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Time correlation functions between inherent structures: a connection between landscape topology and the dynamics of glassy systems

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Abstract

In this work we introduce time correlation functions between inherent structures (IS) of a supercooled liquid. We show that these functions are useful to relate the slowing down of the dynamics to the structure of the energy landscape near the glass transition temperature. They show a short-time regime during which the system remains in the basin of a particular IS and a long-time regime where it explores the neighbourhood of an IS. We compare the behaviour of these functions in a binary Lennard-Jones glass and in a model of traps and show that they behave qualitatively different. This comparison reflects the presence/absence of structure in the landscape of the Lennard-Jones/traps models. Possible scenarios for the structure of the landscape which are compatible with these results are discussed.

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1. Introduction

Potential energy landscape (PEL) studies have contributed to the understanding of the dramatic slowing down of the dynamics of supercooled liquids near the glass transition

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temperature [1]. The introduction of inherent structures (IS) (local minima of the PEL) [2], which divide the phase space into basins of attraction, allows the separation of vibrational motion from more fundamental structural transitions. It is thought that activation over barriers between inherent structures is the main mechanism of diffusion below the mode coupling transition temperature T_{MCT}. Above T_{MCT} also saddles of the potential energy landscape play an important role in the diffusion properties of the system. The decrease of the number of saddles available to the system when the temperature is lowered towards T_{MCT} has been proposed as one of the main reasons of the dramatic slowing down of the dynamics [3–6]. In the framework of the landscape approach to the glass transition it has also been proposed that, at least for some glass formers, the landscape may be organized in *metabasins* that should contain many local minima where the system spends increasingly long times as temperature is lowered [7,8]. However, the definition of metabasins is less rigorous than IS and consequently even when the concept is not new only very recently quantitative results have begun to appear [9–11].

In a previous work we studied the statistics of distances in real space between neighbouring IS [12] in a binary mixture Lennard-Jones glass and the number of saddles as function of temperature following molecular dynamics trajectories. We saw that the distance between minima decreases exponentially near T_{MCT} but does not go strictly to zero implying the existence of saddles even below T_{MCT}. The number of saddles suffers a strong decrease around $T = 1$ and decays abruptly at lower temperatures but stays finite near T_{MCT}. These results together with the vanishing of the diffusivity at T_{MCT} seem to imply the existence of saddles associated with nondiffusional events. The picture that emerges is one where the system spends long times in a kind of metabasins of the energy landscape each one of them containing many IS similar to the one proposed by Doliwa and Heuer [9–11].

Here we show that some dynamical quantities in two systems which have a similar kind of glass transition but possess very different PEL structure behave in qualitatively different ways. This allows to distinguish the mechanisms of confinement in these two kinds of systems. We define time correlation functions between inherent structures visited during the equilibrium time evolution of a binary mixture Lennard-Jones glass. These correlations present two sharply distinguished time regimes which we show to correspond to exploration inside a basin of a particular IS and to exploration of the neighbourhood of a basin. The behaviour of correlations as temperature is lowered towards T_{MCT} implies the emergence of strong spatial confinement in configuration space. In order to test if these confinement is a consequence of the topology of the PEL or if it can be explained as a purely dynamic effect we compare the behaviour of the Lennard-Jones glass with a model of traps where the landscape is flat and only confinement in time is present. In fact both systems behave qualitatively different implying that confinement in the Lennard-Jones glass is a consequence of the nontrivial structure of the energy landscape. We discuss some possible scenarios for this structure which are compatible with the dynamical characteristics observed. While the existence of metabasins is a plausible scenario it is not the only possibility.

In Section 2 we define the quantities of interest in our study. In Section 3 we show and discuss our results for the binary Lennard-Jones model. In Section 4 we show the corresponding results for a model of traps and finally in Section 5 we present our conclusions.

2. Time correlation functions between inherent structures

As mentioned above, every instantaneous state of the system may be associated with an IS of the energy landscape. Given that at an initial time the system is in a configuration corresponding to some IS, we define $C_{IS}(t)$ as the probability that the system *is at the same* IS after a time t. This means that the IS associated with the initial and final states is the same irrespective of where the system was in between. We have observed that the IS can be identified by their energy since the case of degeneracy (interchange of two particles of the same kind, for example) is quite unusual and has no significant statistical weight. So, the computation of $C_{IS}(t)$ is very simple:

$$C_{IS}(t) = \frac{1}{N_t}\sum_{i=1}^{N_t} \delta_{t_i,t_i+t}, \quad \text{with } \delta_{t_i,t_j} = \begin{cases} 1 \text{ if } E_{IS}(t_i) = E_{IS}(t_j)\,, \\ 0 \text{ if not}\,, \end{cases} \tag{1}$$

