Topological Description of the Aging Dynamics in Simple Glasses

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(October 26, 2018)

We numerically investigate the aging dynamics of a monatomic Lennard-Jones glass, focusing on
the topology of the potential energy landscape which, to this aim, has been partitioned in basins of
attraction of stationary points (saddles and minima). The analysis of the stationary points visited
during the aging dynamics shows the existence of two distinct regimes: i) at short times, \( t < t_c \), the
system visits basins of saddles whose energies and orders decrease with \( t \); ii) at long times, \( t > t_c \),
the system mainly lies in basins pertaining to minima of slowly decreasing energy. The dynamics for
\( t > t_c \) can be represented by a simple random walk on a network of minima with a jump probability
proportional to the inverse of the waiting time.

PACS Numbers : 61.20.Lc, 64.70.Pf, 02.70.Ns

The very slow approach to equilibrium of glassy sys-
tems is a very interesting and intriguing physical pro-
cess that, in the last few years, has received consider-
able attention from analytical, numerical and experimental
point of view [1]. When a glassy system is suddenly
brought in the glassy state from an high temperature
(or low density) equilibrium state, it starts to explore
the phase space with an off-equilibrium dynamics which
slows down as the system “ages”. During this aging
regime one time physical quantities, that are time in-
dependent on average at equilibrium, slowly approach
their equilibrium values, while two time quantities, like
the correlation functions, depend on both times due to
the lack of time translation invariance. The study of
the off-equilibrium dynamics of glassy systems, and in
particular of spin-glasses, has allowed to obtain impor-
tant informations on the phase-space properties of the
systems itself (behavior of the order parameter in the
low temperature equilibrium phase [4–6]) and to for-
mat off-equilibrium relations generalizing the usual equi-
librium ones (generalized fluctuation-dissipation relation
[7] with the introduction of an effective temperature
[8]. The investigation of the off-equilibrium properties
seems to indicate the correctness of the conjecture stat-
ing the similarity of structural glasses with some spin
glass model (spin-glasses with one step replica symmetry
breaking) [9–11]. The way a glassy system goes towards
equilibrium is then not only an interesting problem by
itself but it is also of great relevance in view of a deeper
understanding of the nature of glass transition. In this re-
spect, many efforts have been devoted to the understand-
ing of the role played by the potential energy landscape
in the equilibrium dynamics of supercooled liquids [12].
The trajectory of the representative point in the 3N con-
figureation space can be mapped into a sequence of locally
stable points (the so called Inherent Structures, IS [13]),
that are the local minima of the total potential energy \( V \):
to each instantaneous configuration during the dynamical
evolution of the system one can associate an IS by a
steepest descent path in the \( V \) surface. The properties of
the IS has been found to be very useful to clarify many
features in the dynamics and the thermodynamics of su-
percooled liquids in [14–17] and off [18,19] equilibrium.
An extension of such an analysis including all station-
ary points of \( V \) (minima and saddles) [20–22] has been
recently proposed to form a better representation of the
system during the equilibrium dynamics. This approach
gives a novel point of view on the equilibrium dynam-
cics of supercooled liquids based on a detailed topological
analysis of the potential energy landscape. In particu-
lar it emerges [21] that the order of the sampled saddles
during the equilibrium dynamics is a well defined increasing
function of temperature and it appears to vanish at the
so-called mode-coupling [23] transition temperature
\( T_{MCT} \), which then marks the crossover from a dynamics
between basins of saddles \( (T > T_{MCT}) \) to a dynamics
between basins of minima \( (T < T_{MCT}) \). Similar results
have been found [23] in the framework of Instantaneous
Normal Modes analysis [4].

