Reproducibility of Dynamical Heterogeneities and Metabasin Dynamics in Glass Forming Liquids: The Influence of Structure on Dynamics

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The discovery that the propensity for particle motion in a supercooled liquid is completely determined by the initial structure pointed to the existence of a causal link between structure and dynamics in glassy systems. Here we demonstrate that this underlying influence of structure is only local in time, fading out beyond the metabasin lifetime much before the α relaxation time. Thus, our results reveal the irreproducibility of metabasin dynamics and support the scenario of a random walk on metabasins for the long time diffusion.

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The discovery of dynamical heterogeneities in supercooled liquids provided a key to understanding one of the main open problems in condensed matter: the nature of glassy dynamics [1–3]. According to this phenomenology [stated both experimentally [2,4,5] and by means of extensive molecular simulations [3,6–9]], relaxation proceeds through the development of slowly relaxing regions that grow both in size and lifetime as the temperature is lowered in the deep supercooled regime. In turn, the configuration space counterpart of this picture is provided by the landscape paradigm [3,7,8]: at low temperatures such that equilibration within local minima is fast compared to transitions between them, the dynamics of the system can be described as transitions between basins of attraction of its potential energy surface (PES), which in turn are arranged in superstructures called metabasins (MB). A MB is a group of closely related or similar configurations which is separated from the next MB by a long range particle rearrangement [3,7–9]. Within this context, we have demonstrated that the α relaxation is accomplished by means of a small number of fast crossings from one MB to a neighboring one involving the collective motion of a significant number of particles that form a relatively compact cluster [8].

Within this dynamic viewpoint of glassy relaxation the structural details of the system play no explicit role. Furthermore, the existence of a causal link between structure and dynamics that accounts for local dynamics varying by orders of magnitude from one region of the system to another has been regarded as an article of faith [2]. Conversely, a very interesting recent paper [10] determined that certain aspect of dynamical heterogeneity indeed depends on structure: while dynamical heterogeneities and particle motions are not reproducible, the spatial variation of propensities for particle motion is completely determined by the initial structural configuration. However, the extent in time of this constraint of structure on dynamics has not been assessed. In particular, in the light of the scenario put forth in [8], it becomes central to determine whether this influence persists at the MB dynamics. We shall hereby demonstrate that the underlying influence of the structure is only local in time, being relevant to the β but not to the α relaxation, thus making MB dynamics irreproducible. This shall provide further support to the proposed scenario of a random walk on MBs for simple glass formers.

We performed a series of molecular dynamics (MD) simulations within the NVE ensemble for a paradigm model of fragile glass former: the binary Lennard-Jones system (LJ2) consisting of a 3D mixture of 80% A and 20% B particles, the size of the A particles being 10% larger than the B ones [6,8,9,11]. We carried out simulation runs after equilibration for temperature $T = 0.5$, a density of 1.2 and 150 particles [8], but similar behavior was found for other low temperatures and larger system sizes. At such temperature (close and above the Mode Coupling temperature, $T_c = 0.435$) this system conforms to the usual scenario of dynamical heterogeneities [6,8,9]: a small number of particles move cooperatively a distance that is comparable to the interparticle distance. These ''fast moving'' (or ''mobile'') particles are not homogeneously distributed throughout the sample but are arranged in clusters usually made of stringlike groups of particles [6,8,9]. The dynamics is most heterogeneous at a time t^* defined by the maximum in the non-Gaussian parameter, $\alpha_2(t)$, $\alpha_2(t) = \frac{3\langle r^4(t)\rangle}{5\langle r^2(t)\rangle^2} - 1$, which measures the deviation of the self-part of the van Hove function, the probability at a given time of finding a particle at distance r from its initial position, from a Brownian behavior [6,9]. This quantity is located at the end of the β and the beginning of the α relaxation (the crossover from the caging to the diffusive regime) and constitutes the characteristic time for dynamical heterogeneities. Addtionally, t^* depends strongly on temperature and grows quickly as we move towards T_c [6,9]. However, not all the mobile particles within a t^* time span contribute decisively to the α relaxation, as we have recently demonstrated [8]. Instead, the α relaxation is driven by a series

of a few MB transitions which are triggered by the occurrence of large compact clusters of medium-range mobile particles called democratic motions [8]. Additionally, the mean residence time in a MB has been estimated to be close to t^* [8].

