Aging as dynamics in configuration space

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Abstract

The relaxation dynamics of many disordered systems, such as structural glasses, proteins, granular materials or spin glasses, is not completely frozen even at very low temperatures [1,2]. This residual motion leads to a change of the properties of the material, a process commonly called aging. Despite recent advances in the theoretical description of such aging processes, the microscopic mechanisms leading to the aging dynamics are still a matter of dispute [3–5]. In this letter we investigate the aging dynamics of a simple glass former by means of molecular dynamics computer simulation. Using the concept of the inherent structure we give evidence that aging dynamics can be understood as a decrease of the effective configurational temperature $T$ of the system. From our results we conclude that the equilibration process is faster when the system is quenched to $T_c$, the critical $T$ of mode-coupling theory [6], and that thermodynamic concepts [7,8] are useful to describe the out-of-equilibrium aging process.

Despite their constitutive differences, many complex disordered materials show a strikingly similar dynamical behavior [1,9]. In such systems, the characteristic relaxation time increases by many decades upon a small variation of the external control parameters such as $T$ or density. Correlation functions show power-law and stretched exponential behavior as opposed to a simple exponential decay. Also the equilibration process is frequently of
non-exponential nature, and is often so slow to give rise to strong out-of-equilibrium phenomena, commonly named aging. It has recently been recognized that the similarity in the equilibrium dynamics for many systems might be related to a similarity in the structure of their configuration space (often called energy-landscape) \[10\] and that this structure can be studied best in the out-of-equilibrium situation. In this letter we investigate the energy-landscape of an aging system and show that by means of this landscape it is indeed possible to establish a close connection between the equilibrium and out-of-equilibrium properties of the same system.

For the case of glass-forming liquids, whose characteristic relaxation time increases by more than 13 decades when \( T \) is decreased by a modest amount, the configuration space is given by the \( 3N \) dimensional space spanned by the spatial coordinates of the \( N \) atoms. In 1985, Stillinger and Weber introduced the concept of the inherent structure (IS), which can be defined as follows \[10\]: for any configuration of particles the IS is given by that point which is reached by a steepest descent procedure in the potential energy if one uses the particle configuration as starting point of the minimization, i.e. the IS is the location of the nearest local potential-energy minimum in configuration space. By this method configuration space can be decomposed in a unique way into the basins of attraction of all IS of the systems and the time-evolution of a system in configuration space can be described as a progressive exploration of different IS. Here we determine the properties of the IS in equilibrium as well as in the out-of-equilibrium situation. From the comparison of the IS in these different situations we elucidate the dynamics of the system during the aging and learn about the structure of configuration space and the physics of the glassy dynamics.

The system we study is a binary mixture of Lennard-Jones particles whose equilibrium dynamics has been investigated in great detail \[11–13\]. It has been found that this dynamics can be well described by the so-called mode-coupling theory \[8\] with a critical temperature \( T_c = 0.435 \). To study the non-equilibrium dynamics we quench at time zero the equilibrated system from an initial temperature \( T_i = 5.0 \) to a final temperature \( T_f \in \{0.1, 0.2, 0.3, 0.4, 0.435\} \). In Fig. \[4\] we show \( e_{IS} \), the average energy per particle in
the IS, as a function of $T$ (equilibrium case — panel a) and as a function of time (out-of-equilibrium case — panel b), respectively. In agreement with the results of Ref. [13] we find that in equilibrium $e_{IS}$ is almost independent of $T$ for $T \geq 1.0$, i.e. when the thermal energy $k_B T$ is larger than the depth of the Lennard-Jones pair potential. At lower $T$, $e_{IS}$ shows a significant $T$ dependence confirming that on decreasing $T$ the system is resident in deeper minima. The relation $e_{IS}(T)$ can be inverted, $T = T(e_{IS})$, and we propose to use this relation to associate in the non-equilibrium case to each value of $e_{IS}(t)$ an effective temperature $T_e(e_{IS}(t))$ [see Fig. 1] [13]. By associating an equilibrium $T$ value to an $e_{IS}(t)$ value we can describe the (out-of-equilibrium) time dependence of $e_{IS}$ during the aging process as a progressive exploration of configuration space valleys with lower and lower energy or, equivalently, as a progressive thermalization of the configurational potential energy. We find that, for all studied $T_f$, the equilibration process is composed by three regimes (Fig. 1b). An early-time regime, during which the equilibrating system explores basins with high IS energy and in which $e_{IS}(t)$ shows little $t$ dependence. This regime is followed by one at intermediate-time in which $e_{IS}(t)$ decreases with a power-law with an exponent $0.13 \pm 0.02$, independent of $T_f$. This scale-free $t$-dependence is evidence that the aging process is a self-similar process. At even longer $t$ a third regime is observed for the lowest $T_f$, characterized by a slower thermalization rate. The cross-over between these three time regimes is controlled by the value of $T_f$.

