Universal fluctuations in the relaxation of structural glasses

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The presence of strong local fluctuations – dynamical heterogeneities – has been observed near the glass transitions of a wide variety of materials. Here we explore the possible presence of universality in those fluctuations. We compare the statistical properties of fluctuations obtained from numerical simulations of four different glass-forming systems: two polymer systems and two particle systems. We find strong evidence for universality, both in the qualitative behavior of the fluctuations and in the remarkable agreement of the scaling functions describing them.

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Dynamical heterogeneities, i.e. strong fluctuations associated with nanometer-scale regions of molecules rearranging at very different rates compared with the bulk [1, 2], have been observed in a wide variety of glass-forming systems, from small molecules, to polymers, to network glasses, to colloidal glasses [1, 2, 3, 4]. A detailed theoretical explanation for those strong fluctuations is not yet available, although several ideas have been proposed [5, 6, 7, 8, 9]. A growing experimental and numerical literature has been uncovering various aspects of dynamical heterogeneities [1, 2, 3, 4, 10, 11, 12, 13, 14, 15, 16, 17, 18], but the question of universality – to what degree these fluctuations behave in the same way in different kinds of glassy systems – remains open.

Another common feature of glass-forming materials is physical aging [19]: for temperatures below the glass transition, the material falls out of equilibrium, and quantities probing the system at two times, a “waiting time” \( t_w \) and a “final time” \( t \), with \( t > t_w \), depend on both times \( t_w \) and \( t \), and not just on their difference \( t - t_w \). In particular, probability distributions and spatial correlations describing dynamical heterogeneities also show aging [10]. Their time dependences \([11, 12, 13, 14]\) display scaling as a function of the two-time correlation \( C_{\text{global}}(t, t_w) \equiv \langle \sum_{j=1}^{N} \exp(i \mathbf{q} \cdot \mathbf{r}_j(t) - \mathbf{r}_j(t_w)) \rangle \), as predicted by a theoretical framework based on the presence of local fluctuations in the age of the sample [9, 20, 21, 22, 23].

In this work we examine the question of universality in the fluctuation behavior of structural glasses. We perform numerical simulations in four different models of glass-forming systems in the aging regime, and take advantage of the presence of scaling to quantitatively compare the properties of fluctuations in all of them. As a result of those comparisons, we find strong evidence that dynamical heterogeneities do indeed exhibit universal behavior.

We consider a system of polymers (labeled \( lj_p \)) with Lennard Jones (LJ) interactions between the monomers, a system of polymers (labeled \( wp \)) with purely repulsive Weeks-Chandler-Anderson (WCA) interactions [24, 25], a system of particles (labeled \( lj_m \)) with LJ interactions, and a system of particles (labeled \( wm \)) with WCA interactions. In our polymer models, nearest-neighbor monomers along a chain are connected by a FENE anharmonic spring potential, and we use the Nose-Hoover method to simulate at a constant pressure and temperature [24]. Each system, composed of 800 chains of 10 monomers each, is equilibrated at a high temperature of \( T_f = 5.0 \) and then it is instantaneously quenched to a final temperature \( T_f \). All temperatures are measured in units of the energy scale \( \epsilon \) of the LJ or WCA potential. The time of the quench is taken as the origin of times \( t = 0 \). After the quench the systems are allowed to evolve for \( 10^5 \) LJ time units. \( T_f \) is chosen low enough that the systems keep aging during the whole low temperature part of the simulation: \( T_f = 0.4 \) for \( wp \), and \( T_f = 0.6 \) for \( lj_p \).

Our results are an average over 100 (resp. 800) independent runs for the \( lj_p \) (resp. \( wp \)) system. The simulations in the particle systems are as described in Refs. [12, 14].

We present results for the probability distributions of observables which probe local fluctuations in small regions of the system: the local coarse grained two-time correlation function [12, 14] \( C_r(t, t_w) \) and the particle displacements along one direction \( \Delta x_j(t, t_w) = x_j(t) - x_j(t_w) \) [4, 12, 15]. In order to probe the spatial correlations of the fluctuations, we also consider the generalized dynamic susceptibility \( \chi_4 \equiv \int d^3 \mathbf{r} \ g_4(\mathbf{r}, t, t_w) \) [13, 16, 17, 18], where \( g_4(\mathbf{r}, t, t_w) \) is a 4-point (2-time, 2-position) correlation function [13, 16].

The top panel of Fig. 1 shows the probability distributions \( \rho(C_r) \) of the local two-time correlation for \( C_{\text{global}}(t, t_w) = 0.2, 0.4, 0.6 \), for WCA polymers. As in particle systems [12, 14], the probability distributions are approximately independent of \( t_w \), for a fixed value of \( C_{\text{global}}(t, t_w) \). In the bottom panel of Fig. 1 we plot the rescaled probability distributions \( \sigma_C \rho(C_r) \) versus the normalized fluctuation \( (C_r - C_{\text{global}}) / \sigma_C \) in the one-point two-time correlator for \( C_{\text{global}}(t, t_w) = 0.5 \), and find that the results are approximately the same for all four sys-
The distributions look similar to those determined by confocal microscopy in a colloid with repulsive interactions [4] but rather different from those found in an attractive colloid [15]. All the distributions collapse together to a common Gaussian shape for smaller $\Delta x$, but depart from the Gaussian for larger $\Delta x$.

