Distributions of inherent structure energies during aging

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We perform extensive simulations of a binary mixture Lennard-Jones system subjected to a temperature jump in order to study the time evolution of fluctuations during aging. Analyzing data from 1500 different aging realizations, we calculate distributions of inherent structure energies for different aging times and contrast them with equilibrium. We find that the distributions initially become narrower and then widen as the system equilibrates. For deep quenches, fluctuations in the glassy system differ significantly from those observed in equilibrium. Simulation results are partially captured by theoretical predictions only when the final temperature is higher than the mode coupling temperature.

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When a liquid is rapidly brought out of equilibrium, for example by an abrupt change in temperature $T$, it starts to age. The material properties change with the aging time $t_w$ in the attempt to recover equilibrium at the new bath temperature $T_b$. This aging process can be visualized as a path in configurational space, that starts from a typical equilibrium configuration before the quench and which, at long times, should converge to an equilibrium configuration characteristic of $T_b$. When $T_b$ is below the glass transition temperature, the aging dynamics never stops in the experimentally accessible time window, but becomes slower and slower on increasing $t_w$.

In recent years, several studies have revisited the physics of aging\cite{1,2,3,4,5,6,7,8,9}, attempting to associate the aging dynamics with a progressive decrease of the fictive (or effective) temperature $T_f$. In these studies, the configuration of the aging system at time $t_w$ is associated with a typical configuration explored by the equilibrium liquid at $T_f$. In this case, the aging dynamics can be modeled as a progressive thermalization of the system, quantified by the progressive decrease of $T_f$.

A convenient framework for analyzing the thermodynamics of supercooled liquids and aging dynamics in numerical simulations is provided by the inherent structure (IS) formalism\cite{10}. In this framework, each configuration is associated with its closest local minimum, named IS, on the potential energy surface (PES) of the liquid. A formal thermodynamic description of the system can be developed with a proper modeling of the statistical properties of the PES, i.e., the distribution of the energy minima $e_{IS}$ and of their basins of attraction $10,11$. It has been shown that in equilibrium supercooled states, the probability density $P(e_{IS},T)$ of exploring a minimum of depth $e_{IS}$ is approximately Gaussian, with a $T$-independent variance and with an average $e_{IS}$ which decreases monotonically with $T$\cite{12,13,14}. In the IS approach, the aging dynamics can be visualized as the progressive exploration of deeper and deeper minima, and a connection between aging and equilibrium configurations can be made by comparing properties of the explored basins.

Experimental studies of glass forming materials\cite{4,15} and recent numerical simulations\cite{16} have called attention to the fact that aging systems, especially for deep quenches, may not be associated with a single $T_f$, i.e., can not be uniquely associated with a liquid configuration, calling for a further development of the present theories. In this Letter, we bring the level of comparison between equilibrium and aging to a much more detailed level, by studying fluctuations around the average properties. We show that the fluctuations frozen in the glass depend on the thermal history and are significantly different from the fluctuations characteristic of the liquid state.

We perform molecular dynamics (MD) simulations of $N=1000$ particles in a cubic box of length $L=9.4$, for the well characterized Kob-Andersen binary-mixture Lennard-Jones (LJ) model\cite{17}, for which the mode coupling transition has been estimated at $T_x=0.435$. We employ the Nosé-Hoover thermostat with parameters chosen so that the kinetic energy thermalizes in a time between 300 and 1000 time steps. Time is reported here in number of MD time steps, each of which is 0.01\textsuperscript{th}. We calculate the probability density $P(e_{IS},t_w)$ of finding the liquid at a given time $t_w$ in a basin of energy $e_{IS}$, as the system responds to a sudden lowering in $T$. To this end, we perform an ensemble of 1500 independent MD runs, each for $10^6$ steps. The temperature is switched from the initial equilibrium temperature $T_i$ to the new $T_b$ at $t_w=0$. For each MD run we select configurations at 35 different $t_w$, logarithmically spaced. We perform a conjugate-gradient quench on each configuration to obtain the associated IS. Diagonalization of the Hessian matrix evaluated at the IS provides the eigenfrequencies $\{\omega_i\}$. Thus for each studied $t_w$, we produce an ensemble of 1500 IS’s. We study five different $T$ jumps, with sets of $(T_i \rightarrow T_b)$ including $(0.55 \rightarrow 0.466)$, $(0.6 \rightarrow 0.1)$, $(0.8 \rightarrow 0.25)$, $(0.8 \rightarrow 0.446)$ and $(0.8 \rightarrow 0.6)$.

