Information-Theoretic Measurements of Coupling between Structure and Dynamics in Glass Formers

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We analyze connections between structure and dynamics in two model glass formers, using the mutual information between an initial configuration and the ensuing dynamics to compare the predictive value of different structural observables. We consider the predictive power of normal modes, locally favored structures, and coarse-grained measurements of local energy and density. The mutual information allows the influence of the liquid structure on the dynamics to be analyzed quantitatively as a function of time, showing that normal modes give the most useful predictions on short time scales while local energy and density are most strongly predictive at long times.

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As supercooled liquids approach their glass transitions, structural relaxation slows down dramatically, but molecular configurations remain disordered and apparently random [1,2]. However, computer simulations [3–8] and experiments [9,10] show that liquid structure and dynamical relaxation are correlated in these systems, as predicted (or assumed) in several theories [11–18]. Correlations between structure and dynamics can be demonstrated at a microscopic level [3–8], by exploiting the dynamically heterogeneous nature of glassy relaxation [19]. That is, individual particles have different propensities for motion [3], depending on local structure. Here, we use information theory [20] to analyze the strength of these correlations, by measuring the extent to which structural measurements can be used to predict particle dynamics at subsequent times. This quantitative analysis provides a stringent test of proposed causal links between structural features and slow dynamics. In two model glass formers, we find that coarse-grained measurements of energy and density [21–23] give the most predictive information for long times. In one of the models, vibrational modes [4–6,17] are strongly correlated with motion on relatively short time scales. Compared to these effects, the correlation between dynamics and low energy (or low enthalpy) local structures is relatively weak.

We consider the Kob-Andersen (KA) mixture of Lennard-Jones particles [24], and an equimolar five-component hard sphere (HS) mixture, which mimics colloidal suspensions [25]. Both systems contain particles of different sizes, with the diameter of the largest particles being σ = 1 (which sets the unit of length). The KA system evolves with overdamped (Monte Carlo) dynamics as in [26]; we focus on a temperature T = 0.5 and density ρ = 1.2. The HS system evolves by event-driven molecular dynamics [27]; we consider volume fractions φ in the range 0.52–0.58. In both systems, we use Δt to indicate the fundamental unit of time. The relaxation at the state points that we consider is up to 3 decades slower than relaxation in the high-temperature or low-density regime, where it is of order Δt (in both systems). Further system details are given in the Supplemental Material [28].

To characterize particle dynamics in these systems, we define the dynamical propensity [3] of particle i as μi,t = ⟨(r(t) − r(t0))2⟩iso, where r(t) is the particle position at time t, and the isokinetic average is calculated over many independent dynamical simulations, all with the same initial particle positions but with independent random initial velocities (and independent stochastic dynamics in the KA system). The role of the “lag time” t0 is discussed in Supplemental Material [28]: we take t0 ≈ 0.1Δt. We use si,t to denote a structural measurement at time t = 0, which depends in general on particle i and all particles in its vicinity. To quantify the strength of the correlation between si,t and the dynamical propensity μi,t, we use mutual information (MI) measurements [20]. The MI is defined as

Ii(t; s) = ∑ s dμpμ(s)p(s) log2 pμ(s)/pμ(s)

where pμ(s) is the joint probability distribution of μ and s, while pμ(μ) and p(s) are its marginal distributions. In Eq. (1), si,t takes discrete values: for continuous observables si,t, the sum over s is replaced by an integral.