To determine the extent in time of the influence of the initial structure on dynamics we first briefly describe and apply the isoconfigurational (IC) method introduced in [10]. In it, one performs a series of equal length MD runs from the same initial configuration, that is, always the same structure (the same particle positions) but each one with different initial particle momenta chosen at random from the appropriate Boltzmann distribution. For times when the system is dynamically heterogeneous, each run presents mobile particles arranged in open (usually stringlike) clusters. However, the mobile particles and corresponding clusters differ from run to run since the mobility of the particles is not determined by the initial configuration [10]. Propensity of a particle for motion in the initial configuration for a fixed time interval of length t has been defined as [10] $\langle \Delta \mathbf{r}_i^2 \rangle_{\mathrm{IC}}$, (where $\langle\,\rangle_{\mathrm{IC}}$ indicates an average over the IC and $\Delta \mathbf{r}_i^2 = [\mathbf{r}_i(t=t) - \mathbf{r}_i(t=0)]^2$ is the squared displacement of particle i in such time interval). At low temperatures propensities are not uniform throughout the sample and high propensity particles are confined to certain (relatively compact) regions [10]. Thus, while particle mobility is not reproducible from run to run, the spatial variation in the propensity is completely determined by the initial configuration, reflecting the influence of structure on dynamics [10]. We applied this method to the 3D LJ2 system and followed 1200 IC trajectories of length t^*_{IC} so that propensities are given by $\langle \Delta \mathbf{r}_i^2 \rangle_{\mathrm{IC}} = \langle (\mathbf{r}_i(t^*_{\mathrm{IC}}) - \mathbf{r}_i(0))^2 \rangle_{\mathrm{IC}}$. Here t^*_{IC} is the non-Gaussian parameter averaged over all the trajectories generated within the IC. This choice is needed in order to quantify the heterogeneous dynamics for the IC in our small system, since the traditional definition of t^* implies an average between different single trajectories from independent configurations or else, the use of a big system where the result represents an average over many subsystems [6,9]. Thus, were the local MB ''small'' (low mean residence time), t^*_{IC} would be lower than the traditional value, t^*. The opposite would be valid for a ''large'' MB. Indeed, we shall demonstrate later on that t^*_{IC} represents a measure of the MB residence time. Figure 1 displays (top curve) the individual particle propensities for this system. Clearly propensities are not uniform but vary from particle to particle and a few ones display high values (more than 3 times higher than the mean value). Additionally, as in [10] we find that these high propensity particles are confined to certain regions of the sample. The fact that the spatial distribution of propensity for the time interval $[0, t^*_{\mathrm{IC}}]$ is determined by the initial configuration led us to think that what the system is actually doing for the different trajectories of the IC is to explore the same MB. That is, the change in particle momenta generates diverging trajectories from a common origin, which are nonetheless still confined to the same MB. Thus, at $t < t^*_{\mathrm{IC}}$ the main influence of the initial structure on dynamics should be the constraint to explore the local MB (fixing the MB for the IC ensemble).

