

Self-Induced Heterogeneity in Deeply Supercooled Liquids

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A theoretical treatment of deeply supercooled liquids is difficult because their properties emerge from spatial inhomogeneities that are self-induced, transient, and nanoscopic. I use computer simulations to analyze self-induced static and dynamic heterogeneity in equilibrium systems approaching the experimental glass transition. I characterize the broad sample-to-sample fluctuations of salient dynamic and thermodynamic properties in elementary mesoscopic systems. Findings regarding local lifetimes and distributions of dynamic heterogeneity are in excellent agreement with recent single molecule studies. Surprisingly broad thermodynamic fluctuations are also found, which correlate well with dynamic fluctuations, thus providing a local test of the thermodynamic origin of slow dynamics.

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The physical properties of crystals follow from the periodic repetition of a unit cell [1]. By contrast, amorphous solids are aperiodic structures displaying frozen spatial inhomogeneities [2–4] which require special theoretical approaches [5–7]. Simple fluids are also structurally disordered, but spatial fluctuations are weak enough that physical properties can be accurately predicted without explicitly dealing with disorder [8]. Deeply supercooled liquids represent a conceptual challenge as they are structurally disordered, with physical properties driven by the existence of spatial heterogeneities, but these fluctuations are transient, induced by the competition between frustrated particle interactions and thermal fluctuations, and of modest spatial extension [7].

The physics of bulk supercooled liquids has received considerable attention [2–7]. It is established that dynamics becomes spatially heterogeneous over a characteristic length scale that grows modestly approaching the experimental glass transition [9–11]. This mesoscopic dynamic heterogeneity is illustrated in Fig. 1(a), obtained from simulating a hard sphere model introduced shortly. The microstructure of supercooled liquids is very complex and fluctuates broadly at the particle scale [12]. Structural heterogeneity reflects the large variety of amorphous packings that particles can locally adopt. These multiple disordered structures are the real-space signature of a rugged free energy landscape, but this local disorder is *self-induced*, as the original Hamiltonian does not contain quenched random interactions.

Bulk physical properties in supercooled liquids emerge as an ensemble average over locally distributed quantities [10]. Ideally, one would like to understand the fluctuations of local thermodynamic and structural properties to then infer heterogeneous relaxation processes [13]. The disorder strength also represents the microscopic mechanism by

which the ideal glass transition may disappear in finite dimensions [14–16], but this was never measured directly. The emblematic stretched exponential decay of time correlations [17,18] reflects a distribution of local relaxation functions with fluctuating shapes and timescales [9,10]. Recent single molecule [19–22] and electron correlation microscopy [23] studies give direct access to such distributions, but the experimental evidence of fluctuating local distributions is contradicted by simulations [24]. The structural origin of dynamic heterogeneity remains a wide open question. Previous work discussed either particle-based structural indicators [12,25–27] or noncausal correlations between bulk structural and dynamical quantities [28–32]. Statically, self-induced disorder is at the core of the mean-field theory of glasses [6] and random first order transition theory [33], and, ultimately, the reason why configurational entropy is central to glass studies [34]. Some consequences of self-induced disorder on bulk thermodynamics have been analyzed before in simulations [35–37], but very little is known about the distribution of these fluctuations in realistic models and their temperature evolution. Most importantly, a link between local entropy fluctuations and structural relaxation has never been established, although this idea, proposed more than 50 years ago [38], has been analyzed in countless publications.

I numerically analyze self-induced heterogeneity by studying dynamic and static properties of statistically independent mesoscopic systems, attacking three different lines of investigations. As pioneered by Heuer and co-workers [39–41] and illustrated in Fig. 1(a), the study of small systems grants access to fluctuations created by the specific packing adopted locally in each configuration. Also key to our study is the use of the swap Monte Carlo algorithm [42] which provides fast equilibration down to the experimental glass transition and allows to probe, for