The MI gives “the average amount of information about the propensity μi,t that is provided by a measurement of si,t.” Since si,t depends only on the initial condition, the MI
measures predictive information. The MI may be evaluated for any structural observable $s_i$, and it makes no assumptions on the nature of the correlation between $\mu_i$ and $s_i$. As such, it represents a generally applicable figure of merit for comparing the influence on dynamics of different structural measures, going beyond previous comparisons of snapshots [3–6,21,23] or analyses of selected subsets of particles [7,8]. The use of (1) to measure information [20] is similar to the use of entropy as a measure of disorder in statistical mechanics, with the role of disorder being taken by the variation in propensity between different particles. Particles with the same value of $s_i$ typically have less variation in their propensity, so specifying $s_i$ reduces the variation in $\mu_i$, just as introducing a constraint in statistical mechanics reduces the entropy [36]. The MI is equivalent to this entropy reduction. Information is measured in bits, with one bit corresponding to a reduction in entropy of $k_B \ln 2$. Our procedure for estimating MI is described in the Supplemental Material [28]: the method ensures as far as possible that we obtain $I_s(\mu; s) = 0$ if $\mu$ and $s$ are independent; it also provides an estimate of the numerical uncertainty in the MI. For some other recent applications of MI measurements in glassy systems, see [37–41].

To illustrate our use of MI, let $s_i$ be the type (A or B) of particle $i$ in the KA system. The different types have different dynamical relaxation so knowledge of the particle type provides predictive information about particle dynamics. In Supplemental Material [28], we show that measuring a particle’s type provides between 0.1 and 0.7 bits of information about its propensity $\mu_i$, depending on the time $t$. This value is a useful baseline for the results that follow: if a structural measurement is strongly coupled with dynamics, we argue that $I_s(\mu; s)$ should be at least of order 0.1 bit, while MIs much less than this indicate weak coupling.

Figure 1 shows MI measurements between particle propensities and several aspects of liquid structure, for both KA and HS systems. Since the influence of particle type on dynamics is not directly related to glassy behavior, we measure mutual information where the predictability based on particle type has already been taken into account. That is, we measure “the information about $\mu_i$ that is provided by a measurement $s_i$ for a particle whose type is already known.” In the KA system, we achieve this by restricting the distributions in (1) to particles of type A, which form the majority (80%) of the system. In the HS system, we use a conditional MI, $I(\mu; s|\alpha) = \sum_{\mu,a} \int d\mu p(\mu, s|\alpha) \ln \frac{p(\mu|s|\alpha)}{p(\mu|\alpha)}$, where $\alpha$ indicates the particle type [28]. Our choices of observable $s_i$ reflect different theoretical pictures of glassy systems.

Low-frequency normal modes in a supercooled liquid define a set of “soft directions” on its potential energy surface (or energy landscape), and these modes influence particle dynamics [4–6,17]. Some normal mode properties can be predicted from arguments based on jamming, leading to predictions for glassy relaxation [5]. We analyze normal modes [28] by quenching the KA system to its nearest energy minimum (inherent structure), and then diagonalizing the Hessian matrix of the energy. The resulting eigenvectors and eigenvalues are $v_k$ and $\omega_k^2$, for $k = 1\ldots N$, and one defines a “local Debye-Waller (DW) factor” $\Delta^2_{\alpha} = \sum_k |v_k^\alpha|^2/\omega_k^2$ that indicates [6,42] the expected size of fluctuations in the position of particle $i$, based on an expansion about the energy minimum. (Here $v_k^\alpha$ is a vector containing the three components of $v_k$ associated with particle $i$.) Since low frequency modes couple most strongly to structural relaxation [6], we also define a generalized DW factor $\Delta^2_{\alpha n}$, which is calculated using only the $n$ modes with lowest $\omega_k$. In HS systems, normal modes cannot be defined by reference to a potential energy surface so we do not consider them here, although alternative definitions are possible [5,17].