In Fig.\textsuperscript{4} we plot $P(e_{IS},t_w)$ for the $(0.8 \rightarrow 0.446)$ run, as well as the corresponding equilibrium distributions $P(e_{IS},T)$ at $T_i$ and $T_b$. The figure shows that distribu-
tions initially become narrower (equivalently taller), then broader again on approaching equilibrium. Fig. 2 shows the average $e_{ag}$ and the standard deviation $\sigma_{ag}$ of the distributions as functions of $t_w$. In the cases where $T_b > T_s$, the variance, which by construction at $t_w = 0$ coincides with the equilibrium variance, first decreases and then relaxes towards the equilibrium value. For $T_b < T_s$, within the studied time window, we only observe the narrowing. We also evaluate the skewness, though we can not discern any trend outside of statistical noise.

Next we attempt to compare the fluctuations observed in aging with theoretical predictions. In equilibrium, the Helmholtz free energy per particle of the liquid can be written as \[ F = e_{IS} - TS_c(e_{IS}) + f_{vib}(e_{IS}, T), \] where $f_{vib}(e_{IS}, T)$ is the free energy of a basin, averaged over all basins of depth $e_{IS}$, and $S_c(e_{IS}) = N^{-1}k_B \ln \Omega(e_{IS})$ is the configurational entropy. $\Omega(e_{IS})$ counts the number of basins of energy $e_{IS}$. In the Gaussian-harmonic approximation (GHA), one assumes that $S_c$ and $f_{vib}$ are quadratic in $e_{IS}$. In the GHA, $P(e_{IS}, T)$ is Gaussian with a $T$-independent variance, i.e.,

$$ P(e_{IS}, T) = \frac{1}{\sqrt{2\pi\sigma_{p}^{2}}} \exp \left[ -\frac{(e_{IS} - \bar{e}_{IS}(T))^{2}}{2\sigma_{p}^{2}} \right], $$

where the $T$ dependence of $\bar{e}_{IS}$ and the variance $\sigma_{p}^{2}$ are expressed in terms of the statistical properties of the PES (the variance $\sigma_{x}^{2}$ and the average energy $E_0$ of $\Omega(e_{IS})$) and of the parameters connecting depth and shape of the basins ($b$ and $c$) \[21\, 22\]. More precisely, $\bar{e}_{IS}(T) = (E_0 - b\sigma_{x}^{2})/(1 + 2c\sigma_{x}^{2}) - T^{-1}\sigma_{p}^{2}/(1 + 2c\sigma_{x}^{2})$, and $\sigma_{p}^{2} = N^{-1}\sigma_{x}^{2}/(1 + 2c\sigma_{x}^{2})$. Below $T = 0.6$, the GHA provides a good description of the numerical data \[12\, 14\], enabling us to estimate $\sigma_{x}^{2}$, $E_0$, $b$ and $c$.

In the non-equilibrium case, recent theoretical approaches suggest that the free energy can be written as,

$$ F = e_{IS} - TS_c(e_{IS}) + f_{vib}(e_{IS}, T_b), $$

where $S_c$ is weighted by $T, 1$, \[6, 8, 22, 23\]. The introduction of $T_I$ modifies Eq. 2 to yield a non-equilibrium probability density, in the GHA,

$$ P(e_{IS}, T(t_w), T_b) = \frac{1}{\sqrt{2\pi\sigma_{ag}^{2}}} \exp \left[ -\frac{(e_{IS} - e_{ag})^{2}}{2\sigma_{ag}^{2}} \right], $$

where $e_{ag}$ and $\sigma_{ag}$ are given by

$$ e_{ag} = \frac{E_0 T_I - \sigma_{c}^{2} - \sigma_{p}^{2} T_b}{2c\sigma_{c}^{2} T_b + T_I}, $$

and

$$ \sigma_{ag}^{2} = N^{-1} \left( 2c + \frac{1}{\sigma_{c}^{2} T_b} \right)^{-1}. $$

Note that the theory predicts a gradual increase of the variance on increasing $t_w$, i.e., on approaching equilibrium (decreasing $T_I$).

The theoretical predictions for the relation between $e_{ag}$ and $\sigma_{ag}$, parametric in $T_I$, are shown in Fig. 3a. In Fig. 3b) we show the evolution of the same quantities as calculated from the aging runs. In the simulation data, at
short $t_w$, the system possesses by construction a distribution of IS energies identical to that of the starting $T$, and hence it is not surprising that the numerical results initially differ from the value predicted by Eq. 6. For longer times, i.e., for lower $\epsilon_{IS}$ values, a region where the variance increases is indeed observed, but only for quenches above $T_x$. The magnitude of change in the variance predicted by the theory is significantly smaller than the one observed in simulation. Even in the case $(0.55 \rightarrow 0.466)$, where the starting $T$ is such that the GHA should hold the best, the observed narrowing falls outside the uncertainty arising from modeling the equilibrium distributions, as well as from numerical errors.