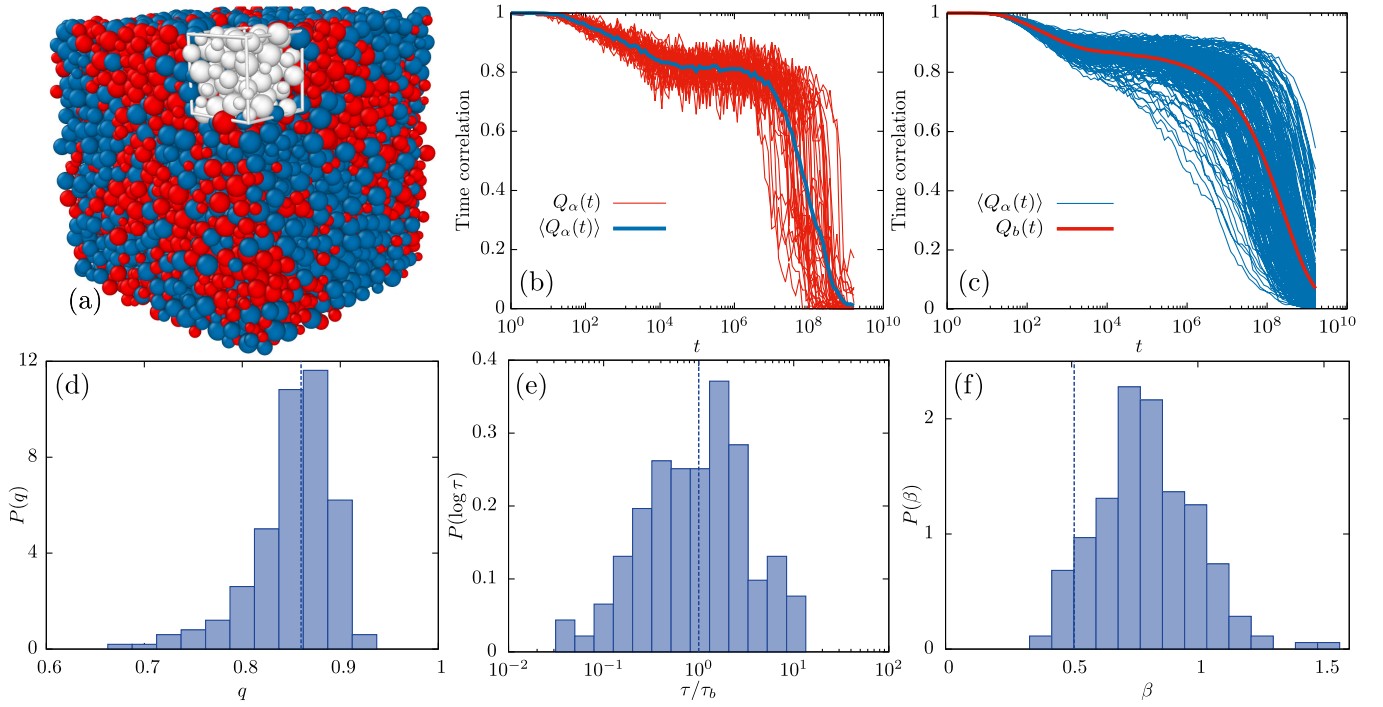


FIG. 1. (a) I highlight a subsystem comprising $N = 111$ particles in a larger system of $N = 8000$ hard spheres, whose spatially heterogeneous dynamics is illustrated by distinguishing fast (red) and slow (blue) particles near τ_b at $P = 30$. (b) Time decay of the overlap $Q_\alpha(t)$ in 40 isoconfigurational trajectories, and the resulting average $\langle Q_\alpha(t) \rangle$ for a single configuration α with $N = 111$ and $P = 30$. (c) Time decay of isoconfigurational average $\langle Q_\alpha(t) \rangle$ for 200 independent configurations with $N = 111$ and $P = 30$ and resulting bulk average $Q_b(t)$. (d),(e),(f) Sample-to-sample fluctuations of the plateau height q , characteristic timescale τ , and stretching exponent β for $P = 30$. Bulk values are marked with vertical dashed lines.

the first time, local fluctuations in the appropriate temperature regime. We first characterize the dynamics of elementary systems using isoconfigurational averaging [43] to obtain smooth time correlations for each sample. We measure both sample-to-sample fluctuations of the relaxation dynamics and the local lifetime of the dynamic heterogeneity, which compare well with recent experiments [20–23]. Second, we characterize sample-to-sample fluctuations of the Franz-Parisi free energy [44], which is directly related, in bulk systems, to the configurational entropy [45]. Third, we show that thermodynamic and dynamic fluctuations are correlated, which amounts to validating a local version of the Adam-Gibbs relation.