where $E_{IS}(t_i)$ is the energy of the corresponding IS at time t_i and with the sum we perform averaging over N_t available times. It will be useful to study also another time correlation function, $C_{IS}^{(rem)}(t)$, given by the probability that the system *has remained* at the same inherent structure during time t. In this case $\delta_{t_i,t_j} = 1$ only if $E_{IS}(t_i) = E_{IS}(t_k)$ for all $t_k \in (t_i, t_j)$. In fact, the calculation of $C_{IS}^{(rem)}(t)$ involves an approximation due to discretization of time. If the system goes to a neighbouring IS and comes back within the interval (t_i, t_{i+1}) our calculation will not notice it, so the calculated $C_{IS}^{(rem)}(t)$ should be taken as an upper bound of the real one.

3. The Lennard-Jones binary mixture

3.1. Size dependence of $C_{IS}(t)$

Unfortunately, these time correlation functions are size dependent. Consider a system S_0 of N particles composed of two noninteracting subsystems S_1 and S_2 of N_1 and N_2 particles, respectively. In this case $C_{IS}(t,N) = C_{IS}(t,N_1)\cdot C_{IS}(t,N_2)$, since the probability of coming back to a given state IS_0 involves the two subsystems coming back to their respective states IS_1 and IS_2. In the present work, we study a system of $N = 130$ particles at several temperatures. In order to study the size dependence of $C_{IS}(t)$ we performed also simulation at $T = 0.55$ for a system with $N = 250$ particles. In Fig. 1a we show $C_{IS}(t,N)$ for the two sizes considered. If the hypothesis of independence between subsystems holds for subsystems of size $N > N_0$ then it is easy to show that for $N > N_1 > N_0$:

$$C_{IS}(t,N) = [C_{IS}(t,N_1)]^{N/N_1}\ . \tag{2}$$

In Fig. 1b we show that this equality is verified quite well for the systems studied. Studying small systems is convenient because the decay of $C_{IS}(t,N)$ is slower for

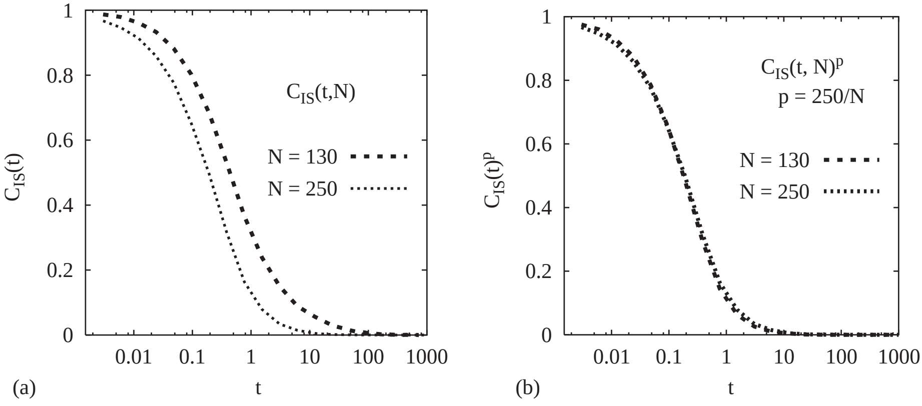

Fig. 1. (a,b) Size dependence of $C_{IS}(t)$ at $T = 0.55$.

smaller N, and so one may access the long-time behaviour of this correlation function. This fact has also been emphasized in other landscape studies of supercooled liquids [13,14]. Having shown that extrapolation to large systems is quite simple, in what follows we will study the properties of correlation functions for the $N = 130$ system. It is important to note that, because of the size dependence, the relaxation times of these correlation functions cannot be straightforwardly related to the typical time scales of the bulk relaxations in supercooled liquids.

3.2. Temperature dependence of $C_{IS}(t)$

Here we show results of molecular dynamics simulations of a binary mixture (80:20), Lennard-Jones system [12] for $N = 130$ at temperatures $2.0, 1.0, 0.8, 0.7, 0.6, 0.55$ and 0.5. We have verified that the mode coupling glass transition for this system is the same as found originally for a sample of 1000 particles ($T_{MCT} = 0.435$ [15]). We repeat the study for two samples with different thermal histories. After having equilibrated the systems we performed long runs in order to collect data. [3] We obtained the IS relaxing the instantaneous coordinates of the system and we computed the time correlation functions from the sequence of $E_{IS}(t_i)$ (Eq. (1)).

