Democratic particle motion for meta-basin transitions in simple glass-formers

G. A. Appignanesi†, J. A. Rodríguez Fris‡, R. A. Montani† and W. Kob‡

† Laboratorio de Fisicoquímica, Departamento de Química,
Universidad Nacional del Sur, Av. Alem 1253,
8000 Bahía Blanca, Argentina.
‡ Laboratoire des Colloïdes, Verres et Nanomatériaux,
Université Montpellier 2, 34095 Montpellier, France.

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We use molecular dynamics computer simulations to investigate the local motion of the particles in a supercooled simple liquid. Using the concept of the distance matrix we find that the $\alpha$–relaxation corresponds to a small number of crossings from one meta-basin to a neighboring one. Each crossing is very rapid and involves the collective motion of $O(40)$ particles that form a relatively compact cluster, whereas string-like motions seem not to be relevant for these transitions. These compact clusters are thus candidates for the cooperatively rearranging regions proposed long times ago by Adam and Gibbs.

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In recent years significant progress has been made in our understanding of the relaxation dynamics of glass-forming liquids at intermediate and low temperatures. Sophisticated experiments and computer simulations have identified many of the salient features of this dynamics, and theoretical approaches have helped to rationalize them, at least to some extent [1, 2, 3, 4]. Despite this progress, many of the most elementary questions have not been answered so far and among them is the nature of the motion of the particles in the $\alpha$–relaxation regime at low temperatures. Experiments and simulations have demonstrated that this dynamics is quite heterogeneous and therefore can be used to explain the observed stretching of the time correlation functions [5, 6, 7, 8, 9, 10, 11]. This heterogeneous dynamics has been shown to be related to cooperative motion in which a small number of particles (a few percent) undergo a collective relaxation dynamics in that they move, often in a string-like fashion, by a distance that is comparable to the one between neighboring particles [8, 10, 12]. Since a qualitatively similar heterogeneous dynamics has also been found in simple lattice models that show a glassy dynamics and for which it is well known that the $\alpha$–relaxation is intimately connected to the dynamical heterogeneities (DH), it has been proposed that these DH are crucial for the relaxation dynamics of all glass-forming systems [13]. However, since in these lattice models all elastic or quasi-elastic effects are completely neglected, it is not at all clear whether or not the DH are indeed the only relevant mechanism for the relaxation.

Another approach to describe the relaxation dynamics on the time scale of the $\alpha$–relaxation is by means of the so-called potential energy landscape (PEL) [14, 15, 16] (or more precisely the free energy landscape) and hence to describe the dynamics of the system by considering its trajectory in configuration space. This PEL is rugged due to the presence of barriers in the free energy and hence at low temperatures the resulting dynamics will be slow. Using the concept of the inherent structures, evidence has been given that (roughly speaking) the motion of the system in the PEL can be decomposed into two types of movements [14, 15]: In the first type the system explores some minima which are locally connected to each other and are not separated by a significant barrier. Therefore such a collection of minima is called “meta-basin” (MB) and its exploration corresponds to the $\beta$–relaxation. As a second type of motion, the system overcomes the barriers that surround a MB and enters a new MB, a motion that has been believed to correspond to the $\alpha$–relaxation [1] or to the elementary events of the $\alpha$–relaxation [13].

Although this picture for the motion of the system within the PEL is certainly appealing from a qualitative point of view, it does not give any insight on the nature of the dynamics of the particles on the microscopic level. Furthermore it remains unclear whether the DH mentioned above have anything to do with the barrier-crossing of the system moving in the PEL. The goal of the present work is therefore to clarify this issue and thus to make an advancement in our understanding of the relaxation dynamics of supercooled liquids. To this aim we have done molecular dynamics computer simulations of a simple glass-former in order to identify the presence of the MB and to investigate the nature of the motion of the particles during the transition from one MB to another. The so obtained results can then be compared with the heterogeneous motion of the particles in order to see to what extend the two motions are related to each other.

The system considered is a binary mixture of Lennard-Jones (LJ) particles. In previous investigations it has been shown that this system shows many features of glass-forming liquids and can thus serve as a simple model for such liquids [19]. The interaction between two atoms of type A (80%) and B (20%) is given by $V_{A\beta}(r) = 4\epsilon_{A\beta}(\sigma_{A\beta}/r)^{12} - 2(\sigma_{A\beta}/r)^6$, where $\alpha, \beta \in \{A, B\}$. The
FIG. 1: Distance matrix $\Delta^2(t', t'')$ of the system for $T = 0.50$. The gray level correspond to values of $\Delta^2(t', t'')$ that are given to the right of the figure.