We simulate three-dimensional nonadditive polydisperse hard spheres with a flat distribution of particle diameters and polydispersity around 23% (details as in Ref. [46]). To probe elementary systems, we use the smallest possible system size with periodic boundary conditions. Too small systems have an incorrect pair correlation [39] and can be structurally unstable [47]. We settle for $N = 111$ particles (a smaller system with $N = 71$ too easily crystallized), which is smaller than the extension of the dynamic heterogeneity, see Fig. 1(a), but has an average behavior comparable to larger systems. We perform constant pressure Monte Carlo simulations at constant temperature (set

to $T = 1$, for convenience in units where the Boltzmann constant k_B is also unity), and use the pressure P as control parameter (constant density simulations would yield equivalent results). This is also convenient as P [or, rather the compressibility factor $P/(\rho k_B T)$, where ρ is the number density] plays for hard spheres a role strictly equivalent to $1/T$ in systems with soft interactions [48]. For this system [46], $P = 20$ corresponds to the onset of slow dynamics, $P = 26$ to the mode-coupling crossover, and $P = 37$ is a conservative estimate of the experimental glass transition. One Monte Carlo timestep represents N attempts to perform a translational move. The unit length is the average particle diameter, and the particle sizes are kept constant in each sample.

We analyze sample-to-sample fluctuations of the structural relaxation up to $P = 30$, much beyond the mode-coupling crossover. We run 40 distinct trajectories starting from each configuration α equilibrated using swap Monte Carlo during which we record the time overlap $Q_\alpha(t) = 1/N \sum_i \theta(a - |\mathbf{r}_i^\alpha(t) - \mathbf{r}_i^\alpha(0)|)$, with $a = 0.2$, $\mathbf{r}_i^\alpha(t)$ the position of particle i at time t starting from configuration α at $t = 0$, and $\theta(x)$ the Heaviside function (this choice ensures that the overlap probes equivalent physics to the self-intermediate scattering function [49,50]). By averaging over distinct trajectories from the

same initial condition α we obtain the isoconfigurational average $\langle Q_\alpha(t) \rangle$, see Fig. 1(b). Whereas $Q_\alpha(t)$ is not smooth and fluctuates among individual trajectories, $\langle Q_\alpha(t) \rangle$ has a smooth time dependence which fully characterizes the relaxation dynamics of configuration α . The isoconfigurational average advantageously replaces the time average needed in single molecule studies. In a final step, we perform an additional average over 200 independent configurations to obtain the bulk correlation function, $Q_b(t) = \overline{\langle Q_\alpha(t) \rangle}$, see Fig. 1(c). To analyze the fluctuations, each isoconfigurational correlation is fitted to a stretched exponential,

$$\langle Q_\alpha(t) \rangle = q \exp[-(t/\tau)^\beta], \quad (1)$$

where (q, β, τ) are three fitting parameters, taking values (q_b, β_b, τ_b) for the bulk function $Q_b(t)$.

In Figs. 1(d)–1(f) we show histograms of their sample-to-sample fluctuations for $P = 30$. The plateau height q has surprisingly large fluctuations, of order 20%, with a pronounced tail towards small values. The relaxation time τ varies over about 3 orders of magnitude, with again a significant tail corresponding to systems relaxing much faster than the bulk. This broad distribution represents a direct probe of spatially heterogeneous dynamics. Surprisingly, the stretching exponent β is also broadly distributed, with a most probable value $\bar{\beta} \simeq 0.75$ much larger than the bulk $\beta_b \simeq 0.5$. Elementary systems do not have the same stretching exponent as the bulk, and sample-to-sample fluctuations are massive. As shown in Fig. 1(b), the overlap in individual trajectories $Q_\alpha(t)$ is typically more compressed than its isoconfigurational average $\langle Q_\alpha(t) \rangle$, but is quite stretched in samples with small β . Our results contradict a recent study obtained using frozen cavities [24], perhaps because relatively large cavities were used. Our simulations reveal that the stretched exponential relaxation of the bulk system stems both from a broad distribution of local relaxation times and from strong deviations from a local exponential decay. They also support results from single molecule studies [20] and electron correlation microscopy [23], and differ from some earlier conclusions [51].