In this Letter we numerically investigate the off-
equilibrium dynamics of a simple model glass, by map-
ping the true dynamics in the configuration space on to
the stationary points of \( V \). In our glass the particles in-
teract via a Lennard-Jones potential modified in such
a way as to avoid crystallization [20]. The system is
brought in an off-equilibrium initial condition by a sud-
den isothermal density jump (crunch) across the liquid-
glass transition line. We find a rather sharp cross-over
between two dynamical regimes: i) a short times regime
where the system point travels between basins of saddles
of decreasing energy and order and ii) a long time regime
where the system point moves between basins of saddles
of zero order (minima) and decreasing energy, crossing
basins of saddles of low order. The existence of two well
separated dynamical regimes shows up also in the Mean
Square Displacement (MSD). Here a logarithmic behav-
ior is found at long times suggesting the picture of a sys-
tem point performing a random walk between basins of
minima with a jump probability per unit time inversely proportional to time elapsed since crunch. This picture is quantitatively supported by the very good agreement found between the MSD measured along the MD trajectories and the MSD reconstructed via a random walk model.

The system under study is a monatomic Modified-Lennard-Jones (MLJ) [24] that is the usual 6-12 Lennard-Jones pair interaction (truncated and shifted at $R_e = 2.6$, standard Lennard-Jones units are used hereafter) plus a small many body term which inhibits crystallization with negligible corrections to the equation of state of a monatomic Lennard-Jones system (see [11,26] for details). The system is composed of $N = 256$ particles enclosed in a cubic box with periodic boundary conditions. The initial liquid equilibrium configurations ($\rho_0 = 0.95$, $T_0 = 0.5$) are prepared by standard isothermal MD. At time $t = 0$ the density is suddenly increased to the value $\rho_1 = 1.24$, where the glass transition temperature ($T_g$($\rho_1$) $\sim 1.4$ [11]) is well above the simulation temperature $T_0$. The subsequent evolution of the system is generated up to time $t = 3 \cdot 10^4$ by means of standard microcanonical MD with time step $\tau = 0.01$. For each MD trajectory we quenched a set of logarithmically equally spaced configurations to the corresponding IS and saddle following the steepest descent path respectively on the potential energy surface $V$ in the former case and on the auxiliary potential $W = \frac{1}{2}|\nabla V|^2$ [20–22] in the latter.

In Fig.1 we report in a logarithmic scale the time evolution of: a) the instantaneous configuration potential energy per particle $e_i$, subtracted by the constant term $\frac{3}{2}T_0$ (open circles), inherent structure saddle energy $e_s$ (full triangle) and the inherent structure minimum energy $e_m$ (open diamonds). Error bars are shown only when larger than symbol size. The arrow indicates time $t_c$, where the crossover from dynamics between basins of saddles to dynamics between basins of minima takes place.

In Fig.2, where we report $e_s$, together with $e_m + n_s \Delta E/N$ with $\Delta E$ a fit parameter. This result confirms the picture of an energy landscape where the saddles of the IS energy $e_m$ (open diamonds). The remarkable coincidence between $e_s$ and $e_i - \frac{3}{2}T_0$ suggests to think of the instantaneous energy $e_i$ as the sum of two contributions: the saddle’s energy (slowly approaching equilibrium) and the energy of nearly $N$ fast harmonic equilibrated degrees of freedom. It is evident the presence of a rather sharp transition in dynamical behavior of $e_s$ and $e_i$ at time $t_c \sim 20$. In particular the time evolution of $e_s$ for $t > t_c$ seems to be driven by the inherent dynamics between minima as suggested by the underlying time evolution of $e_m$.

In Fig.3, the mean saddle’s order $n_s$ (number of negative eigenvalues of the potential energy Hessian computed on the saddle configurations) is reported as a function of time. The dynamic transition observed at $t_c$ in the energy time evolution in Fig.2 corresponds here in the mean order $n_s$ falling below the value $n_s = 1$ or, in other words, for times longer than $t_c$ the system point starts to explore extensively the basins of saddles of order zero (minima). The inset in Fig.2 shows the order $n_s$ computed along a single MD trajectory. One can see that for times $t > t_c$ the systems visits basins of minima passing through basins of low order saddles.
order \( n_s + 1 \) lay above the saddles of order \( n_s \) of a constant quantity \( \Delta E \). From the data we obtain the value \( \Delta E = 10 \). The value of \( \Delta E \) could also be obtained from an equilibrium analysis, as in [21] where a value of \( \Delta E = 3.6 \) is found for the case \( \rho = 1 \). We have not carried out such an equilibrium analysis for the density \( \rho = 1.24 \) used here.