LJ parameters used are $\epsilon_{AA} = 1.0$, $\sigma_{AA} = 1.0$, $\epsilon_{AB} = 1.5$, $\sigma_{AB} = 0.8$, $\epsilon_{BB} = 0.5$, and $\sigma_{BB} = 0.88$. These interactions have been truncated and shifted at $r_{cutoff} = 2.5\sigma_{AA}$.

In the following we will use $\sigma_{AA}$ and $\epsilon_{AA}$ as units of length and energy, respectively, and measure time in units of $(m\sigma_{AA}^2/4\epsilon_{AA})^{1/2}$. The equations of motion were solved for the NVE ensemble at a particle density of 1.2, using the velocity form of the Verlet algorithm with a time step of 0.02. All the presented results correspond to the situation in equilibrium.

In order to identify the MBs we define the following “distance matrix” (DM) [20]:

$$\Delta^2(t', t'') = \frac{1}{N} \sum_{i=1}^{N} |r_i(t') - r_i(t'')|^2 , \quad (1)$$

where $r_i(t)$ is the position of particle $i$ at time $t$. Thus $\Delta^2(t', t'')$ gives the system averaged squared displacement of a particle in the time interval that starts at $t'$ and ends at $t''$. Note that the time average of $\Delta^2(t', t' + \theta)$ over $t'$ gives the $r$-average of $G_s(r, \theta)$, the self-part of the van Hove correlation function for time displacement $\theta$. The same is true if one averages over a very large system. Since we are interested in individual MB-MB transitions, one has to avoid that the presence of several independent local rearrangements, that will occur in a large system almost simultaneously, obscures the analysis of the individual event. Therefore we have considered a rather small system of 150 particles, the smallest possible system that does not affect the interactions, i.e. the box size was two times $r_{cutoff}$ for the $A - A$ interaction [21].

Figure 1 shows a typical graph of the DM at $T = 0.50$ as a function of the two time arguments $t'$ and $t''$, with darker areas corresponding to configurations that have a smaller distance. At this temperature the dynamics is already slow with an $\alpha$–relaxation time $\tau$ of the order of $4 \cdot 10^3$ [14]. ($\tau$ can, e.g. be defined by requiring that the self intermediate scattering function $F_s(q, t)$ has decayed to 10% of its initial value.) From this figure we see immediately that the dynamics of the system is quite heterogeneous in time in that it stays for a significant time relatively close to one region in configuration space, dark square-like regions, before it finds a pathway to a new region. Thus this is clear evidence that the system explores the present MB before it moves on to a neighboring one. At this temperature the typical sojourn time within one MB is around 300-800 time units, which is around 10% of $\tau$. Thus this sojourn time corresponds to the time scale of $t^*$, the time that previous investigations have shown to be relevant for the dynamical heterogeneities in the system and which is defined as the time at which one observes the maximum in the non-gaussian parameter $\alpha_2(t)$ [21, 22], and which at this temperature is 400 time units [11]. Hence we can conclude that the MB-MB transitions are relevant for the DH whereas it takes about 5-10 such transitions in order to make an $\alpha$–relaxation. We also point out that from Fig. 1 it becomes evident that the time for a MB-MB transition is quite short, on the order of 100 time units, which thus corresponds to about 20% of $t^*$. Thus the transition is significantly faster than the $\alpha$–relaxation times $\tau$.

In Fig. 2 we show for the same run and time interval $\delta^2(t, \theta)$, the (particle) averaged squared displacement (ASD) of the particles within a time interval $\theta$ (solid curve). This function is defined as

$$\delta^2(t, \theta) = \Delta^2(t - \theta/2, t + \theta/2)$$

$$= \frac{1}{N} \sum_{i=1}^{N} |r_i(t - \theta/2) - r_i(t + \theta/2)|^2 \quad (3)$$

Thus $\delta^2(t, \theta)$ is $\Delta^2(t', t'')$ measured along the diagonal $t'' = t' + \theta$ and hence the average of this quantity over
different start times $t$ gives the usual mean-squared displacement for time lag $\theta$. A comparison of this ASD with Fig. 1 shows that $\delta^2(t, \theta)$ is showing pronounced peaks exactly then when the system leaves a MB. Thus we see that changing the MB is indeed associated with a rapid motion as measured in the ASD.