For the shorter waiting times, $t_w = 30.2$, the tails of the distributions in the four systems are very close to each other, but they significantly separate for longer $t_w$. In all systems the tails of the distributions become wider as $t_w$ increases; this is shown in more detail for the $w_p$ system in the middle panel of Fig. 2. In all four systems, the tails can be fit in the region $|\Delta x| > 0.5$ by a nonlinear exponential form $\rho(\Delta x) \approx N \exp(-|\Delta x/a|^\beta)$. However, the bottom panel of Fig. 2 shows that for WCA polymers, the exponent increases at long $t_w$, while for LJ particles, it decreases at long $t_w$. According to [15] the tails of the distribution are representative of particles which have escaped their cages, whereas the peak of the distributions are due to the particles which vibrate in place. This suggests that the difference in the evolution of the tails could be due to the different diffusive behavior between small molecules.
and polymers.

We now consider the spatial correlations of dynamical fluctuations. The top panel of Fig. 3 shows that \( \chi_4(t, t_w) \) has a peak as a function of \( t - t_w \), and that this peak’s height and position grow with \( t_w \). Similar behaviors are observed in experiments in granular systems [18] as the area fraction is increased, and in numerical simulations of supercooled liquids as the temperature is reduced [16, 17]. In the middle panel, we plot the ratio \( \chi_4/\chi_4(C=1/e) \) as a function of \( 1 - C = 1 - C_{\text{global}}(t, t_w) \), for WCA polymers; all the curves collapse into a single master curve. Both behaviors are identical to those found in LJ and WCA particles [13, 14]. In the bottom panel of Fig. 3, the same ratio is plotted for LJ particles, WCA
particles and WCA polymers. The scaling function is similar but apparently not identical in the polymer and small molecule cases.

By Fourier transforming the correlation function $g_4(r, t, t_w)$, we obtain the 4-point dynamic structure factor $S_4(q, t, t_w)$ [13, 16, 17]. We fit its small $q$ behavior $(q < 1.9)$ with an empirical scaling form: $S_4(q) = (S_4^0 - K) f(\xi_4(q)) + K$, with $f(x) = 1/(1 + x)^\mu$, for the $w_p$ and $l_{jm}$ systems. The dynamic correlation length $\xi_4(t, t_w)$ and the parameters $S_4^0(t, t_w)$ and $K(t, t_w)$ are extracted from each fit. The unknown scaling function $f(x)$ is the same for all the fits. It has sometimes been assumed [16] that it has an Ornstein-Zernicke (OZ) form, corresponding to $\mu = 1$. More recently, however, it has been shown [26] that the function $\chi_q$, which is believed to have a similar behavior to $S_4(q)$, does not have an OZ form, and indeed has an asymptotic behavior $\chi_q \sim |q|^{-4}$ for large $q$. Indeed, forms other than OZ are better at describing the data in the supercooled regime of various glassy models [17], and they provide significantly better fits to the aging regime data presented here. By minimizing the average square error over the whole set of fits, we determine $\mu = 1.8$ [27]. Although our fits are performed only for moderate to small values of $x = \xi_4 q$, the asymptotic behavior for large argument, $f(x) \sim x^{-3.6}$, is not far from the prediction of [26].

The top panel of Fig. 4 shows that all the data sets agree rather well with the scaling function. The middle panel of Fig. 4 shows the extracted correlation lengths vs. $t - t_w$ for different waiting times, for WCA polymers. We see an initial increase in the correlation length in all the curves, but when the time difference gets larger, the correlation length either remains constant or it decreases slightly [28]. As in LJ particles [13], the plateau value of $\xi_4$ is a growing function of $t_w$. The bottom panel of Fig. 4 shows plots of the ratio $\chi_4/\xi_4(C = 1/e)$ against $1 - C$, for the $w_p$ and $l_{jm}$ systems. In both cases we find that there is a moderately good collapse, and it appears that $\xi_4$ goes to a nonzero constant when $(1 - C) \to 1$, (i.e. $(t - t_w)/t_w \to \infty$). However, the scaling function for monomers grows with $1 - C$ for $1 - C > 0.5$, while for the polymers it appears to become approximately constant.

In summary, we have explored the possible presence of universality in the fluctuations of relaxing structural glasses, by comparing simulation data from two polymer models and two particle models. As we pointed out before, some differences are observed: (a) the scaling plots for $\chi_4/\xi_4(C = 1/e)$ and $\xi_4/\xi_4(C = 1/e)$ versus $1 - C$ show some small discrepancies between polymers and particles; and (b) the behavior of the tails of the distributions of displacements, $\rho(\Delta x(t, t_w))$, show a qualitatively different evolution with $t_w$ in the small molecule and polymer cases (which might be due to their different diffusible behaviors). However, there is remarkable similarity in the behavior of fluctuations in all the systems considered, and we find the evidence for universality to be very strong. In particular, the following aspects of the fluctuations appear to be universal: (i) the fact that the probability distributions $\rho(C_r(t, t_w))$ approximately collapse for different waiting times $t_w$ when $C(t, t_w)$ is held constant; (ii) the very peculiar shape of the scaling function $\rho(C_r - C_{\text{global}})/\sigma_C \equiv \sigma_C \rho(C_r)$; (iii) the qualitative behavior of the 4-point density susceptibility $\chi_4(t, t_w)$ and the dynamic correlation length $\xi_4(t, t_w)$ as functions of $t_w$ and $t - t_w$; and (iv) the fact that the rescaled quantities $\chi_4/\chi_4(C = 1/e)$ and $\xi_4/\xi_4(C = 1/e)$ plotted versus $1 - C$ approximately collapse for different waiting times $t_w$.

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[27] The minimization yields a value of $\mu = 1.769 \pm 0.001$. The statistical error is small, but the systematic errors due to the choice of interval and possible differences between monomer and polymer systems are more difficult to estimate, and probably much larger.

[28] Deciding between these two possibilities would require even longer time spans and larger statistics.