Another interesting quantity in describing the dynamical processes is the mean square displacement of the configuration at time \( t \) from that at time \( t_w \) after crunch:

\[
r^2(t, t_w) = \frac{1}{N} \sum_i \langle |r_i(t) - r_i(t_w)|^2 \rangle ,
\]

where \( \langle ... \rangle \) is an average over initial configurations. In Fig. 4 we report \( r^2(t, t_w) \) as a function of time \( t \) for four selected \( t_w \) values: \( t_w = 1, 5, 20, 200 \). Also in this case \( t_c \sim 20 \) marks a transition in the dynamical behavior. In particular the long time regime shows a well defined logarithmic dependence on time. This suggests the picture of the diffusion process proceeding through elementary uncorrelated events occurring with a probability per unit time \( p(t) \propto 1/t[27] \). As previously observed, in the long time regime the system point travels between basins of minima. It is therefore natural to identify the elementary diffusion events as jumps between adjacent basins of minima. In order to give further support to this conjecture we calculated the cumulative number of jumps \( N_{jumps}(t) \) defined as the number of jump events in which the constantly monitored energy of the IS makes a sharp transition.

The quantity \( N_{jumps} \) is plotted in Fig. 5(a). For times \( t > t_c \) \( N_{jumps} \) displays a nice logarithmic behavior that
is what one would expect if the probability per unit time of a jump event is $p(t) = c/t$. In other words the time needed to escape from an IS reached by the system after a time $t_w$ from *crunch* is proportional to time $t_w$ itself (a similar behavior is found in the off-equilibrium dynamics of a ferromagnetic Ising system where the persistence time of a bubble in which spins have a similar value is proportional to time $t_w$). In Fig. 5(a) the solid line represents the fitting function $c \log(t)$ with $c = 1.0$. In Fig. 5(b) we report the mean square distance $d^2$ between adjacent minima probed by the system during the aging dynamics:

$$d^2(t) = \frac{1}{N} \sum_i (|r_i^S(t^+) - r_i^S(t^-)|)^2,$$

where $t$ is the time of the jump between two different basins of minima and $r_i^S(t^+)$, $r_i^S(t^-)$ are the coordinates of IS respectively before and after time $t$. The quantity reported in figure approaches the long time constant value $d_0^2 \sim 0.019$. For uncorrelated jumps, the mean square displacement would be simply given by

$$r^2(t, t_w) = d_0^2 c \log(t/t_w).$$

This is in a remarkably good agreement with the MD data as shown in Fig. 4 where we draw straight lines with slope $d_0^2 c = 0.019$ (as obtained from the values of $d_0^2$ and $c$ derived from Fig. 5) and intercept chosen as to best fit the data for $t > 20$.

In conclusion we have numerically studied the off-equilibrium dynamics of a monatomic Modified-Lennard-Jones system by sudden isothermal density jumps from the liquid to the glassy phase. Analyzing the time evolution of the energy and the mean square displacement we found two well defined dynamical regimes, which can be related to the different ways the system explores the potential energy landscape: i) at short times the system point moves downward passing through basins of saddles with decreasing energy and order, and ii) at longer time the relevant dynamical processes are jumps between basins of minima with slower decreasing energy. In the whole time regime the instantaneous potential energy $e_i$ can be thought as due to a sum of two contributions: the energy of the underlying saddle’s configurations $e_s$ plus a nearly harmonic term of the fast degrees of freedom $3/2T$. Moreover the linear energy gap between saddles and underlying minima $e_s - e_m$ as a function of saddles order $n_s$ supports the picture of a simple energy landscape with only a single energy barrier parameter $\Delta E$ which represents the energy gap between a saddle of order $n_s$ and a saddle of order $n_s + 1$. The relevant processes in the long time aging regime are well represented by a simple random walk model with elementary events corresponding to jumps between minima with a probability per unit time proportional to the inverse of time elapsed since the system has been brought out of equilibrium.

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