Our strategy probes structural relaxation locally without any time averaging. We can then ask how long the dynamic heterogeneity persists, i.e., how long it takes a spontaneous fluctuation to return to average behavior. To this end, we promote the overlap to a two-time correlation, $Q_\alpha(t_w + t, t_w)$, by recording the dynamics between times t_w and $t_w + t$ starting from configuration α at $t_w = 0$. The case $t_w = 0$ was considered in Fig. 1. In the opposite limit, $t_w \rightarrow \infty$, the system loses memory of the initial condition: $\lim_{t_w \rightarrow \infty} \langle Q_\alpha(t_w, t_w + t) \rangle = Q_b(t)$. Our goal is to quantify how this limit is reached in different samples, allowing us to define a local lifetime for dynamic heterogeneity, as opposed to global ones discussed before [20]. We define

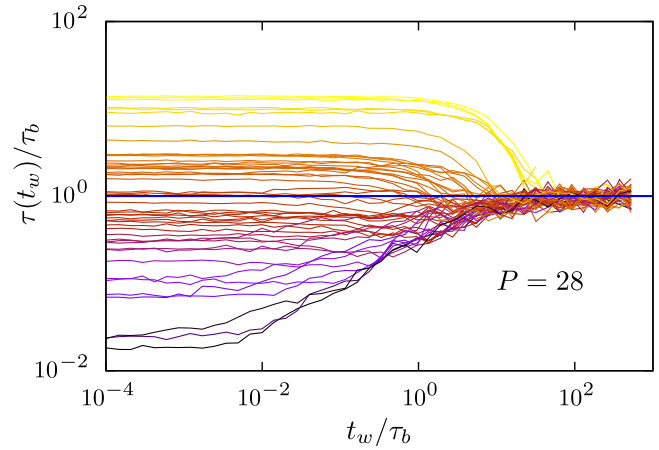


FIG. 2. Evolution of the local relaxation time $\tau(t_w)$ as the system progressively loses the memory of its initial condition and returns to the average behavior. Fast and slow samples display asymmetric behavior, but have a similar lifetime of about $50\tau_b$.

$\tau(t_w)$ from the time decay of $\langle Q_\alpha(t_w + t, t_w) \rangle$ for each configuration α .

The results are shown in Fig. 2 for $P = 28$. For each sample, we observe that $\tau(t_w)$ displays a plateau of duration $t_w \sim \tau(t_w = 0)$, which simply confirms that no useful dynamics is happening at times shorter than τ . However, all samples (fast and slow) return to the bulk value τ_b over a similar timescale $t_w \approx 50\tau_b$, but they do so in a very asymmetric manner reminiscent of nonlinear aging studies [52]. Over the explored time window, no pronounced pressure dependence was detected for this lifetime. These results are again in harmony with experimental findings from single molecule studies [20] and earlier determinations of heterogeneity lifetime [53].

We turn to thermodynamic fluctuations. The order parameter for a static glass transition is the overlap $Q_{\alpha\beta} = 1/N \sum_{i,j} \theta(a - |\mathbf{r}_i^\alpha - \mathbf{r}_j^\beta|)$ between a pair (α, β) of equilibrium configurations. From the fluctuations of the overlap, the bulk Franz-Parisi (FP) free energy $V_b(Q)$ is constructed [44]. This is well studied numerically [37,45,54]. Here, we focus instead on sample-to-sample fluctuations, about which little is known at low temperatures. The equilibrium fluctuations of $Q_{\alpha\beta}$ between a fixed reference configuration α and fluctuating configurations β define the distribution $P_\alpha(Q) = \langle \delta(Q - Q_{\alpha\beta}) \rangle$, which yields $V_\alpha(Q) = -(T/N) \log P_\alpha(Q)$ for each sample α . The bulk free energy $V_b(Q)$ is obtained after averaging over α : $V_b(Q) = \overline{V_\alpha(Q)}$.

Figure 3(a) shows the evolution with P of the bulk FP potential $V_b(Q)$. For $P = 35$ (near the experimental glass transition), we show $V_\alpha(Q)$ for individual samples. The evolution of $V_b(Q)$ resembles previous results [54], and demonstrates the approach to a random first-order phase transition (possibly) occurring at larger P . The non-convexity of $V_b(Q)$ at large P stems from using a small

