intense focus on understanding dynamical heterogeneity in a wide variety of systems, the structural origin of this phenomenon is not well understood [2,3]. Simulations of model supercooled liquids are useful for understanding the connections between structure and dynamics because particle locations may be followed precisely for all times. Nonetheless, new theoretical tools are needed to filter out extraneous detail from the key structural and dynamical fluctuations in glassy systems.

One particularly useful simulation-based tool for quantifying the influence of structure on dynamics is the isoconfigurational ensemble, where a large number of molecular dynamics simulations are initiated from the same starting configuration with momenta sampled randomly from a Boltzmann distribution [4,5]. Under glassy conditions, spatial heterogeneities are immediately evident in the isoconfigurational displacement (or propensity) field. A reasonable hypothesis is that particles with low propensity have a larger measure of local structural stability. Surprisingly, however, simple structural quantities, such as free volume and local potential energy, show little correlation with the heterogeneity of the propensity field [6]. In some models, localized soft modes [7–9] or unstable modes [10] appear to correlate strongly with propensity, but the degree of universality of this connection has not been thoroughly investigated.

Recently, focus has turned to the study of specific structural motifs and their putative connection with the dynamics of supercooled liquids. The notion that the frustration of local order incommensurate with bulk crystalline periodicity may be related to glass formation is an old one [11–14]. New evidence for the growth of domains associated with local packing motifs has been presented for several simple [15] and realistic model systems [16], where particles tend to be found in certain locally preferred structures (LPS) with increased supercooling. As a general rule, more fragile systems display a more rapid increase in LPS concentration and domain extent [15,16]. In some systems, a correlation between the size and location of LPS and slow dynamics has been observed [17,18], although the quantitative meaning of the correlations observed remains, in a statistical sense, obscure.

Point-to-set (PTS) correlations have emerged as an alternative quantifiable metric of amorphous ordering. PTS correlations measure the decrease of configurational entropy imposed by the presence of particles pinned in an equilibrium configuration [19,20]. The length scale associated with PTS correlations has been demonstrated to grow upon increased supercooling in several systems [20–22], although its variation is rather modest over the dynamical range currently accessible in simulations [23]. Nonetheless, several observations indicate that the growing PTS length scale should ultimately drive the dramatic increase in relaxation times in supercooled liquids [24–26]. It should be noted that PTS correlations, as well as other recently proposed measures of static correlations [27,28], are "order agnostic" [23], and therefore, their growth does not necessarily connect to the emergence of specific local structures, such as those identified in the LPS studies.

In this Letter, we quantify the correlation between static structure and dynamical heterogeneity in supercooled liquids in a statistically precise sense and within a coherent simulation framework. We demonstrate that seemingly similar systems may differ dramatically with respect to the degree to which specific local structural motifs correlate with dynamics. Our results indicate that scenarios connecting LPS cluster formation and glassy behavior [29,30] cannot be

generically correct. The observed model dependence suggests instead that local structural quantities play a key role in systems with large deviations from mean-field glassy behavior. Finally, we show that a connection exists between growing PTS correlations and LPS in systems where LPSs are strongly predictive of dynamical heterogeneity.

The first two models we study are binary Lennard-Jones mixtures, namely the Kob-Andersen (KA) system [31] and the Wahnström (Wahn) system [32]. The definition of these models and their LPS statistics have been extensively detailed in Ref. [33]. The KA system is an 80:20 mixture, while the Wahn system is equimolar. As a third system, we study a binary mixture of harmonic spheres (Harm) at a density such that that jamming is approached by lowering temperature near to zero ($\rho = 0.675$) [34]. In all cases, one species is smaller (B for KA and Wahn, A for Harm) and is intrinsically more mobile. Results for the small particles will be reported in the main text and for the large particles in the Supplemental Material [35]. In the following, we discuss all quantities using standard reduced units. For all three systems, we study systems with $N = 1000$. Further simulation details and a description of the LPS in each system can be found in the Supplemental Material [35].

