Quenches and crunchs: Does the system explore in aging the same part of the configuration space explored in equilibrium?

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Abstract

Numerical studies are providing novel information on the physical processes associated to physical aging. The process of aging has been shown to consist in a slow process of explorations of deeper and deeper minima of the system potential energy surface. In this article we compare the properties of the basins explored in equilibrium with those explored during the aging process both for sudden temperature changes and for sudden density changes. We find that the hypothesis that during the aging process the system explores the part of the configuration space explored in equilibrium holds only for shallow quenches or for the early aging dynamics. At longer times, systematic deviations are observed. In the case of crunches, such deviations are much more apparent.
1 Introduction

At the glass transition temperature $T_g$ (Debenedetti 1997), the characteristic relaxation time of a liquid becomes of the same order of the experimental time, thus preventing equilibrium studies at lower $T$. Material properties below $T_g$ depend on the previous history (i.e. on the preparation technique, on the cooling/compression rate and so on) as well as on the time spent in the glass-state. This time dependence, generically known as physical aging, highlights the out-of-equilibrium (OOE) condition of glasses and their extremely slow equilibration processes.

Substantial amount of work has been devoted to the understanding and to the formal description of the supercooled liquid dynamics (Götze 1999, Cummins 1999), of the physics beyond the glass transition (Angell 1995) and of physical aging (Bouchaud et al. 1998, Cugliandolo et al. 1996, Latz 2000). Numerical simulations of supercooled states, both in equilibrium and in controlled out-of-equilibrium conditions, have played an important role in the present developments (Kob 1999). Although the time scales probed by numerical simulations are very different than experimental ones (100ns compared to s), the numerical “experiments” appear to be able to reproduce features of real materials (Utz et al. 2000, Barrat and Berthier 2001).

The description of the aging dynamics as motion in configuration space, has been very fruitful (Kob et al. 2000). It has been shown that, during aging, the system explores deeper and deeper basins of the potential energy surface. The search for deeper basins during aging resembles the exploration of deeper and deeper basins which takes place in equilibrium on cooling. This similarity has been interpreted in term of a decrease of the internal configurational temperature $T$ of the system under aging (Kob et al. 2000). An analysis of the curvatures of the PES basins supported the possibility that during the aging process the system visits the same type of minima as the one visited in equilibrium. This analysis supported also the possibility of a thermodynamic description of the aging system and a prediction of the internal configurational temperature in full agreement with the numerical estimates (Sciortino and Tartaglia 2001a).

The outcome of these studies, which are still far from being settled, suggest that the out-of-equilibrium glassy state, notwithstanding its out of equilibrium condition, can be uniquely determined by its kinetic temperature, its volume and the properties of the basin in which the system is trapped. These quantities allow to develop a thermodynamic description of the glass state (Davies and Jones 1953, Nieuwenhuizen 1998, Speedy 1998, Mezard and Parisi 1999, Sciortino et al. 1999) which is currently tested in experiments (Grigera and Israeloff 1999, Knaebel et al. 2000) and further simulations (Sciortino and Tartaglia 2001b).

From an experimental point of view, aging experiments are performed at constant pressure. Moreover, often a change in pressure (and hence in density) is used to bring the system from an equilibrium to an out-of-equilibrium state. The change
in density produces a much more dramatic change in the PES than a change in temperature. This opens the possibility that the hypothesis of out-of-equilibrium dynamics as succession of quasi equilibrium states may not apply to the crunch experiments and hence that a more refined thermodynamic approach is requested for glass materials produce with a crunch route.

In this manuscript we revisit the hypothesis that during the aging process the system explores the same part of the configuration space by performing a more accurate analysis of the relation basin-depth as a function of the basin-curvature, made nowadays possible by the increased computational facilities. We also present a comparison of this relation for different quenching temperatures and for a crunch (Di Leonardo et al 2000).

2 The models

We consider two models, an atomic one and a molecular one.

The first microscopic model we consider is a binary (80:20) mixture of Lennard-Jones particles (BMLJ), 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 $V_{\alpha\beta} = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6]$. 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 $r_{\text{cut}} = 2.5\sigma_{\alpha\beta}$. $\sigma_{AA}$ 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 $\sqrt{m\sigma^2_{AA}/48\epsilon_{AA}}$, where $m$ is the mass of the particles. 1000 particles were placed in a box of side 9.4. The studied isochore has density of 1.2. To study the quenches, we have equilibrated several independent configurations at $T = T_i$ in the $NVT$ ensemble (Nosé-Hoover thermostat). Each of the configuration has been quenched to $T_f$ by changing at $t = 0$ the thermostat temperature to $T_f$. The thermostat constant is chosen in such a way that, within 1000 MD steps, the average kinetic energy thermalizes to $T_f$. To study the crunches, we have equilibrated 280 independent configurations at $T = 0.35$ in the $NVT$ ensemble at density of 1.103. The coordinates of each atom has been rescaled by 0.9714 at $t = 0$ to simulate a 10% density increase. In this way, the final density of the crunches coincides with the density of the quenches. Inherent structures of a system are calculated by conjugate gradient algorithms. The minimization procedure is iterated until the energy change is less than $10^{-15}$. The density of states is then calculated by diagonalizing the corresponding Hessian matrix.