Figure 1(a) shows that for relatively short time scales $t \approx \Delta t < \tau_\alpha$ in the KA model, the mutual information between propensity and DW factors is large (up to 0.5 bits), so $\Delta^2_\alpha$ and $\Delta^2_{\alpha n=150}$ are strongly correlated with particle

![Figure 1](image_url)

**FIG. 1** (color online). MI measurements $I_s(\mu; s)$ in the KA system at $T = 0.5$, and $I_s(\mu; s|\alpha)$ in the HS system. We show MI between propensity and (a) Debye-Waller factors $\Delta_\alpha$ and $\Delta_{\alpha n=150}$ in the KA system; (b) coarse-grained energy and density in the KA system; (c) coarse-grained density in the HS system. Arrows indicate the structural relaxation time $\tau_\alpha$ and error bars indicate numerical uncertainties in the MI. In (c), the MI signals at short times are comparable with numerical uncertainties. The behavior of the MI at long times is discussed in the main text.

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motion. This indicates that the normal modes accurately mimic the fluctuations of the system within its initial metastable state. On longer time scales, the MI decreases strongly: as structural relaxation takes place, the “soft directions” for further motion decorrelate from those at $t = 0$ [10,43], reducing the predictive power of the normal mode analysis. While $\Delta^2_{i,n=150}$ provides significant predictive information even at $t = \tau_a$ [5,6,17], it appears that dynamical correlations on these time scales are not fully determined by motion along the “soft directions” that are present at $t = 0$. To make stronger predictions for relaxation on long time scales, one might consider correlations between successive relaxation events, for example through dynamical facilitation [15,44] or avalanches [10].

In addition to normal modes, coarse-grained energy and density measurements are also correlated with dynamical fluctuations [21–23,45]. In particular, field-theoretic descriptions of particle motion [18,22] are built on hydrodynamic fields such as the density. We define a local density, coarse-grained on a length scale $l$, as

$$\bar{\rho}_i = \rho_i - 3\sum_j e^{-r_{ij}/\ell^2} / (\ell^2 p_i^2),$$

where the sum runs over all particles $j$ and $r_{ij}$ is the distance between particles $i$ and $j$ [23].

Similarly, the locally-averaged energy is

$$\bar{\varepsilon}_i = \sum_j \varepsilon_j e^{-r_{ij}/\ell^2} / (\ell^2 p_i^2),$$

where $\varepsilon_j$ is the energy of particle $j$. Figures 1(b), 1(c) show that for $\ell = 2\sigma$ these quantities have strong predictive power on time scales longer than the structural relaxation time, but the MI is smaller for times $t < \tau_a$. The results are broadly similar for both models. We show data for $\ell = 2\sigma$ which illustrates the typical behavior: dependence on $\ell$ is discussed in Supplemental Material [28].

Throughout the glassy regime, we expect $I(\mu; \bar{\rho})$ and $I(\mu; \bar{\varepsilon})$ to have peaks at some ($\ell$-dependent) time $t'_c$, before decreasing at longer times (see for example the HS data at $\phi = 0.55$). However, for the largest volume fractions it is clear that $t'_c$ is significantly larger than $\tau_a$, and exceeds our sampling window. We attribute this large time scale to hydrodynamic effects that are largely independent of glassy behavior: on general grounds we expect regions of size $\ell > \sigma$ to relax on a time scale $t'_c$ that increases with $\ell$ and is significantly larger than $\tau_a$. Relaxation in high-density or low-energy regions of size $\ell$ will therefore be predictably slower than average up to $t \approx t'_c$. On these large time scales, almost all memory of the initial structure has been lost, leaving only the hydrodynamic energy or density fluctuations as the dominant predictive factor for dynamics. We argue that this effect leads to the large MI values at long times in Figs. 1(b), 1(c). In the simplest theoretical description, one expects $t'_c \sim \ell^2 / D$ where $D$ is a diffusion constant; a more accurate estimate of $t'_c$ would account for the relationship between diffusion constants and relaxation times [46,47]. However, we focus in this study on times $t$ of order $\tau_\rho$, where the system has significant dynamical heterogeneity and the motion is complex and co-operative. For the HS system, Fig. 1(c) shows that the MI at $\tau_a$ increases at large $\phi$, indicating that the coupling of dynamics to local density is increasing as the glass transition is approached, consistent with [18,22,45]. The MIs at $\tau_a$ are less than 0.1 bits for all states considered, but they increase rapidly for later times. Overall, Figs. 1(b), 1(c) show that simple observables like local energy and density couple strongly to dynamics, giving useful predictive information, particularly on relatively long time scales. We argue that these correlations merit further study, either theoretically [18] or numerically, presumably via three-point correlations [22].

