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Aging as dynamics in configuration space

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Abstract. – Using molecular dynamics computer simulation we calculate for a simple glass former $e_{\rm IS}$, the energy of the inherent structure, in equilibrium and in the out-of-equilibrium situation. We show that $e_{\rm IS}$ can be used to define for the aging system an effective time-dependent temperature $T_{\rm e}(t)$. In particular we demonstrate that during the aging process the system visits at time t configurations which are typical for the equilibrium system at temperature $T_{\rm e}(t)$.

In the last few years our understanding of the dynamics of supercooled liquids has increased significantly. This progress has become possible due to novel experimental techniques to investigate such systems [1] and to remarkable advances to describe them theoretically [2]. Very recently strong efforts have been made to investigate also the out-of-equilibrium dynamics (OOED) of supercooled liquids [3–5]. One motivation for these attempts is the analytic result [3] that for certain simple models this OOED can be described by equations which are formally very similar to the ones found in the so-called mode-coupling theory (MCT) [2], the theory which is so successful to describe the (supercooled) equilibrium dynamics. A further reason is that it is believed that the long-time OOED is dominated by the *structure* of the phase space of the system (*i.e.* the way the local minima are connected with each other, or the distribution of the barrier heights between them) and that this information can then be used to gain a better understanding of the *equilibrium* dynamics at low temperatures and hence the glass transition. For the case of spin glasses such connections between the OOED and the equilibrium properties of the system have already been shown to exist [6,7], but for structural glasses only the first attempts in this direction have been made.

In the present paper we discuss the results of computer simulations in order to demonstrate that the concept of the inherent structure (IS), introduced by Stillinger and Weber [8] and discussed in more detail below, can be used to make interesting connections between the equilibrium properties of supercooled liquids and their OOED dynamics. Thus our results establish a link between the properties of such systems above the glass transition temperature and the ones below it and hence should allow us to get a better understanding of this transition as well as of the dynamics above and below it.

The idea of the IS can be described as follows: 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 for the minimization. By this method the configuration space can thus be decomposed in a unique way into the basins of attraction of all IS of the systems. In this framework, the time evolution of a system in configuration space can therefore be described as a progressive exploration of different IS. In the following we will 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 will gain a better understanding of the dynamics of the system during the aging and hence improve our understanding of the structure of configuration space and thus the glassy dynamics.

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 α and β, with $\alpha, \beta \in \{\mathrm{A}, \mathrm{B}\}$, is given by $V_{\alpha\beta} = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^{6}]$. The parameters $\epsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are given by $\epsilon_{\mathrm{AA}} = 1.0$, $\sigma_{\mathrm{AA}} = 1.0$, $\epsilon_{\mathrm{AB}} = 1.5$, $\sigma_{\mathrm{AB}} = 0.8$, $\epsilon_{\mathrm{BB}} = 0.5$, and $\sigma_{\mathrm{BB}} = 0.88$. The potential is truncated and shifted at $r_{\mathrm{cut}} = 2.5\sigma_{\alpha\beta}$. In the following we will use σ_{AA} and ϵ_{AA} as the unit of length and energy, respectively (setting the Boltzmann constant $k_{\mathrm{B}} = 1.0$). Time will be measured in units of $\sqrt{m\sigma_{\mathrm{AA}}^2/48\epsilon_{\mathrm{AA}}}$, where m is the mass of the particles.

In the past the equilibrium dynamics of this system has been investigated in great detail [9, 10] and it has been found that this dynamics can be described very well by MCT with a critical temperature $T_{\mathrm{c}} = 0.435$. This system has also been used to study the OOED of simple glass formers [5] and it was shown that this dynamics is in qualitative agreement with the one predicted by recent mean-field theories. In the present study the system was equilibrated at a (high) temperature $T_{\mathrm{i}} = 5.0$, using 1000 particles in a box of size of $(9.4)^3$, and subsequently quenched to a temperature $T_{\mathrm{f}} \in \{0.1, 0.2, 0.3, 0.4, 0.435\}$. This quench was done by means of a stochastic heat bath in which every 50 time steps the velocities of all the particles were exchanged with the ones drawn from a Maxwell-Boltzmann distribution corresponding to a temperature T_{f}. Between these exchanges the system was propagated in the microcanonical ensemble by means of the velocity form of the Verlet algorithm, using a step size of 0.02.

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 procedure was also used to determine the IS for the system at equilibrium in the temperature range $5.0 \geq T \geq 0.446$.