While all of the above models are simple binary mixtures with short-ranged interaction potentials, their local structures differ significantly. For each model, we identify particles participating in LPS through a Voronoi analysis [35]). These LPS correspond to icosahedra, bicapped square antiprisms, and distorted icosahedral structures in Wahn, KA, and Harm, respectively. The relative abundance of these LPS at low temperatures is model dependent: it is fairly significant in the Wahn model (about 10% of the particles are at the center of a LPS) and weaker in the other models. In the KA model, this is due to the fact that twisted bicapped prisms are mostly centered around the small particles, which constitute the minority species.

In order to investigate the connection between the LPS in each system and dynamical behavior, we perform simulations in the isoconfigurational ensemble at supercooled temperatures, $T = 0.588$ for the Wahn, $T = 0.45$ for the KA, and $T = 5.5$ for the Harm. These temperatures correspond roughly to the same degree of supercooling, as measured by the relative distance (about 3%–6%) from their fitted Mode-Coupling temperatures, T_c [35]).

We select 40 (20) equilibrated configurations for the KA and Wahn (Harm) systems and perform the Voronoi analysis as discussed above. For each configuration, we performed 200 (100) NVT simulations in the isoconfigurational ensemble. From the simulations starting from each configuration, we compute the particle mobilities $\mu_i(t) \equiv \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)| \rangle_{\rm iso} \equiv \langle |\delta \mathbf{r}_i(t)| \rangle_{\rm iso}$. To quantify the number of LPS associated with a given particle, we count the number of structures deemed locally preferred in a spherical region of radius l around each particle ($n_{\rm LPS}$). All results reported here are nearly insensitive to this l value in the range we have investigated $1.5 \leq l \leq 3.0$, and we chose to report results only for $l = 2.5$.

In Figs. 1(a)–1(c), we show the combined probability distribution of μ_i and $n_{\rm LPS}$ for the three systems introduced above. We quantify correlation by using the Spearman rank correlation coefficient K [45], which has been used previously in a similar context [6]. K is 1 if two quantities are related by a monotonically increasing function and -1 if by a decreasing one. K values are shown in the top-right corner of each histogram. We see visually and quantitatively that the correlation is much stronger in the Wahn system than in the KA and Harm systems. For comparison, the probability distributions for correlation between mobility and local energy ($E_i = (e_i + \sum_{j \in \text{neigh}(i)} e_j)/(1 + |\text{neigh}(i)|)$, where $|\text{neigh(i)}|$ is the number of neighbors in the Voronoi structure around particle i) are shown in Figs. 1(d)–1(f). The correlation is fairly significant in the two Lennard-Jones mixtures and much weaker in the Harm system.