We show next that during the equilibration process the system visits the same type of minima as the one visited in equilibrium. We evaluate the curvature of the potential energy at the IS as a function of $T$ (for the equilibrium case) and as a function of time $t$ (for the out-of-equilibrium case) by calculating the density of states $P(\nu)$, i.e. the distribution of normal modes with frequency $\nu$. Before we discuss the frequency dependence of $P(\nu)$ we first look at its first moment, $\bar{\nu}$, a quantity which can be calculated with higher accuracy than the distribution itself. The $T$-dependence of $\bar{\nu}$ in equilibrium and its $t$-dependence in non-equilibrium are shown in Figs. 2a and 2b, respectively. Note that Fig. 1 and Fig. 2 are quite similar. This demonstrates that during the progressive thermalization, the aging system
explores IS with the same $e_{1S}$ and with the same curvature as the one visited in equilibrium, i.e. the same type of minima. The similarity of Fig. 1 and Fig. 2 also demonstrates that $T_e(e_{1S})$ can indeed serve as a $T$ which characterizes the typical configuration occupied by the system. We also consider the frequency dependence of $P(\nu)$, which is shown for the equilibrium case in Fig. 3. In the inset we show $P(\nu)$ at the highest and lowest $T$ investigated and we find that the dependence of $P(\nu)$ on $T$ is rather weak. To better visualize the weak $T$-dependence of $P(\nu)$ we discuss in the following $P(\nu) - P_0(\nu)$, where $P_0(\nu)$ is the (equilibrium) distribution at $T = 0.446$, the lowest $T$ at which we were able to equilibrate the system. In Fig. 3 we show $P(\nu) - P_0(\nu)$ and from it we see that the main effect of a change in $T$ is that with decreasing $T$ the modes at high $\nu$ disappear and that more modes in the vicinity of the peak appear. We also find that if an analogous plot is made for the out-of-equilibrium data the same pattern is observed, i.e. that with increasing $t$ $P(\nu)$ becomes narrower and more peaked.