In Fig. 2a we plot $C_{IS}(t)$ for the set of temperatures considered. It is clear that the decay of $C_{IS}(t)$ slows down very quickly as T_{MCT} is approached. Fig. 2b shows that at low temperatures $C_{IS}(t)$ may be approached by two stretched exponentials with quite different exponents. In the short-time regime (STR) the value of β is around 0.8 and it is almost constant for T varying between 0.6 and 0.5. In the long-time regime (LTR) the value of beta is very small ($\beta = 0.2$ for $T = 0.5$) and is decreasing sharply on approaching T_{MCT}. The deviation from stretched exponential behaviour at the longer times of Fig. 2b for $T = 0.5$ is due to limited statistics. We have verified in some longer

[3] Typically $t_{\rm run} \sim 1000\ \tau$. The MD time step in our simulations is 0.003 Lennard-Jones time units which amounts to runs of 2×10^7 time steps for the smaller temperature studied.

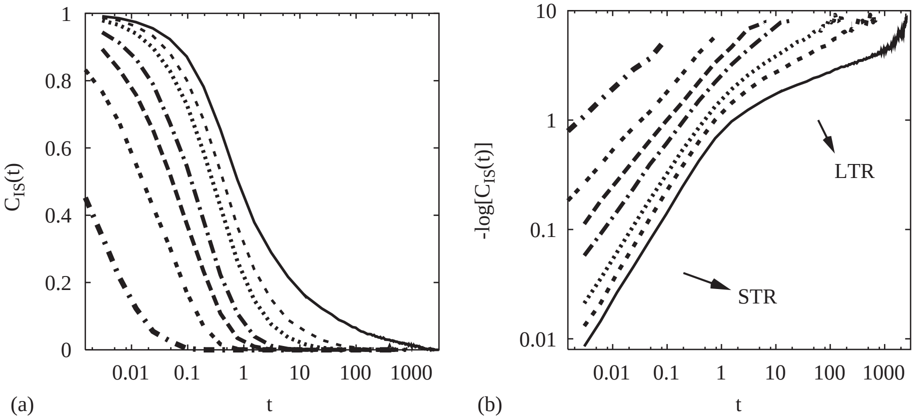

Fig. 2. (a) Temperature dependence of $C_{IS}(t)$ for $N = 130$. From left to right $T = 2.0, 1.0, 0.8, 0.7, 0.6, 0.55$ and 0.5. (b) –log $[C_{IS}(t)]$ for the same set of temperatures; plotted in this way a stretched exponential $exp[-(t/\tau)^{\beta}]$ is a straight line with slope β. The short-time regime (STR) and long-time regimes (LTR) are indicated.

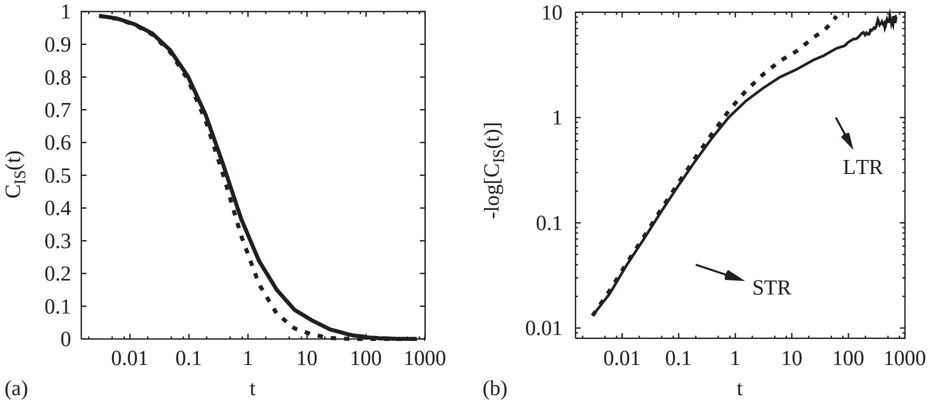

Fig. 3. $C_{IS}(t)$ (continuous line) vs $C_{IS}^{(rem)}(t)$ (dotted line) for $N = 130$ and $T = 0.55$. The fit to stretched exponentials of $C_{IS}(t)$ gives $\beta = 0.83$ for the STR and $\beta = 0.28$ for the LTR.

runs that the stretched exponential behaviour extends at least for the whole range of times of Fig. 2b. In order to explain the meaning of the two regimes observed we show in Fig. 3 $C_{IS}(t)$ together with $C_{IS}^{(rem)}(t)$ for $T = 0.55$. We see that the STR is the region of time where both correlation functions are almost equal. So the STR of $C_{IS}(t)$ may be interpreted as the time the system remains at the same IS while the LTR accounts for the time the system is *around* one IS, exploring neighbouring inherent structures and with a finite probability of coming back to the original IS.