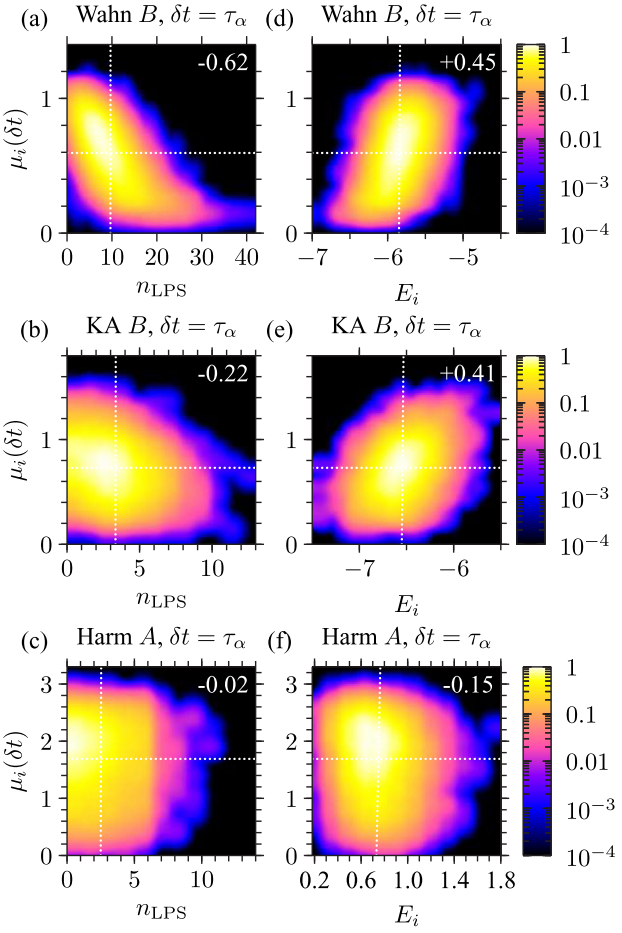

FIG. 1 (color online). Interpolated histograms of particle mobility. Numbers at the top right indicate Spearman rank correlation coefficients K [45]. The first column shows the correlation between mobility and $n_{\rm LPS}$ with the LPS defined in the text. The second column shows correlation with E_i, the sum of a particle and its neighbors' pair energies. White dotted lines show the average value of the quantity on the horizontal and vertical axes.

Inspection of Fig. 1(a) reveals a long tail in the histogram of n_{LPS} values. From these data, we can predict that a particle in a domain rich in icosahedral structures will be very immobile. Looking at the data at $n_{\mathrm{LPS}} = 0$ instead, we see that such particles will have higher than average mobility. However, slow and fast particles have a wide range of n_{LPS} values. In Fig. 2 we show the level of "precision" [45] in predicting which particles are slow based on n_{LPS} and E_i for the models studied, as well as the K values. Here, precision is defined as the percentage of particles in the top (bottom) 2% of n_{LPS} (E_i), which are also in the bottom 10% of $\mu_i(\delta t)$. All trends discussed are insensitive to the particular percentiles chosen for this definition of precision (see the Supplemental Material [35] for further details, including a discussion of sample-to-sample fluctuations in these quantities).

When viewed from this statistical perspective, several striking features are observed. For the Wahn system, LPSs are highly predictive of slow dynamics. In particular, using our definition of precision, one may "predict" the location of slow particles with near perfect accuracy up to τ_α, and such a correlation continues to grow to the longest times we investigated. In the KA system, local energy is more predictive of slow dynamics than LPS locations, and the correlation for both local energy and n_{LPS} in KA and Harm is far lower than in the Wahn system.

We may thus conclude that the correlation between dynamics and local structural metrics such as n_{LPS} is highly system dependent. What may be taken from this dramatic degree of variability? Among the three models studied, the Wahn system shows the largest departures from mean-field behavior. Namely, Wahn exhibits large violation of the Stokes-Einstein relation, sizable deviations from time-temperature superposition, and large inconsistencies between fitted mode-coupling exponents [35,46]. From this perspective, the KA system shows moderate deviations from mean-field behavior. This leads us to consider whether the correlation between local structural order and slow dynamics might be connected to how much a model system conforms to the mean-field paradigm. While the Harm system does not uniformly display mean-field behavior, results from finite size studies [47] and the existence of a nonmonotonic dynamical length scale [34] suggest that its behavior is at least partially harmonious with mean-field theory. This leads us to posit a connection between a high degree of local structure-dynamics correlation and strong spatial fluctuations which are manifest in systems that deviate from mean-field behavior.

To better test this notion, we study a fourth system, the high-density ($\rho = 2.0$) Gaussian core model (GCM). The GCM is a single-component fluid with Gaussian repulsions [48,49], which has all the hallmarks of glassy behavior while matching mean-field predictions of dynamical exponents, strongly suppressed non-Gaussian fluctuations and minimal Stokes-Einstein violation [49]. This mean-field behavior seems to arise naturally from the long ranged and ultrasoft interaction potential (see discussion in the Supplemental Material [35]).