The second model we consider is a simple three-sites molecular model (LW), introduced by Wahnström and Lewis (Wahnström and Lewis 1993). The model is constructed by gluing in a rigid molecule three identical Lennard Jones (LJ) atoms. The shape of the molecule (an isosceles triangle) and the LJ parameters were chosen
Figure 1: Inherent structure energy as a function of $T$ in equilibrium (left) and as a function of waiting time $t_w$ following a quench (center) or a crunch (right). In the central panel, $T_f = 0.25$ and $T_i$ is 5, 0.8, 0.6, 0.55 and 0.5 from top to bottom.

to mimic as close as possible one of the most studied glass-forming, liquid, ortho-terphenyl. The slow dynamics of this model has been recently revisited (A. Rinaldi \textit{et al.} 2001) in great details. For this model we present preliminary results for a quench, starting from $T = 480$ K down to $T = 280$ K at constant density 1108.4907 Kg / m$^3$. The simulated system is composed by 343 molecules. The integration time step is 0.01 ps and the aging dynamics is followed up to 1 ns. Averages over more than 50 independent realizations are presented.

3 BMLJ model

3.1 Energies

Following a quench or a crunch, the system finds itself in a region of configuration space which is not explored in equilibrium under the externally imposed temperature and volume. The motion of the system in configuration space evolves in the attempt of reaching the typical equilibrium configuration. A clear indicator of this evolution is the time evolution of the potential energy. In the PES paradigm, the potential energy of the system can be expressed as $E = e_{IS} + E_{vib}$, where $e_{IS}$ is the IS energy and $E_{vib}$ describes the thermal excitations about the IS (harmonic plus anharmonic vibrations). While the vibrational energy does not show a significant aging depen-
3.2 Basins’ curvatures

In equilibrium, below $T = 1$, the system starts to explore deeper and deeper basins, whose shape is depth dependent. A simple way to characterize the shape of the PES basins is to calculate the density of states in harmonic approximation, expanding the potential energy around the local minimum configuration. The resulting distribution of frequencies characterizes, in harmonic approximation, the volume in configuration space associated to the basin. The density of states allows to estimate the vibrational free energy $f_{\text{basin}}$ in harmonic approximation, since

$$f_{\text{basin}}(T) = \frac{k_B T}{N} \sum_{i=1}^{3N-3} \log(\beta \hbar \omega_i)$$

A $T$-independent indicator of the basin shape can be defined as $S \equiv \sum_{i=1}^{3N-3} \log(\hbar \omega_i / \epsilon_{AA})$.

Studies on several models of liquids shows that along isochoric paths, the depth dependence of the average curvature of the basins is model and density dependent.

In the case of the BMLJ at the studied density, the average shape of the basins...
becomes wider and wider on moving to deeper and deeper basins, as shown in Fig. 2.

Fig. 2 also shows \( S(e_{IS}) \) during the aging dynamics following quenches and crunches, from different initial and bath conditions. The important observation is that during \( T \)-changes, there is an initial part of the aging process were the system explores in aging the same set of basins explored in equilibrium. For longer times, deviations start to take place and the system finds itself located in region of the configuration space which are not commonly explored in equilibrium conditions. The effect is negligible (and indeed it was not noted in previous studies) at sufficiently high \( T_f \) values (shallow quenches), but is becomes detectable in deeper quenches. In future studies, it will become important to correlated the time at which the aging dynamics significantly separates from the equilibrium one with the different mechanism of exploration of configuration spaces which characterize also the dynamics of the system in equilibrium (i.e. saddle-dominated dynamics as compared to activated dynamics (Sciortino and Tartaglia 1997, La Nave et al 2000, Angelani et al 2000, Cavagna et al 2000)).

A related interesting question is the validity of the description of the aging system as composed by two system in quasi-equilibrium at different temperatures (Sciortino and Tartaglia 2001) in conditions where the aging system explores basins which are not populated in equilibrium.

In the crunch case, in the time window accessible to numerical simulations the system never explores region of configuration space which are visited in equilibrium. The starting configuration is different from any configuration visited in equilibrium. In this respect, the ensemble of configuration of the system after an initial crunch can not be identified with an equilibrium ensemble at a different temperature, not even at infinite temperature.

Having said so, we call the reader attention on the fact that the differences observed in \( S \) are smaller than the entire variation of \( S \) with aging. We also recall that the time windows accessible to numerical experiment is such that the system, even after the longest waiting time simulated, has not completely forgot the initial configuration (or, in other words, the correlation functions never decay to zero in the simulated time period). In this respect, it is not that surprising that the basins explored in crunches are different from the basins explored in aging and in equilibrium. Finally we note that \( S \), being the sum of logarithms, is driven by the low frequency values. The small frequencies are the most affected by size effects and by artificial localization of the eigenmodes. Future studies should focus on the size effect on the data reported in Fig. 2.