We next show that $T_e(e_{1S})$ completely determines $P(\nu)$ during the aging process. For this we see from Fig. 1 that $T_e = 0.6$ corresponds to $t \approx 1600$ for $T_f = 0.435$, 0.4, and 0.3, and to $t \approx 4000$ and $t \approx 25000$ for $T_f = 0.2$ and 0.1, respectively (see dashed lines in Fig. 1). If $T_e$ has thermodynamic meaning the non-equilibrium $P(\nu)$ at these times should be the same as the equilibrium $P(\nu)$ at $T = 0.6$. These functions are plotted in Fig. 4 (curves with filled symbols). We find that the different distribution functions are superimposed, demonstrating the validity of the proposed interpretation of $T_e$ as effective $T$. That this collapse of the curves is not a coincidence can be recognized by the second set of curves which is shown in Fig. 4 (curves with open symbols). These curves correspond to $T_e = 0.5$ for which the corresponding times from Fig. 1 are $t \approx 16000$ for $T_f = 0.435$, and 0.4, and the $t \approx 25000$ for $T_f = 0.3$ [19]. Also for $T_e = 0.5$ the different $P(\nu)$ can be considered to be identical within the accuracy of the data. Note that the two set of curves corresponding to the two values of $T_e$ are clearly different, showing that our data has a sufficiently high precision to distinguish also values of $T_e$ which are quite close together. From the present data we conclude that minima with the same value of $e_{1S}$ do indeed have the same distribution of curvature.
To discuss the results of this paper it is useful to recall insight gained from the analysis of instantaneous normal modes (INM) of supercooled liquids [17]. The INM studies have demonstrated that the slowing down of the dynamics in supercooled liquids is accompanied by a progressive decrease in the number of so-called double-well modes, i.e. the number of directions in configuration space where the potential energy surface has a saddle leading to a new minimum, a condition stronger than the local concavity. It has been demonstrated [18] that the number of double-well modes vanishes on approach to $T_c$. Thus for $T > T_c$ the system is always located on a potential energy landscape which, in at least one direction, is concave (i.e. the system sits on a saddle point) whereas at $T < T_c$ the system is located in the vicinity of the local minima, i.e. the landscape is convex. This result can be rephrased by saying that $T_c$ is the $T$ at which the thermal energy $k_B T_c$ is of the same order as the height of the lowest-lying saddle point above the nearest IS, i.e. above $e_{\text{IS}}$. The energy difference between $k_B T + e_{\text{IS}}$ and the lowest-lying saddle point energy can be chosen as an effective ($T$-dependent) barrier height. This observation, which should hold true also for the Lennard-Jones system studied here, and the results presented here lead us to the following view of the energy landscape and the aging process. For high $T$, $k_B T$ is significantly higher than the lowest lying saddle energy and the effective barriers between two minima are basically zero, i.e. the system can explore the whole configuration space. At $T \approx 1.0$ the system starts to become trapped in that part of configuration space which has a value of $e_{\text{IS}}$ which is less than the one at high $T$ (Fig. 1 and Ref. [13]) and the properties of the IS start to become relevant. This point of view of the structure of phase space can now be used to understand the aging dynamics. At the beginning of the quench the system is still in the large part of configuration space which corresponds to (high) $T_i$. Although $k_B T_f$ is now relatively small, the effective barriers are still zero and the system can move around unhindered and it moves to minima which have a lower energy. The rate of this exploration is related to the number of double-well directions accessible within $k_B T_f$, which explains why in Fig. 1b the curves with small $T_f$ stay at the beginning longer on the plateau than the ones with larger $T_f$. With increasing $t$ the system starts to find IS which have a lower
and lower energy and $e_{IS}(t)$ starts to decrease. Note that apart from the $T_f$ dependence of the rate of exploration just discussed, this search seems to be independent of $T_f$, since in Fig. 1b the slope of the curves at intermediate times does not depend on $T_f$.

With increasing $t$ the system finds IS with lower and lower energies and decreases its $T_e$. From the above discussion on the INM we know that with decreasing $T$ the height of the effective barriers also increases and it can be expected that the search of the system becomes inefficient once it has reached a $T_e$ at which the energy difference between the lowest-lying saddle and $e_{IS}$ becomes of the order of $k_B T_f$. Therefore we expect that once this stage has been reached the $t$-dependence of $e_{IS}$ will change and this is what we find, as shown in Fig. 1b in the curves for $T_f = 0.2$ and 0.1 at $t \approx 10^4$. We also note that the $T_e$ at which this crossover occurs will increase with decreasing $T_f$, in agreement with the result shown in Fig. 1. For times larger than this crossover $t$ the system no longer explores the configuration space by moving along unstable modes but rather by means of a hopping mechanism in which barriers are surmounted. This hopping mechanism, although not efficient for moving the system through configuration space, still allows the system to decrease its configurational energy and its $T_e$ further. Thus the cross-over from the self-similar process to the activated dynamics, which in equilibrium is located close to $T_c$, is in the non-equilibrium case $T_f$ dependent. We conclude that in order to obtain configurations which are relaxed as well as possible (within a given time span) one should quench the system to $T_e$ in order to exploit as much as possible the low-lying saddle points.