In fig. 1 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. [10] we find that in equilibrium e_{IS} is almost independent of T for $T \geq 1.0$, *i.e.* when the thermal energy $k_{\mathrm{B}}T$ 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. In this temperature range the relation $e_{\mathrm{IS}}(T)$ can be inverted, $T = T(e_{\mathrm{IS}})$, and we propose to use this relation to associate, *in the non-equilibrium case*, to each value of $e_{\mathrm{IS}}(t)$ an effective temperature $T_{\mathrm{e}}(e_{\mathrm{IS}}(t))$ (see fig. 1) [11]. By associating an equilibrium T value to an $e_{\mathrm{IS}}(t)$ 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 of three regimes (fig. 1b): An early-time regime, during which the equilibrating system explores basins with high IS energy and in which $e_{\mathrm{IS}}(t)$ shows little t-dependence. This regime is followed by one at intermediate time in which $e_{\mathrm{IS}}(t)$ decreases with a time dependence which is compatible with a power law with an exponent

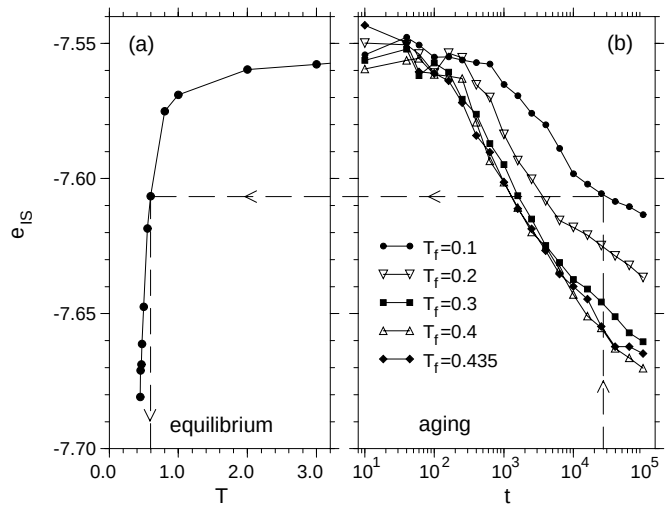

Fig. 1 – $e_{\rm IS}$, the potential energy of the inherent structure in equilibrium as a function of temperature (panel a) and as a function of time during the aging process (panel b). The dashed line is used to define the effective temperature $T_{\rm e}(t)$ in the non-equilibrium case.

0.13 ± 0.02, independent of $T_{\rm f}$. 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 $T_{\rm f}$, characterized by a slower thermalization rate. Very recently similar results have been obtained for a finite-size spin model [12].

We show next that during the equilibration process the system visits the same type of minima as the one visited in equilibrium. For this we evaluate the curvature of the potential

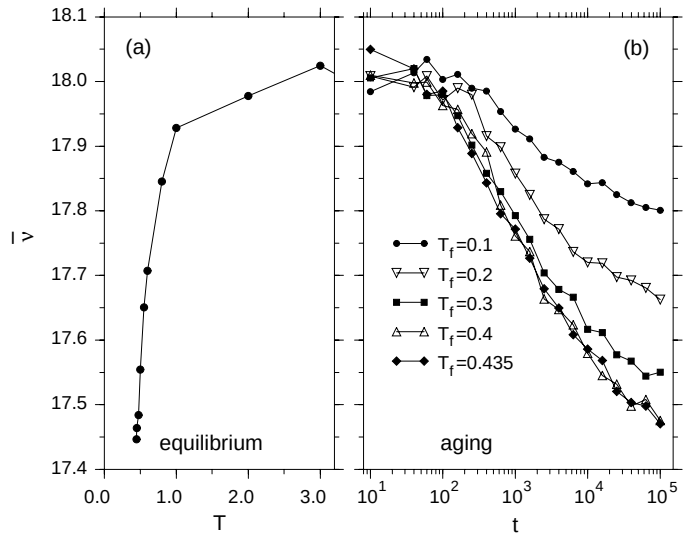

Fig. 2 – a) Temperature dependence of $\bar{\nu}$, the first moment of the density of states, in equilibrium. b) Time dependence of $\bar{\nu}$ during the aging process.