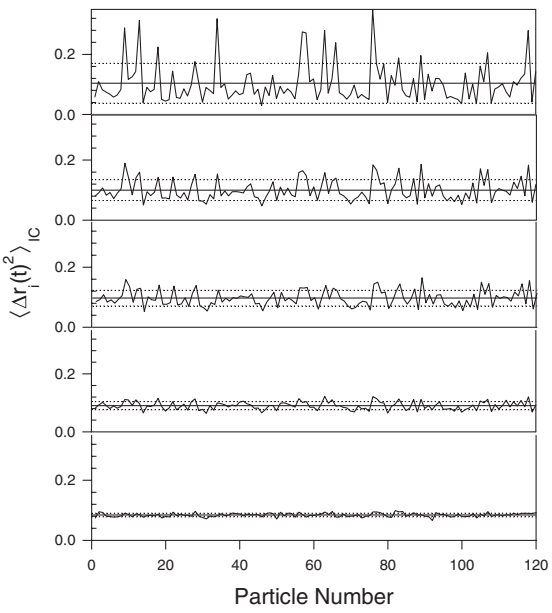

FIG. 1. $\langle \Delta \mathbf{r}_i^2(t) \rangle_{\mathrm{IC}}$ for each of the 120 A particles ($t^*_{\mathrm{IC}} = 700$). From top to bottom: $t = 0$, $0.5t^*_{\mathrm{IC}}$, t^*_{IC}, $3t^*_{\mathrm{IC}}$, and $9t^*_{\mathrm{IC}}$. Solid and dotted lines indicate the corresponding mean propensity and standard deviation (σ), respectively.

At this point we define a time-dependent propensity for a fixed time interval. That is, propensities have been defined for a fixed time interval, for example, here of length t^*_{IC} and starting at $t = 0$ (at the initial configuration), but we now leave the origin of the time interval as a variable: We start 1200 IC runs at $t = 0$ but calculate propensities as: $\langle \Delta \mathbf{r}_i^2(t) \rangle_{\mathrm{IC}} = \langle (\mathbf{r}_i(t + t^*_{\mathrm{IC}}) - \mathbf{r}_i(t))^2 \rangle_{\mathrm{IC}}$. We note that this definition preserves the value of the mean propensity (the value of propensity averaged over all the particles) for each time interval. This procedure is apt to study the persistence on the propensities of the memory of the initial configuration. In Fig. 1 we plot propensities for different values of t (note that for the top curve $t = 0$ we recover the original definition). From direct inspection of the propensity values and of the standard deviation, σ, we can learn that particle propensities clearly make uniform very quickly (they quench and fluctuate smoothly around the mean value) for times greater than t^*_{IC}, much before the time for the α relaxation (estimated to be ≈ 7700, averaged over the IC). This is also evident from Fig. 2 which shows an abrupt decay of the variance of the propensity, σ^2. Hence, a main conclusion emerges: the influence of structure on dynamics is only local in time in which concerns the propensity for motion, being thus influential for the β but not for the α relaxation.

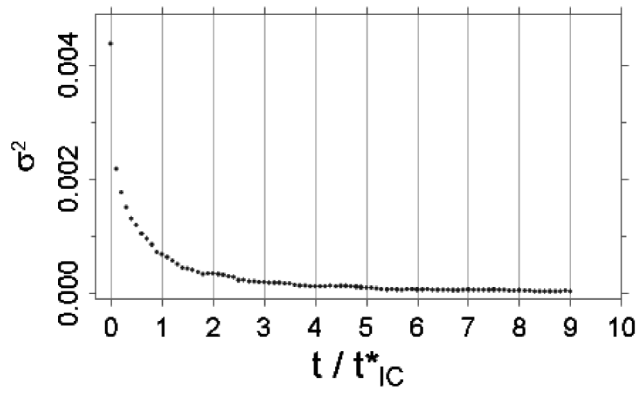

FIG. 2. The time evolution of the variance of the propensity, σ^2 (calculated every $0.1t^*_{\mathrm{IC}}$).