In Fig. 2(d) we show results for $N = 3456$ Gaussian core particles at $T = 3.2$ with 100 isoconfigurational runs initiated from 20 independent configurations. We note that this temperature is slightly higher, relative to $T_c = 2.7$, than the one used in the other models, but corresponds instead to the same relative increase in relaxation time as observed for the Wahn system [35]. We found that distorted crystal-like structures constitute the LPS of the model (the underlying stable crystal at the studied density is bcc). In agreement with our expectations, the correlation between n_{LPS} and dynamics in the GCM system is very low, just as in the Harm system, and only marginally improves as t increases [50]. It may appear that the correlation between n_{LPS} and dynamics in both the KA and GCM system are superficially similar. However, the LPS in the GCM system are simple crystalline motifs that exist because of the difficulty of avoiding such particle arrangements in a monatomic system. In this sense, we view the correlation of *both* n_{LPS} and E_i as significantly weaker in the GCM system when compared with KA.

It would be natural to speculate that in systems such as the Harm and GCM models, there simply exists *no* connection

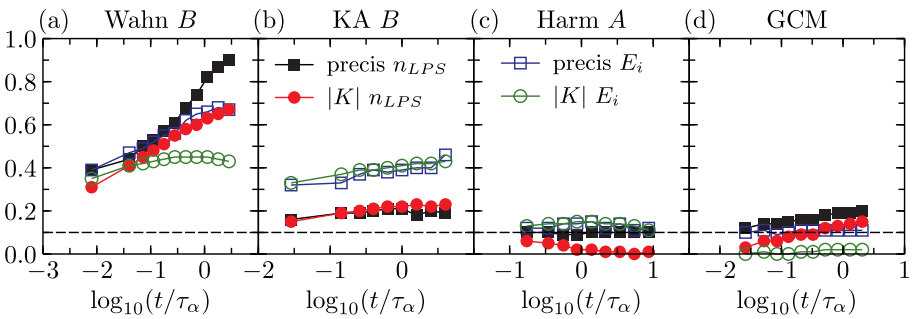

FIG. 2 (color online). Time dependence of predictability metrics and correlation coefficients as a function of time for four models. Closed symbols correspond to data comparing mobility with n_{LPS} as in the left-hand column of Fig. 1 and open symbol comparing local energy E_i (defined in text) to mobility, as in the right-hand column of that figure. K is the Spearman rank correlation coefficient [45]. Precision is defined as the percentage of particles in the top (bottom) 2% of n_{LPS} (E_i), which are in the bottom 10% of μ_i. Horizontal dashed lines show the result for the precision metrics that would result from random classification of particles as slow.

between structure and dynamics. However, this statement is incorrect. We have used the R_4-ratio analysis of Berthier and Jack [51] to quantify the structural component of the dynamic fluctuations. As detailed in the Supplemental Material [35], we found that all four systems analyzed in Fig. 2 show a marked correlation between structure and dynamics, despite the fact that no *specific* structural motif connects to dynamics in the more mean-field like models. These striking results will be a subject for future investigations. Here we just point out an interesting analogy with the behavior of mean-field p-spin models [52], which *do* display large values of R_4 close to the dynamic transition.

One may take the inability of specific structural metrics, such as LPS determined from Voronoi analysis, to correlate universally with dynamics in supercooled liquids as an indication that a more general form of growing amorphous order must be implicated. In the remaining of this work, we focus on structural correlations embodied in point-to-set and related length scales [21,22,25,26]. In order to show that this type of order may subsume specific structural metrics, we investigate the connection between local order as measured by n_{LPS} and PTS correlations.

The PTS length scale is extracted by calculating the range over which spatial correlations imposed by an equilibrium amorphous spherical boundary decay. We first establish that it is possible to ergodically sample cavities at some R_{cav} using the particle size annealing (PSA) method detailed in Ref. [22]. In brief, we monitor the overlap q, a measure of the similarity between the initial configuration in the cavity and that at a later time t. The overlap is defined as $q(R_{\mathrm{cav}}, t) = (\rho l^3 \tilde{N})^{-1} \sum_{i=1}^{\tilde{N}} \langle n_i(t) n_i(0) \rangle$ where the center of the cavity has been tiled into $\tilde{N} = 125$ cubes of side length $l = 0.36$, small enough such that the cell occupancy $n_i(t)$ is always zero or one. We use both regular Monte Carlo (MC) sampling and a sampling where the particle diameters are shrunk to 60% of their original size and grown back in and check that the q values agree at long times. In the limit of large cavity and long time, $q(t)$ will tend to the bulk value $q_b = \rho l^3$, and thus, this value is conventionally subtracted from q.