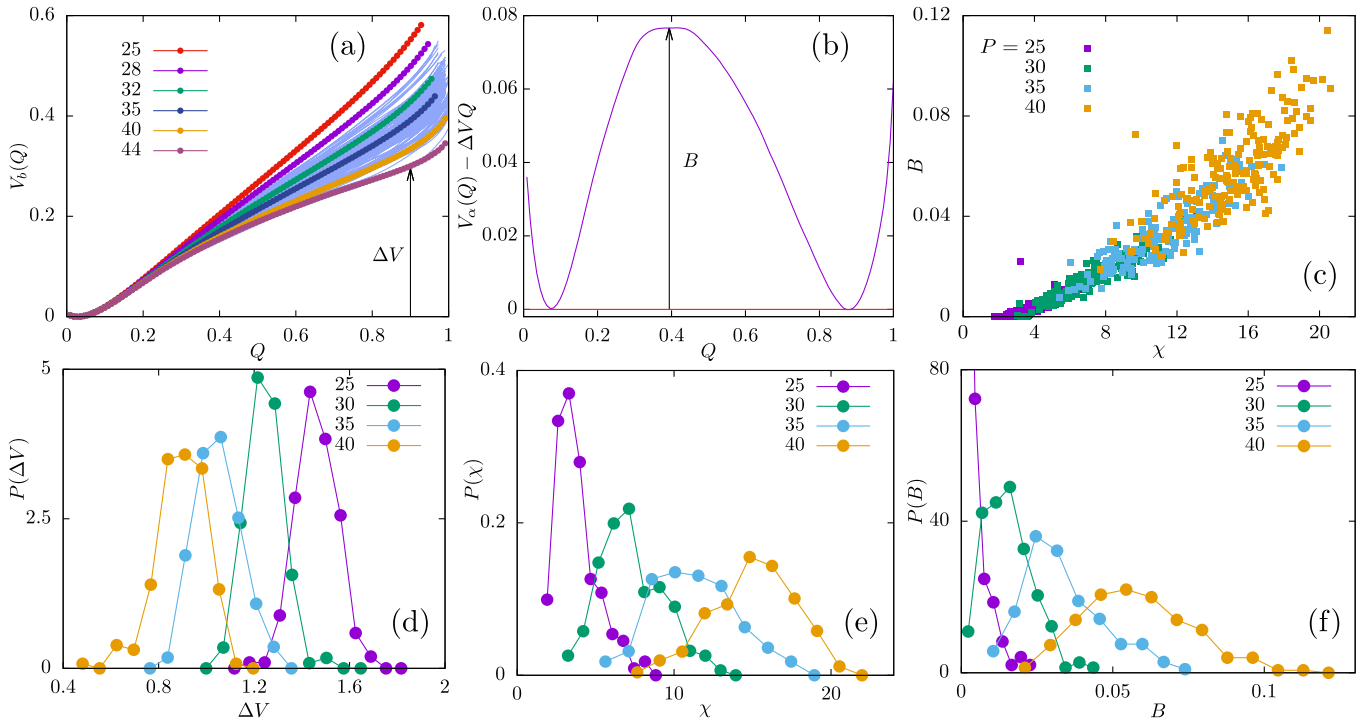


FIG. 3. (a) Evolution of the bulk Franz-Parisi potential $V_b(Q)$ with pressure. For $P = 35$, we also show $V_\alpha(Q)$ from multiple independent samples (thin lines), showing the breadth of self-induced free energy fluctuations. (b) Definition of the free energy difference ΔV and the barrier B for an individual sample at $P = 35$. (c) Scatter plot of the barrier B versus the susceptibility χ for independent samples at different pressures. (d),(e),(f) Histogram of sample-to-sample fluctuations of ΔV , χ , and B .

N and is absent in larger systems [37]. An estimate of the bulk configurational entropy [45] follows the free energy difference ΔV_b between high and low Q values, see Fig. 3(a).

The evolution of $V_b(Q)$ is smooth, but the sample-to-sample fluctuations observed at each state point are surprisingly large. For $P = 35$, we obtain a range of $V_\alpha(Q)$ resembling the measured $V_b(Q)$ over the range $P \in [28, 40]$, i.e., from the mode-coupling crossover to below the experimental glass transition. This shows that spatial fluctuations of the configurational entropy are surprisingly large, which, to our knowledge, has never been observed before.

To start quantifying these observations, we introduce three measures: $(\Delta V, B, \chi)$. For each sample, ΔV is the critical value of the field needed for the function $V_\alpha(Q) - \Delta V Q$ to have two minima of the same height [see Fig. 3(b)], and thus to induce a discontinuous transition between high and low Q phases; B is the barrier separating the two minima, see Fig. 3(b); the susceptibility χ is the variance of overlap fluctuations at coexistence. Scatter plots reveal that these three quantities are strongly correlated [for instance B vs χ in Fig. 3(c)], and thus they describe well local fluctuations of the FP free energy. The histograms in Figs. 3(d)–3(f) show the evolution of these fluctuations over a broad range of pressures. There is considerable overlap between the distributions measured at

well-separated state points, reflecting the large amount of disorder in supercooled liquids. These fluctuations represent a coarse-grained, agnostic, nonmechanical measure of the thermodynamic stability of the local particle packing, with no reference to a potential energy landscape [40] (which is not appropriate for hard spheres anyway). These results also confirm and quantify the central role played by self-induced disorder in the thermodynamics of supercooled liquids, thus reinforcing analogies with random field Ising models [14,35,37,55,56].