In order to rationalize this result in terms of the landscape approach we now study the reproducibility of MB dynamics. Thus, we first describe briefly the distance matrix method to study MB dynamics [8]: for each IC trajectory we recorded 100 configurations for a total run time close to the α relaxation and built the following distance matrix [8,12], DM: $\Delta^2(t', t'') = \frac{1}{N}\sum_{i=1}^{N} |\mathbf{r}_i(t') - \mathbf{r}_i(t'')|^2$, where $\mathbf{r}_i(t)$ 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''. In other words, this distance matrix contains the averaged squared distances between each recorded configuration and all the other ones. For this study [as all studies dealing with MBs [7,8,12]], we must investigate small systems, since for large systems the results originated from different subsystems would obscure the conclusions [7,8,12]. Thus, we used 150 particles. However, we also found the same qualitative results for small subsystems immersed in a big one, thus ruling out the possibility for finite size effects. Figures 3(a) and 3(b) show two examples which display the typical behavior for runs with $T = 0.5$. The gray level of the squares in the DM depicts the distance between the corresponding configurations, the darker the shading indicating the lower the distance between them. From the island structure of this matrix a clear MB structure of the landscape is evident. That is, islands are made up of closely related configurations (low Δ^2) which are separated from the configurations of other islands by large distances. We can estimate the typical residence time in the MBs for this T (from island sizes) as qualitatively on the order of t^*_{IC}. Given the small system size we expect this to be a good estimate (however, this time scale clearly depends on system size, since for a large system different subsystems would be undergoing MB transition events at different times). Thus, MB transitions (which last 1%–2% of the α relaxation) are fast events compared to the times for the exploration of the MBs. From the average squared displacement plot (not shown here but represented by the first row of the DM) we can learn that MB transitions imply jumps more than 5 times

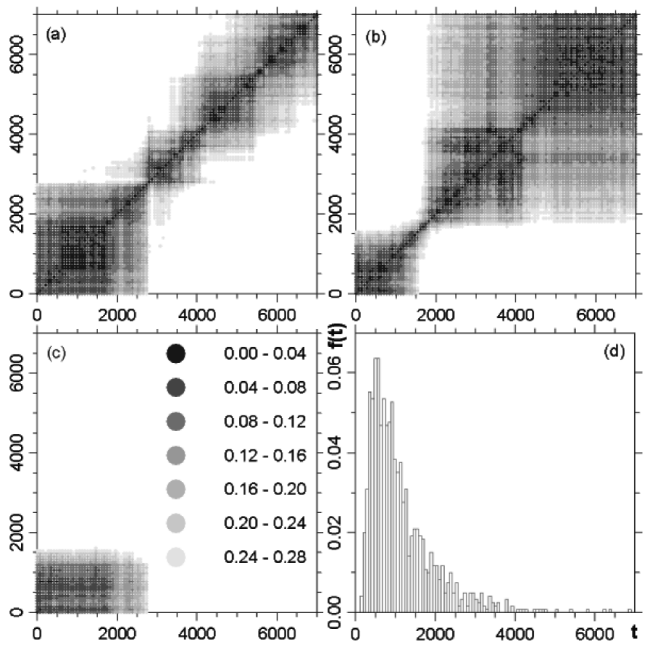

FIG. 3. (a) and (b) DM for a pair of IC trajectories. (c) DDM between the two trajectories. The gray levels of the scale are the same for Fig. 3(a)–3(c). (d) Distribution of MB residence times for the IC.

higher than the mean squared distance between consecutively recorded structures within a MB and any pair of structures differing by more than 0.2 clearly belong to different MBs [8]. The study of MB transition events has been done previously [8], revealing the decisive role of large compact clusters of particles: ''democratic'' clusters or d clusters. These clusters are responsible for the α relaxation (completed after 5–10 such events) and represent potential candidates for the cooperatively relaxing regions of Adam and Gibbs [8].