Another theory of glassy relaxation is based on locally-favored structures (LFS): atomic or molecular packings that have low energy (or enthalpy) [14]. Particles in LFS typically have slower than average dynamics in glassy systems [7,8,48,49] and the theory [14] predicts that glassy relaxation is controlled by the formation of locally stable regions that are rich in these LFS. The LFS considered here are illustrated in Fig. 2; full details are given in the Supplemental Material [28]. For both KA and HS models, we consider an LFS that is associated with local fivefold symmetry, which we expect to be associated with lower propensity for motion [8,25,49–51]. Let $n_{155}(i)$ be the number of these structures in which particle $i$ participates. In the KA model we also consider a particular 11-particle LFS that is correlated with slow dynamics [7,8]: we define

$$I(\mu; n_{155}) = \sum_{i=1}^{N} n_{155}(i) \log_2 n_{155}(i),$$

where $N$ is the number of particles. We find that $I(\mu; n_{155})$ is larger than the MI for the same system, indicating that the LFS are good indicators of slow dynamics.

![Figure 2](image-url)  
**FIG. 2** (color online). MI between propensity and LFS measurements. These MIs are smaller in magnitude than those of Fig. 1, and all are less than 0.1 bit. (a) KA system, including pictures of the relevant LFS. (b) HS system, for which we consider only the ‘155’ LFS. Representative error bars are shown in (a), while (b) shows error bars only at $t = \tau_a$. 

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high temperatures, indicating that structure is more strongly
much larger at low temperatures in the KA model than at
environment.

As with the low-frequency normal modes, the MI is largest
on times $t \approx \Delta t$ indicative of (fast) $\beta$-relaxation [1],
but there is still some correlation at the structural relaxation
time. However, the strength of the correlation is smaller for
the LFS than for the normal modes, less than 0.1 bit in all
cases. Figure 2(b) shows similar results for the HS system.

It is also useful to compare $I_i(r; \mu)$ with “the average
amount of information about a particle’s dynamics
that is provided by specifying its propensity,” which is

$$I_i(r; \mu) = \int \text{d}r \text{d}p_i(r, \mu) \log (p_i(r, \mu) / p_i(\mu) p_i(r)),\quad$$

where

$$p_i(r, \mu) = \int \text{d}r \text{d}p_i(r, \mu) \log (p_i(r, \mu) / p_i(\mu) p_i(r)),\quad$$

and indicate that single-particle motion in glass formers has
a large unpredictable component, as well as predictable
aspects that are encoded by the propensity.

From Fig. 3, the two quantities in (3) are almost equal for
the KA model. Eq. (3) is an “information-processing
inequality” [20], so this result indicates that the propensity
captures almost all predictable information about single-
particle displacements. For the HS system, we use a
conditional MI between $r$ and $\mu$, to account for particle
type, as above. In this case, the two MIs in (3) differ
somewhat more strongly than they do in the KA model: this
situation might arise (for example) if some particles have
finite average displacements $\langle r_i(t) - r_i(t_0) \rangle$ that are only
weakly correlated with their propensities.

Nevertheless, we have $I_i(r; \mu) \approx I_i(r; \mu)$ in both models,
indicating that the propensity captures almost all predict-
able aspects of the single-particle dynamics [3]. This
further validates the MI as a measure of the influence of
liquid structure on dynamics—possible generalizations of
this work include the use of other structural observables $s_i$, or
investigation of collective dynamical measurements
(instead of single-particle propensities).

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