An implicit assumption in the theory is that, during aging, the liquid explores configurations typical of equilibrium \[24, 25\] and hence that the landscape parameters derived from the equilibrium study can be used to calculate the out-of-equilibrium distributions. Previous work has shown that this is not necessarily so \[23\]. Here we analyze our extremely large database of inheritance and in aging to address the question of whether the basin curvature during aging differs from the equilibrium case. The quantity $M \equiv N^{-1} \sum_{i=1}^{3N-3} \ln \frac{\nu_i}{\Lambda_i}$ constitutes a good indicator of the curvature of a single basin in the harmonic approximation \[21, 23\]. In Fig. 4(a) we plot average values $\langle M \rangle_{eq}(\epsilon_{IS})$ and $\langle M \rangle_{ag}(\epsilon_{IS})$ for equilibrium and aging runs. This plot shows that for all aging experiments with $T_b > T_x$, the $\epsilon_{IS}$ dependence of $M$ is the same in equilibrium and in aging, and hence that the aging liquid explores basins the shape of which is the same as the one explored in equilibrium. In contrast, for $T_b < T_x$, the aging system explores basins of different shape. In the $(0.8 \rightarrow 0.25)$ case, the system begins to explore basins of higher $M$ relative to equilibrium values near $\epsilon_{IS} \approx -7.6$. In the deep quench $(0.6 \rightarrow 0.1)$ case, the system stays in basins of roughly constant $f_{vib}$. It is as though the system explores basins of lower energy, but not of correspondingly lower $f_{vib}$. To discern the origins of the differences in basin sampling in aging and equilibrium, we calculate the distribution of $M$, $P(M)$, for four different cases (Fig. 4(b)). More specifically, we want to assess if differences in $\langle M \rangle$, at the same average $\epsilon_{IS}$ value, arise from differences in the distributions of sampled $\epsilon_{IS}$ or...
if they arise from intrinsic differences in sampled basin shapes. For this reason we show, together with the equilibrium case for $T = 0.55$ (for which $e_{IS} = -7.6228$), the $P(M)$ for basins of depth $e_{IS} = -7.6228 \pm 0.002$, explored in the shallow $0.8 \rightarrow 0.446$ and deep $0.8 \rightarrow 0.25$ quenches (independent from $t_w$) and basins explored in equilibrium (independent from $T$). Data in Fig. 4(b) show that the equilibrium $P(M)$ coincides with the distributions evaluated from all sampled basins with depth equal to $e_{IS} = -7.6228$. It also coincides with the distributions evaluated during aging in the $T_b > T_x$ runs. But it does not coincide with the distributions evaluated during aging in the $T_b < T_x$ case. Hence, differences between equilibrium and aging cannot be ascribed to the the non-linear dependence of $M$ on $e_{IS}$. We conclude that in aging runs with $T_b < T_x$ the system explores narrower basins (higher $M$) as compared to equilibrium.

In conclusion, the results reported in this Letter provide high quality data for the evolution of the energy distribution in aging, for several different aging scenarios, and hence provide an important starting point for a detailed master equation description [26, 27, 28, 29] of the dynamics in configuration space. In our simulations, when $T_b > T_x$, we find that the distribution initially narrows during aging, broadening again as the system re-equilibrates. We also find that the system samples configurations which are typically explored in equilibrium. In this $T$ range, a description of the aging dynamics via a master equation is feasible, provided equilibrium properties are fully characterized. By contrast, when $T_b < T_x$, we only observe the narrowing of the distribution. Furthermore, the vibrational states explored during aging differ from the equilibrium ones. We note that the out-of-equilibrium theory, which is built on the hypothesis that states explored in aging are the same as those explored in equilibrium, predicts only broadening associated with the approach to equilibrium. Hence a theory based on a single $T_i$ may only apply to the $T_b > T_x$ case. We also stress that the results reported in this Letter suggest that fluctuations in arrested states (which on the time scale of simulation correspond to $T_b < T_x$) depend on the previous thermal history [28]. Glasses with the same average values may strongly differ in their frozen fluctuations. For deep quenches, the fluctuations frozen in the glass are significantly different from the fluctuations experienced in the liquid state, a feature which could explain the cross-over effect [22, 24] and the failure of the theories based on one $T_i$. Finally, we note that the decrease of the variance at short times (as shown in Fig. 2), suggests that the initial aging dynamics—which may well be the only one accessible on the observation time scale for deep quenches—acts in the direction of increasing the differences between the equilibrium liquid and glass distributions.

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