In order to understand the nature of the motion of the particles when the system leaves a MB, we have calculated $\hat{G}_s(r, t, t + \theta)$, the distribution of the displacement $r$ of a particle for a given time difference $\theta = 40$. (Note that the average of $\hat{G}_s(r, t, t + \theta)$ over $t$ gives $G_s(r, \theta)$.) This distribution is shown in Fig. 3a for starting values $t$ that correspond to times at which the ASD shows a plateau, i.e. when the system explores a MB. Also included in the graph is the self part of the van Hove function, $G_s(r, \theta)$, and we see that the distributions $\hat{G}_s(r, t, t + \theta)$ are narrower and more peaked than $G_s(r, \theta)$ thus showing that in a MB the system moves more slowly than on average. In Fig. 3b we show the same distributions but now for times in which the system is about to leave a MB (compare the values of $t$ with Fig. 1). For these values of $t$ the distributions are displaced to the right with respect to $G_s(r, \theta)$, showing that in this time regime the motion of the system is faster than on average. Most noteworthy is the observation that this shift is relatively uniform, i.e. a substantial part of the particles moves quicker than on average. Thus we can conclude that the rapid increase of the ASD is not due to the presence of a few fast moving particles, but instead to a “democratic” movement of many particles, in contrast to the results for cooperative motion on the time scale of $t^*$ which has been documented in earlier work [11, 10, 12]. Thus this movement is very different in nature from the “string-like” motion found in the context of the dynamical heterogeneities [12, 23].

To demonstrate that the number of particles that participate at this democratic motion is indeed substantial and strongly correlated with a strong increase in the ASD, we have defined as “mobile” all those particles that in the time interval $\theta = 40$ have moved more than $r_{th} = 0.3$, and denote the fraction of such particles by $m(t, \theta)$ [24]. In Fig. 2 we have included the fraction of mobile particles as a function of time (vertical bars) and a comparison of this data with the ASD in the same graph shows that the fraction of mobile particles is indeed large whenever the ASD increases rapidly. This fraction is on the order of 30% of the particles and thus significantly larger than one would expect from $G_s(r, \theta)$ if one integrates this distribution from $r_{th}$ to infinity and which gives 0.09.

In order to give an idea on the nature of the motion of the mobile particles during a MB-MB transition, we show in Fig. 4 a typical configuration of mobile particles before such a transition event and attach to each particle an arrow which points to the location of the particle after the event, i.e. a time $\theta = 40$ later. From this graph we recognize that the MB-MB transitions correspond to a movement in which the particles form a relatively compact cluster. Thus this is in contrast to the type of motion found in the context of the DH in which the particles form string-like objects [12, 23]. These compact regions have, at the temperature considered, around 30-60 particles and can be considered as potential candidates for the cooperatively rearranging regions (CRR) proposed long time ago by Adam and Gibbs [26] and which are also at the heart of the approach of Goldstein for the relaxation dynamics of glass-forming systems [27].

Finally we mention that we have found that upon a decrease of temperature the sojourn time of the system within one MB increases rapidly. This is in agreement with previous results in which the concept of inherent structures was used [13, 15], although here we have used a significantly simpler method to identify the MB and which can notably also be used in real experiments such as colloidal systems [8, 10]. (We emphasize, however, that we have obtained qualitatively the same results by considering the inherent structures, although this approach is computationally much more involved.) On the other hand an increase of the temperature makes that the structure of the MB is basically washed out and the ASD does no longer show the pronounced peaks.

The present result indicate that the $\alpha$—relaxation is not directly related to the presence of strings that are
formed by a small number of particles but instead is due to a cooperative rearrangement of a substantial fraction of the particles. This cooperative rearrangement is responsible for the transition between adjacent MBs and involves, at the temperature considered, on the order of 40 particles. During such a MB-MB transition the majority of the particles outside this CRR does not contribute significantly to the relaxation. Therefore one needs on the order of 5-10 such transition events in order to complete an α-relaxation on the scale of the local neighborhood. Since these transitions take only a few percent of the α-relaxation time, one thus can envision, at least at low temperatures, the α-relaxation as a sequence of rapid, localized, cooperative relaxation events in which a substantial number of particles participate. This result is thus in surprisingly good agreement with the picture put forward long time ago by Adam and Gibbs and Goldstein.

Finally we mention that in view of the proposed connection between the geometrical properties (distribution of barrier heights, size of meta-basins,...) and the fragility of glass-forming systems \(^1\), \(^2\), \(^3\), \(^4\) it will be of great interest to do the analysis presented here for a strong glass former. This will allow to obtain a better understanding of the difference between strong and fragile glass-formers \(^5\).

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