We carry out these tests for the Wahn model. The strong icosahedral ordering in this model makes it an ideal system to probe the connection between local order and the spatial distribution of the overlap. In Fig. 3(a) we show that for $R_{\mathrm{cav}} = 3.0$ q is sampled ergodically. We then take 30 of the Wahn configurations used earlier and perform two standard MC simulations for cavities centered at 27 positions in each. The longtime overlap value is extracted from each cavity, and the number of icosahedral centers within the cavity as well as the one within the inner $R = 2.5$ of the cavity is calculated. We find that high overlap cavities generally have high n_{LPS} and vice versa. This implies that (for the Wahn system) the cavity simulations are mostly probing the same type of local ordering measured by the Voronoi construction, although it does not necessarily mean that the correlation *length* measured by doing cavity simulations at a series of radii is the same as would be measured by the extent of LPS domains.

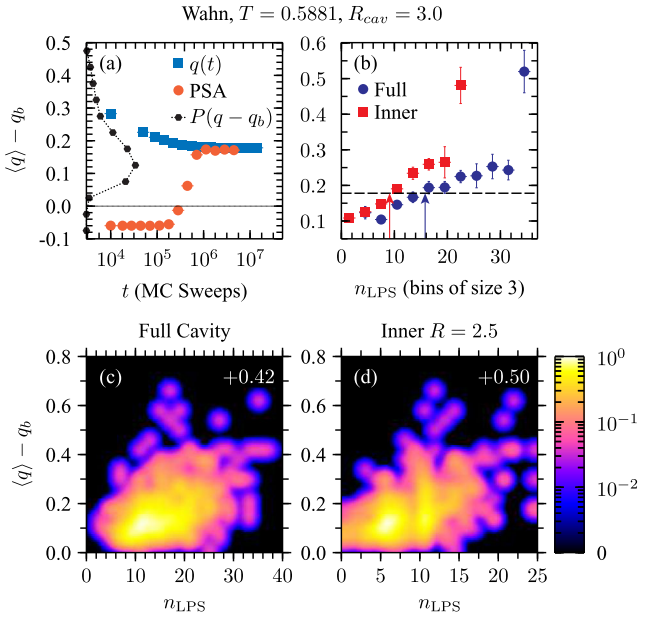

FIG. 3 (color online). (a) Cavity overlaps and PSA overlaps (with the value for a bulk system q_b subtracted) indicating ergodic sampling at this cavity size and temperature. The dashed line shows the overlap probability distribution $P(q - q_b)$. (b) On average, cavities containing a large number of LPS centers have high overlap. "Inner" points count only LPSs which are within $R = 2.5$ of the center of the cavity. The dashed line shows the average overlap and arrows show the average number of LPS. (c) and (d) show the full data distribution and Spearman rank correlation coefficients [45]. The data in (b) are obtained from (c) and (d) by averaging over vertical slabs of width 3.

In conclusion, we have demonstrated that the correlation between local structural metrics (e.g., E_i and n_{LPS}) and dynamics in supercooled liquids is highly system dependent. In models such as the Wahn mixture, accurate predictions of heterogeneous dynamics may be made on the basis of a single structural marker while essentially no correlation exists in mean-field like systems such as the GCM. However, a strong link between *some* aspect of static structure and dynamics does exist, as signified by the sizable R_4 ratio observed in all the systems we have studied. Despite being order agnostic, PTS correlations appear to show a connection with specific types of local order such as Voronoi signatures in systems whose dynamics may be predicted by the location of such structural motifs. Furthermore, previous work has detected an apparent connection between the growth of relaxation times and order agnostic length scales in systems where the connection between relaxation times and specific structural metrics is not very strong [22,25,26]. These facts suggest that PTS correlations may provide a more general description of the key static fluctuations that determine dynamical behavior in supercooled liquids.

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