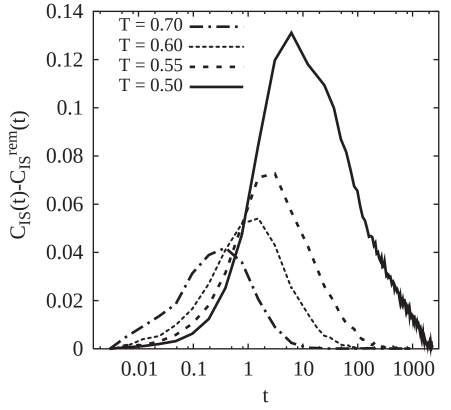

Fig. 4. The difference $C_{IS} - C_{IS}^{(rem)}$ for the LJ binary mixture for different temperatures.

In order to filter from the $C_{IS}(t)$ the effect of remaining in a single basin all the time, we show in Fig. 4 the difference $C_{IS} - C_{IS}^{(rem)}$ which represents the probability of the system to be at the same IS after a time t *knowing that it has gone away at least once during this time interval*. This probability shows two important characteristics: the first one is that there is a characteristic time at which the probability of coming back to the original IS is maximal. This time scale grows when temperature is lowered: if the system goes out of a basin it takes more time to come back as temperature is lowered. The second feature is more important: the probability to come back **grows** as the glass transition temperature is approached. This is a signature of *spatial confinement*. To show more clearly this point and closely inspect the relation between the studied correlation functions and landscape topology, we study in the next section a random walker on a lattice with traps.

4. The traps model

The model of traps in a d-dimensional hypercubic lattice is realized as a random walk of a particle hopping between traps attached at each lattice site with a given trap energy distribution $\rho(E)$ [16,17]. Depending on the form of the distribution, different interesting dynamical behaviours are observed. If the energies are exponentially distributed the model has a dynamical phase transition at a finite temperature T_0 below which it presents typical glass phenomenology as aging effects. Other possibilities like, e.g. Gaussian distribution of energies lead to a dynamical transition only at $T_0 = 0$ and show stretched exponential relaxations. The trap model has been proposed as a phenomenological or toy model for describing the physics of glasses and spin glasses. From a physical point of view, the dynamics proceeds through activation over barriers corresponding to the depth of the traps. Besides the difference in the depths, the landscape can be considered flat, structureless. This is the essential point we want to compare with the Lennard-Jones glass which is known to possess a complex PEL topology. In an interesting study, Denny et al. [18] compared some properties of the Lennard-Jones glass with the model of traps. They found that there are collections of IS of nearly the same energy which they associated with metabasins and present a nearly Gaussian distribution of energies, similar to the distribution of single inherent structures energies. Some relaxation functions do indeed behave in agreement with results on a model of traps, a result which implies that activated processes are important in the dynamics of the LJ binary mixture also above the mode coupling transition temperature.

Here we also make a comparison between the Lennard-Jones glass and the model of traps. But our aim here is to calculate the time correlation functions defined in Section 2 for a simple model where the probability of the system to return to a given basin is exclusively of random character. So, we associate a trap to a basin (not to a collection of basins as Denny et al. did) and study the probability that the system returns to a given basin. We considered two and three dimensional lattices, and assigned to every site a trap of energy E that is determined randomly from an exponential distribution of the form e^{E/T_0}. The energy associated with a given site is kept fixed during the simulation, i.e., when the walker returns to a given site it finds the same trap (quenched-disorder case [17]). In order to make the comparison with the results for the binary LJ model as close as possible we choose the typical energy of the exponential distribution as $T_0 = T_{MCT}$, so both models are expected to have a dynamical transition at the same temperature $T_{MCT} = 0.435$. Because of computational limitations periodic boundary conditions in a lattice of size L^d are imposed on the values of the energies although the walker moves in an infinite lattice limited in practice only by the largest time considered in the correlation functions. We have used $L = 100$ for $d = 3$ and $L = 1000$ for $d = 2$. To obtain enough statistics at the lowest temperatures studied for $d = 2$, we needed to perform rather long walks of 10^8 steps that we averaged over 1000 realizations of disorder. We then computed the time correlation functions defined in II along these runs. In fact, because of the periodic boundary conditions imposed in the energies, in this case we use the position of a site instead of its energy in order to compute the delta function in expression 1. Note that the function $C_{IS}^{(rem)}(t)$ defined above corresponds exactly to the equilibrium correlation $C_{eq}(t)$ defined in Eq. (4) of [16]. We verified that $C_{IS}^{(rem)}(t)$ presents the expected long-time behaviour at low temperatures: $C_{IS}^{(rem)} \propto t^{-(x-1)}$ with $x = T/T_{MCT}$, obtained theoretically by Monthus et al. [16] (Eq. (14)).