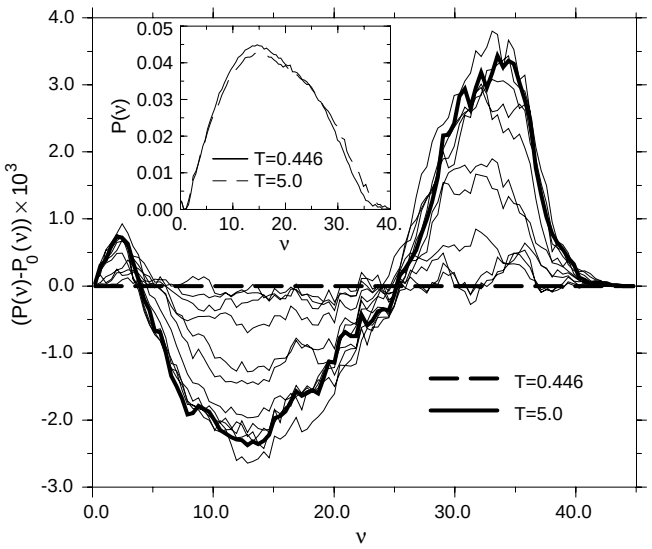

Fig. 3 – Frequency dependence in equilibrium of $P(\nu)$, the density of states at frequency ν. Main figure: temperature dependence of $P(\nu)$ for all temperatures investigated. In order to see this dependence more clearly we have subtracted from these distributions $P_0(\nu)$, the equilibrium distribution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

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 ν. 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 b, respectively. Note that fig. 1 and fig. 2 are very similar. This demonstrates that the aging system visits during the progressive thermalization local minima which have the same curvature as the equilibrium system at the temperature $T_{\rm e}$. This shows that $T_{\rm e}(e_{\rm IS})$ can indeed serve as a temperature which characterizes the typical configuration occupied by the system.

Now we consider the full 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 temperatures investigated and we find that the dependence of $P(\nu)$ on T is rather weak. To better visualize this 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 ν 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 time $P(\nu)$ becomes narrower and more peaked, in agreement with the experiments of ref. [13].

We next show that $T_{\rm e}(e_{\rm IS})$ completely determines $P(\nu)$ during the aging process. For this we read off from fig. 1 that $T_{\rm e} = 0.6$ corresponds to $t \approx 1600$ for $T_{\rm f} = 0.435$, 0.4, and 0.3, and to $t \approx 4000$ and $t \approx 25000$ for $T_{\rm f} = 0.2$ and 0.1, respectively (see dashed lines in fig. 1). If $T_{\rm e}$ has a thermodynamic meaning, the *non-equilibrium* $P(\nu)$ at these times should be the same

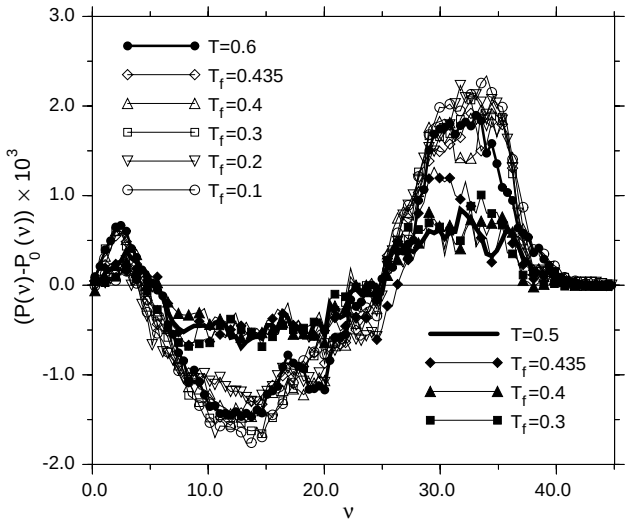

Fig. 4 – Comparison of $P(\nu)$ in the out-of-equilibrium situation at different values of $T_{\rm f}$ and different times (but at the same $T_{\rm e}$) with $P(\nu)$ at equilibrium with $T = T_{\rm e}$. Open symbols: $T_{\rm e} = T = 0.6$. Filled symbols: $T_{\rm e} = T = 0.5$.

as the *equilibrium* $P(\nu)$ at $T = 0.6$. These functions are plotted in fig. 4 (curves with open symbols). We find that the different distribution functions are superimposed, demonstrating the validity of the proposed interpretation of $T_{\rm e}$ as an effective temperature. 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 filled symbols). These curves correspond to $T_{\rm e} = 0.5$ for which the corresponding times from fig. 1 are $t \approx 16000$ for $T_{\rm f} = 0.435$, and 0.4, and the $t \approx 25000$ for $T_{\rm f} = 0.3$ [14]. Also for $T_{\rm e} = 0.5$ the different $P(\nu)$ can be considered to be identical within the accuracy of the data (fig. 4). Note that the two set of curves corresponding to the two values of $T_{\rm e}$ are clearly different, showing that our data has a sufficiently high precision to distinguish also values of $T_{\rm e}$ which are quite close together. From the present data we thus conclude that minima with the same value of $e_{\rm IS}$ do indeed have the same distribution of curvature [15].