Within the IC method we define now a new DM for any pair of IC trajectories, the distinct distance matrix (DDM), as: $\Delta^2(t'_a, t''_b) = \frac{1}{N}\sum_{i=1}^{N} |\mathbf{r}_i(t'_a) - \mathbf{r}_i(t''_b)|^2$, where $\mathbf{r}_i(t_a)$ is the position of particle i at time t in trajectory a and $\mathbf{r}_i(t_b)$ is the position of particle i at time t in trajectory b (both trajectories within the IC). That is, we measure the averaged squared distance between each configuration of a given trajectory and each configuration of the other. Note that the DM we used previously [8] was defined for a single trajectory while now we measure distances between different trajectories. We expect this matrix to begin with a dark rectangle indicating the common MB explored by both trajectories. Note that the first row and the first column shall depict the averaged squared displacement for each trajectory from the initial configuration [the same averaged squared displacement plot that arises from the DMs of Fig. 3(a) and 3(b)]. Figure 3(c) shows typical results. From it we can note that after the exploration of the first MB, the two trajectories enter different MBs, as can be learnt from the large distances between them. Since struc-

tures differing by more than 0.15 belong to different MBs, the time a given trajectory exits the first MB can be detected as the time when its mean squared displacement exceeds such value. By using this, the probability calculated over the IC ensemble that after exit of the first MB any pair of trajectories visit structures whose mean squared distance is lower than 0.15 (a value compatible with typical distances between structures within a given MB) gives roughly 1%. Hence, the IC study indicates that the MB dynamics is not reproducible, with many different MBs accessible by different IC trajectories after exploration of the local MB. This also means that the influence of the initial structure is only local in time (not extending beyond the first MB), a fact consistent with particle propensities becoming uniform and thus loosing their heterogeneous nature at relatively short times ($\approx t^*_{\mathrm{IC}}$ cf. Fig. 1). A random walk scenario (spatially uncorrelated hopping processes between MBs) has been proposed for the long time diffusion of glassy systems [13] and has recently received support from LJ2 systems [14] (the mean squared displacement as a function of MB jumps follows a linear behavior with slope 1 in a log-log plot). Our finding that the memory of the initial structure on the propensities does not survive a MB transition event with the concurrent irreproducibility of MB dynamics brings new support to such a picture.

Now we justify the assumption that t^*_{IC} represents a measure of the local MB residence time. In the IC method each trajectory explores the MB by a different pathway and resides in it a different amount of time before escaping it to enter another MB. Thus, the time a single run explores a MB might not be necessarily representative of the mean MB residence time and a single MD run can provide a misleading picture of the MB superstructure of the PES. However, by using many IC trajectories a greater portion of the MB volume can be sampled (thus, this technique represents a powerful statistical tool to locally explore MBs, that is, to determining MB lifetimes and sizes, escape pathways, MB connectivity, etc.). In this sense, we calculated the residence times within the original MB for the set of 1200 IC trajectories. As noted earlier, we used a threshold of 0.15 in the mean squared distance to locate exits from the first MB. Figure 3(d) shows the distribution of residence times obtained. In such figure we are plotting the fraction of configurations, $f(t)$, that leave the first MB at given time intervals (we recall we recorded configurations each $10\% t^*_{\mathrm{IC}}$). The most probable residence time (given by the maximum of the distribution) is very close to t^*_{IC}, while the mean residence time is around $t = 1150$ ($\approx 1.7 t^*_{\mathrm{IC}}$). Thus, t^*_{IC} represents a measure of the confining influence of the local MB. This fact reveals the existence of a direct connection between the time scale for dynamical heterogeneities and the MB residence time. As expected [8], we have found that the exit of the first MB for each trajectory is marked by the occurrence of a d cluster. The d clusters for the different trajectories are different, but in all cases a significant portion of the particles that comprise them are high propensity particles. This reinforces the idea that the regions of high propensity constitute less ''jammed'' (more ''active'') regions of the sample. Furthermore, propensity studies are able to determine the ''degree of jamming'' of a given structure: when one studies (for a fixed time interval commensurable with the dynamical heterogeneity time scale) a pair of different initial structures, each presenting a local MB with a different value of t^*_{IC}, the initial structure with the less confining local MB (lower t^*_{IC}) displays a greater number of particles with high propensity, thus revealing the existence of a larger ''unjammed'' region.

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