The presented picture implies that, if hopping processes were not present, $T_e$ for the system would always be above $T_e$. Although hopping processes are always present, they might be so inefficient that even for long times the value of $T_e$ is above $T_e$. From Fig. 1 we recognize that this is the case for the present study. We note that theoretical mean-field predictions derived for $p$–spin models [20] and recent extensions of the ideal MCT equations to non-equilibrium processes [21] conclude that system quenched below $T_e$ always remain in that part of configuration space corresponding to $T > T_e$.

Finally we stress that the present analysis of the aging process strongly support the use
of the IS as an appropriate tool for the identification of an effective $T$ at which the configurational potential energy is at equilibrium. This opens the way for detailed comparisons with recent out-of-equilibrium thermodynamics approaches \[8\] and for detailed estimates of the configurational entropy.
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FIGURES

FIG. 1. a) $\epsilon_{IS}$, the potential energy of the inherent structure in equilibrium as a function of temperature (panel a) and as a function of time during the aging process (panel b). The dashed line is used to define the effective temperature $T_e(t)$ in the non-equilibrium case. The microscopic model we consider is a binary (80:20) mixture of Lennard-Jones particles, which in the following we will call type $A$ and type $B$ particles. The interaction between two particles of type $\alpha$ and $\beta$, with $\alpha, \beta \in \{A,B\}$, is given by $V_{\alpha\beta} = 4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r}\right)^{6}\right]$. The parameters $\epsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are given by $\epsilon_{AA} = 1.0$, $\sigma_{AA} = 1.0$, $\epsilon_{AB} = 1.5$, $\sigma_{AB} = 0.8$, $\epsilon_{BB} = 0.5$, and $\sigma_{BB} = 0.88$. The potential is truncated and shifted at $r_{cut} = 2.5\sigma_{\alpha\beta}$. $\sigma_{AA}$ and $\epsilon_{AA}$ are chosen as the unit of length and energy, respectively (setting the Boltzmann constant $k_B = 1.0$). Time is measured in units of $\sqrt{m\sigma_{AA}^2/48\epsilon_{AA}}$, where $m$ is the mass of the particles. 1000 particles were used at a fixed density of 1.2. Further information on the equilibrium and non-equilibrium simulations can be found in Refs. [11,12,14]. By using copies of the system at different times $t$ since the quench, we calculated the IS of the system by means of a conjugate gradient method. To improve the statistics of the results we averaged them over 8-10 independent runs. The same method was also used to determine the IS for the system at equilibrium in the range $5.0 \geq T \geq 0.446$.

FIG. 2. a) Temperature dependence of $\bar{\nu}$, the first moment of the density of states, in equilibrium. b) Time dependence of $\bar{\nu}$ during the aging process.

FIG. 3. Frequency dependence in equilibrium of $P(\nu)$, the density of states at frequency $\nu$. Main figure: Temperature dependence of $P(\nu)$ for all temperatures investigated. In order to see this dependence clearer we have subtracted from these distributions $P_0(\nu)$, the equilibrium distribution function at $T = 0.446$. Inset: Comparison of $P(\nu)$ at $T = 5.0$ and $T = 0.446$.

FIG. 4. Comparison of $P(\nu)$ in the out-of-equilibrium situation at different values of $T_f$ and different times (but at the same $T_e$) with $P(\nu)$ at equilibrium with $T = T_e$. Filled symbols and bold dashed line: $T_e = T = 0.5$. Open symbols and bold solid line: $T_e = T = 0.6$. 10
FIG. 1. W. Kob, F. Sciortino and P. Tartaglia
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