To discuss the results of this paper it is useful to recall some of the insight gained from the analysis of instantaneous normal modes (INM) of supercooled liquids [16]. The INM studies have demonstrated that the slowing-down of the dynamics in supercooled liquids is accompanied by a progressive decrease of 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 which is stronger than the local concavity. It has been found [17] that the number of double-well modes vanishes on approach to $T_{\rm c}$. Thus for $T > T_{\rm c}$ the system is always located on a potential energy landscape which, in at least one direction, is concave (*i.e.* the system sits close to a saddle point), whereas for $T < T_{\rm c}$ 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 $T_{\rm c}$ is the temperature at which the thermal energy $k_{\rm B}T_{\rm c}$ becomes comparable to the height of the lowest-lying saddle point above the nearest IS, *i.e.* above $e_{\rm IS}$. Therefore the energy difference between the lowest-lying saddle point energy and $k_{\rm B}T + e_{\rm IS}$ can be chosen as an effective (T-dependent) barrier height. These observations, which hold true also for the Lennard-Jones system studied here [18], and the results presented in the

present paper thus lead us to the following view of the energy landscape. For high T, $k_{\rm B}T$ is significantly higher than the lowest-lying saddle energy and the effective barriers between two adjacent minima are basically zero, *i.e.* the system can explore the whole configuration space. At $T \approx 1.0$ the system starts to populate that part of configuration space which has a value of $e_{\rm IS}$ which is less than the one at high T (fig. 1 and ref. [10]) 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) $T_{\rm i}$. Although $k_{\rm B}T_{\rm f}$ is now relatively small, the effective barriers are still zero and the system can move around relatively unhindered and thus 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 $k_{\rm B}T_{\rm f}$, which explains why in fig. 1b the curves with small $T_{\rm f}$ stay at the beginning longer on the plateau than the ones with larger $T_{\rm f}$. With increasing t the system starts to find IS which have a lower and lower energy and $e_{\rm IS}(t)$ starts to decrease. Note that, apart from the $T_{\rm f}$ dependence of the rate of exploration just discussed, this search seems to be independent of $T_{\rm f}$, since in fig. 1b the slope of the curves at intermediate times does not depend on $T_{\rm f}$, within the accuracy of the data.

With increasing t the system finds IS with lower and lower energies and decreases its $T_{\rm e}$. 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 $T_{\rm e}$ at which the energy difference between the lowest-lying saddle and $e_{\rm IS}$ becomes of the order of $k_{\rm B}T_{\rm f}$. Therefore we expect that once this stage has been reached the t-dependence of $e_{\rm IS}$ will change and this is what we find, as shown in fig. 1b in the curves for $T_{\rm f} = 0.2$ and 0.1 at $t \approx 10^4$. We also note that the $T_{\rm e}$ at which this crossover occurs will increase with decreasing $T_{\rm f}$, in agreement with the result shown in fig. 1b. 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 $T_{\rm e}$ further. Thus the crossover from the "self-similar" process to the activated dynamics, which in equilibrium is located close to $T_{\rm c}$, is in the non-equilibrium case $T_{\rm f}$-dependent. We conclude that in order to obtain configurations which are relaxed as much as possible (within a given time span) one should quench the system to $T_{\rm c}$ in order to exploit as much as possible the low-lying saddle points.

The presented picture implies that, if hopping processes were not present at all, $T_{\rm e}$ would always be above $T_{\rm c}$, even after an infinite amount of time. Although in reality hopping processes are always present, they might be so inefficient that even for long times the value of $T_{\rm e}$ is above $T_{\rm c}$. 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 [19] and recent extensions of the ideal MCT equations to non-equilibrium processes [20] conclude that system quenched below $T_{\rm c}$ always remain in that part of configuration space corresponding to $T > T_{\rm c}$.

The summary of the present work is thus that by investigating the inherent structure of the system in the equilibrium and out-of-equilibrium situation we have been able to show that during the aging process the system visits configurations which can be characterized by an effective temperature $T_{\rm e}(t)$. This opens the way for detailed comparisons with recent out-of-equilibrium thermodynamics approaches [21] and with the IS-thermodynamic approach, discussed in refs. [22]. In particular, it will be important to find out how $T_{\rm e}(t)$ compares with the temperature T_X, introduced in the recent work on the non-applicability of the fluctuation dissipation theorem [3–5, 23].

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