In Fig. 5 we show the difference $C_{IS} - C_{IS}^{(rem)}$ for the traps model in two and three dimensions. The behaviour of these correlation functions as a function of temperature is qualitatively the same for $d = 2$ and $d = 3$. They present a characteristic time that increases as temperature is lowered as we observed for the curves of Fig. 4 corresponding to the binary LJ model. In the case of traps, the maximum of the probability of coming back to a given trap moves towards increasing times as temperature is lowered because the walker is caught increasing times in the traps of the surroundings. The confinement can only be attributed to the time the walker spends in the individual traps. Since every trap is spatially equivalent to each other, there is no spatial confinement as the walker moves in a flat landscape. More importantly, the fact that the height of

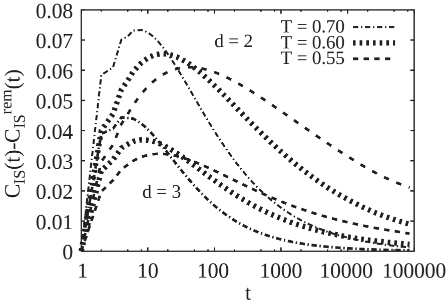

Fig. 5. The difference $C_{IS} - C_{IS}^{(rem)}$ for the traps model when $d = 2$ and $d = 3$ and at different temperatures $T = 0.7, 0.6, 0.55$ and 0.5.

the maximum of these curves increases for the binary LJ model while it goes down for the traps model is a clear indication that an additional type of confinement exists in the energy landscape of the LJ model. An arrangement of the energy landscape in metabasins that contain several basins (as has been suggested by Doliwa et al. [9–11]) could explain the qualitative features of the curves we observe in Fig. 4 since the system would be forced to explore several IS within a metabasin before leaving it for a time that increases on approaching T_{MCT}. But inspection of Fig. 5 suggests another possible picture for the topology of the energy landscape. From Fig. 5 it is clear that reduction of the dimension of the space where the walker moves increases sharply the absolute value of the studied probabilities. So, another possible mechanism that may account for the increasing confinement of the binary LJ system is a reduction of dimensionality of the space where the system moves. In this picture, as temperature lowers, the system is forced to move in a landscape of reduced dimensionality where the different accessible regions of configuration space need not be separated by any energy barrier.

5. Summary and conclusions

In the present paper, we defined time correlation functions between inherent structures of an energy landscape and studied them for a LJ binary mixture at different temperatures. We observed that the probability of being at the same IS after a time t, $C_{IS}(t)$, presents two time regimes: a short-time regime which is related to exploration of basins, and a long-time regime which corresponds to exploration of the neighbourhood of a given basin. The weak dependence of β on temperature for the STR at low temperatures indicates that the basin topology does not change on approaching T_{MCT}, while the contrary holds for the inter-basins topology given the strong variation of β with T in the LTR. The study of the difference $C_{IS}(t) - C_{IS}^{(rem)}(t)$ for this system and comparison of the same function for a traps-model give clear evidence that in the LJ model there is a spatial mechanism of confinement that is not present in the traps-model. From our results two possible mechanisms emerge to account for the confinement at low temperatures. One possibility is that inherent structures are arranged in superstructures, like in the metabasins scenario [9–11]. This scenario implies as a basic ingredient the existence of energy barriers, necessary to define the metabasins and consequently the landscape appears to be broken into pieces (metabasins). Nevertheless, the confinement observed in our results can also be explained by a gradual reduction of the dimensionality accessible to the system as the temperature is lowered. In this second scenario, as energy barriers are not implied a priori, the landscape is not necessarily broken in metabasins but its structure can be that of a network composed of connected funnels. In this scenario the confinement is consequence of a reduction of the dimension of the funnels as temperature is lowered.

We have shown that the time correlation functions introduced in this paper are useful tools to get information on the structure of the PEL in supercooled liquids and can also be straightforwardly calculated in trap like models. It would be interesting to analyse their behaviour in other models in which one could a priori define some structure or hierarchical organization of states which seems to be present in the LJ binary mixture.

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