We come to the third point of the paper. Both the bulk relaxation time τ_b and FP potential $V_b(Q)$ (therefore, the configurational entropy $\approx \Delta V_b$) evolve noticeably with P . A “correlation” necessarily relates $\log \tau_b$ to ΔV_b , but this does not imply any causality between configurational entropy and relaxation time. All previous work thus instead tested the validity and universality of the Adam-Gibbs relation [28,29,32], which reads $\log(\tau_b/\tau_\infty) = (P/\rho k_B T)(k_B T/\Delta V_b) \sim P/\Delta V_b$, using notations where physical dimensions are transparent. Collecting static and dynamic sample-to-sample fluctuations, we can directly test whether local fluctuations of the configurational entropy correlate with local fluctuations of the dynamics. Such demanding test of a putative structure-dynamics correlation has never been performed. Our approach also differs from most parallel studies [12,25–27], because we (intentionally [57]) do not work at the single particle level.

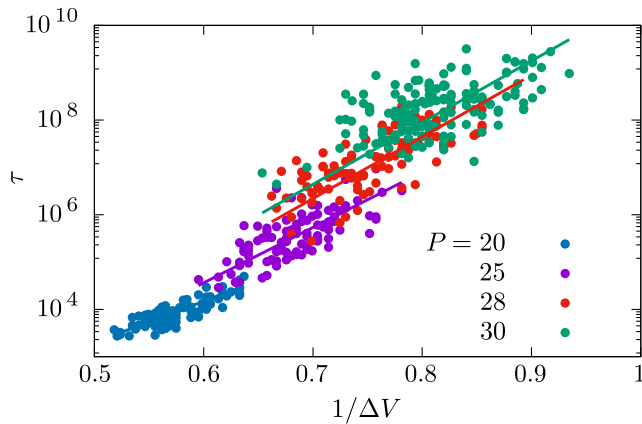


FIG. 4. Scatter plot of the relaxation time τ of individual samples against the free energy difference ΔV . The straight lines represent a local version of the Adam-Gibbs relation, where $\log \tau \propto (P/\Delta V)$. This shows that self-induced dynamic and thermodynamic fluctuations are locally correlated.

A scatter plot of $\log \tau$ vs $1/\Delta V$ independently obtained for multiple samples at multiple equilibrium state points is shown in Fig. 4 to test the Adam-Gibbs relation directly at the level of local fluctuations. Note that each point represents a substantial numerical treatment to obtain accurate and independent values for τ (using isoconfigurational dynamic average) and ΔV (using umbrella sampling techniques). The observed correlation is quite good and the data align along the Adam-Gibbs relation, shown with the straight lines. Interestingly, since $B \sim 1/\Delta V$, this correlation can be recast as $\log \tau \sim B$, suggesting that B represents a meaningful candidate for the effective barrier to structural relaxation. By contrast, we find that the plateau height q (local Debye Waller factor) correlates weakly with the dynamics, which appears to contradict models where short-time dynamics is used to infer structural relaxation [30,31]. Several more tests along these lines could be performed following the methods introduced above, and the quality of the various correlations could be quantified further.

Deeply supercooled liquids display broad distributions of their local physical properties, which are extensively probed here numerically at extremely low temperatures by analyzing mesoscopic systems equilibrated with a swap Monte Carlo algorithm. Each configuration is “typical,” yet each sample displays static and dynamic properties that fluctuate wildly, directly impacting all observed bulk properties. Our results directly establish that deeply supercooled liquids are found, at the mesoscale, in a very large number of distinct packings with distinct properties. This *self-induced heterogeneity* represents the real space signature of the metaphorical rugged free energy landscape. Static fluctuations are central to random first order transition theory, but they also exist in simpler plaquette models [58], although both approaches provide distinct general perspectives on their dynamical consequences [59,60].

We focused here on an important subset of questions regarding dynamic heterogeneity and thermodynamic fluctuations, but many more can be tackled using similar tools, from experimentally relevant questions (e.g., rheology) to fundamental ones (e.g., extracting coupling constants of effective field theories).

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