We note on passing that some model potentials, like for example the BKS model for silica do not show, along an isochoric path any dependence of the basin shape on the potential depth (Saika-Voivod et al 2001). This class of models (and their corresponding materials) may provide simple aging and crunching dynamics compared to the BMLJ model here studied.
Figure 3: Radial distribution function for the AB atoms for eight different temperatures ranging from 2 to 0.446, evaluated in the IS configurations. The right panels show the enlargement of two different $r$-regions. A significant enlargement is requested to highlight the very subtle changes accompanying the population of basins of deeper and deeper IS energy.

Figure 4: Dependence on $e_{IS}$ of $g_{AB}(r = 0.8675)$ in equilibrium and during aging (crunch and quench). Note that states with same $e_{IS}$ value are realized with different pair distribution functions.
3.3 Structure of the liquid in the inherent structures

The inherent structure energy is, by definition, the integral of the pair potential over \( r \), weighted by the radial distribution function \( g(r) \). The changes in inherent structure energy on cooling does reflect changes in the local structure. In this section we look in detains these differences, with the aim of characterizing in a microscopic way the differences in states with the same inherent structure but different density of states.

Fig. 3 shows the AB radial distribution function in equilibrium as evaluated in the IS configurations, i.e. once the thermal distortion has been subtracted. The structure of the liquid changes in a very minor way and can be visualized only with a very fine resolution. The net effect of cooling in \( g_{AB}(r) \) appears as a shift of less than 0.001 in the average interatomic distance.

To emphasize the \( T \)-changes we show in Fig. 4 the relation between the basin potential energy and \( g(r) \) for a fixed \( r \) value. The data confirm that under crunch, the local liquid order is different from the equilibrium ones.

Fig. 5 shows the enlargements of \( g(r) \) in equilibrium and contrast them with the one during aging at the same \( e_{IS} \) value. Again, we note that the quench configuration is closer to the equilibrium one as compared with the crunch one.

Figure 5: Equilibrium, crunch and quench \( g_{AB} \) at the same \( e_{IS} \) values. To maximize the differences, the equilibrium \( g_{AB}(r) \) at \( T = 2.0 \) has been subtracted to all curves.
Figure 6: Equilibrium $T$-dependence of the IS energy for the LW model (left) and as a function of time during a quench from $T = 480$ to $T = 280K$ (right).

Figure 7: Equilibrium $T$-dependence of the average frequency for the LW model (left) and as a function of time during a quench from $T = 480$ to $T = 280K$ (right).
4 LW model

In the case of the LW model for ortotherphenyl (Wahnström and Lewis 1993), all results refer to a quench case.

4.1 Energies

The $T$-dependence of the inherent structure energy for the LW model is shown in Fig.6 together with the time evolution under aging. As for the BMLJ model, the aging dynamics is characterized by a slow progressive reduction of the IS energy.

4.2 Basins’ curvatures

As in the BMLJ case, the basin curvature is correlated with the basin’s depth. The $T$-dependence of the average frequency in equilibrium and the $t_w$ dependence in aging is shown in Fig.7. The frequency decreases on cooling or on aging as in the BMLJ case.

The $e_{IS}$ dependence of the local curvatures in equilibrium and in aging is shown in Fig.8. We note that for the case of the LW potential, in the time window explored by the numerical simulation and for the chosen $T_f$, the basins explored during aging coincides with the basins explored in equilibrium.

5 Conclusions

In this manuscript we have compared the properties of configuration space explored in equilibrium and in out of equilibrium conditions, with the aim of deepening our understanding of the physical mechanisms behind the aging process in disordered materials.

A careful analysis of the relations between curvature and depth of the potential energy basins reveals that basins which are not statistically explored in equilibrium are visited during the aging dynamics, especially during the dynamics following a crunch. In quenches, such conditions appears to hold also in the case of deep quench depth. At long times, the hypothesis that during the aging process the system explores the same part of the configuration space does not seem to hold any longer, at least on the scale of present day numerical calculations.

The differences in the basins appear to be located in the region of very small frequencies and may not be clearly seen if the average frequency is used as indicator of the basin curvature. We have shown here that the average of the logarithm of the
frequency (a quantity which weigh more the very low frequency spectrum) is indeed a better indicator. Such quantity is important since it quantifies the basin’s vibrational free energy. On the other hand, the very low frequency part of the spectrum is very sensitive to size effects. It could be that spurious localized modes are stabilized by the limited size of the simulated system. This call for a size-dependence detailed analysis of the relation between curvature and depth in equilibrium and in aging.

Finally, we recall that the hypothesis that the part of configurations space explored in aging and in equilibrium are similar is an important element to be able to predict the value of the internal temperature of the system and the associated response of the aging system to an external perturbation. Indeed, in the case where such detailed comparison was performed, the basin shape and curvature in aging and equilibrium do coincide. Unfortunately, no evaluation of the internal temperature has been performed yet for $t_w$ values where the possibility of predicting the value of $T_{int}$ should fail. It would be very interesting to perform such accurate study (i.e. the comparison between predictions and numerical calculations) in the near future, in particular for crunches, where the breaking of the assumption is apparent even at short waiting times.
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