Connections between structural jamming, local metabasin features, and relaxation dynamics in a supercooled glassy liquid

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Dynamics in glass-forming liquids in the supercooled regime vary considerably from one point of the sample to another suggesting the existence of regions with different degrees of jamming. In fact, the existence of relatively compact regions with particles with an enhanced propensity for motion has been detected in model glassy systems. In turn, the structural relaxation has been shown to be accomplished by means of a series of fast transitions between metabasins in the potential energy landscape involving the collective motion of a substantial number of particles arranged in relatively compact clusters (democratic clusters or *d* clusters). In this work we shall complete this picture by identifying the connections between local structural jamming, metabasin confining strength, and *d* clusters. Thus we shall demonstrate that the degree of jamming of the local structure dictates the confining strength of the local metabasin and that the local high propensity regions and the *d* clusters are not only similar in nature but that they share a significant amount of particles.

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I. INTRODUCTION

The relaxation dynamics of glass-forming systems in the deep supercooled regime has been shown to be characterized by the presence of dynamical heterogeneities [1–8]. This phenomenological picture implies that relaxation proceeds through the development of slowly relaxing regions that grow both in size and lifetime as the temperature is lowered. A complimentary related approach is provided by the landscape paradigm [4,6,7,9–15] which considers the relaxation dynamics as the exploration the system performs of its potential energy surface (PES) (the multidimensional surface generated while considering potential energy as a function of particle coordinates). At low enough 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 the PES, which in turn are arranged in superstructures called metabasins (MB) (MB is a group of closely related or similar configurations which is separated from the next MB by a long range particle rearrangement [4,6–8,13–15]). The portion of the PES sampled by the trajectory is more rugged as temperature lowers [12]. That is, at high temperatures the trajectory visits shallow minima that are separated by low barriers while at low temperatures it gets trapped in low-lying minima separated by high barriers [12]. Within this context, we have shown the α relaxation to be accomplished by means of a series of fast transitions between metabasins, each one triggered by the collective rearrangement of a significant number of particles arranged in a relatively compact cluster (the democratic clusters or *d* clusters) [7]. These events resemble the cooperatively rearranging regions proposed long ago by Adam and Gibbs.

The aforementioned findings reconcile the real dynamics of the particles with the relevant jumps on the PES. However, this dynamical viewpoint bears no explicit connection with the local structure of the system. It seems intuitive that the occurrence of such collective motions that drive the system from one MB to another and that become responsible for the structural relaxation of the system must be related to the existence of sizeable "less jammed" regions of the sample. The first step in this direction has been taken by recognizing the fact that while dynamical heterogeneities and particle motions are not reproducible, the spatial variation of the propensities for particle motion is completely determined by the initial structural configuration [16]. Moreover, the particles with high propensity for motion have been determined to conform relatively compact regions of the sample [16]. The fact that the structure of these regions bears certain similarity to that of the *d* clusters (contrary to the situation of the open stringlike clusters of dynamical heterogeneity discovered in the past) makes it interesting to study the possible connections between them. Additionally, in a previous work on binary Lennard-Jones systems [17] we have determined that the above indicated influence of local structure on dynamics is very limited in time, not extending much beyond the local metabasin lifetime and thus practically not surviving the occurrence of a *d* cluster. In this sense, we have shown that the metabasin topology of the PES is complicated, with each MB connected with a multiplicity of neighboring ones. This fact implies the consequent irreproducibility of MB dynamics and brings support to a MB random walk scenario for the long time diffusion [17].

In summary, a plethora of results indicate that a clear link exists between the local structure of the system, its potential energy landscape, and the resulting dynamics. In this sense, in the present work we complete the picture initiated in previous works [7,17] by providing a detailed study that brings together findings from each context. Thus we shall hereby study in detail the structure of different MBs and the corresponding distributions of particle propensities for motion and size of unjammed regions. This will enable us to demonstrate the relationship between the degree of jamming of the local structure (the size of the high propensity region) and the confining strength of the local MB. We shall also show that any given particular realization (a single trajectory) of the real dynamics (implying a particular exploration of the local MB) leads to the occurrence of a *d* cluster that comprises a

significant subset of the particles of the corresponding high propensity unjammed region. In other words, we shall make clear the fact that the *d* clusters are involved in the relaxation of (substantial portions of) such regions, thus linking these dynamically relevant events to local structural features or "defects." The work is organized as follows. In Sec. II we briefly discuss the model and simulation details, the isoconfigurational method used to determine unjammed regions and the distance matrix method to locate MB transitions and democratic clusters. In Sec. III we study propensity distributions and sizes of unjammed regions while Sec. IV links structural jamming to metabasin properties and *d* clusters. Finally, Sec. V is devoted to stressing the conclusions of the work.

II. METHODOLOGY

In order to be comprehensive, this section is aimed at describing briefly the methods we use and also to present previous finding upon which the rest of the work is built (see [7,17] for more details).

A. Model and computational details

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 three-dimensional (3D) mixture of 80% *A* and 20% *B* particles, the size of the *A* particles being 10% larger than the *B* ones [5,7,8,18]. We carried out simulation runs after equilibration for a series of low temperatures. We shall show results mainly from systems at temperature $T=0.5$, density of 1.2, and 150 particles [7]. The need for this system size will be given later on, but similar results were obtained for larger system sizes and for subsystems of this size immersed in larger systems. At low temperatures (close to and above the mode coupling temperature, $T_c=0.435$) this system conforms to the usual scenario of dynamical heterogeneities [5,7,8]: 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 [5,7,8]. The dynamics is most heterogeneous at a time t^* defined by the maximum in the non-Gaussian parameter, $\alpha_2(t)$, $\alpha_2(t)=3\langle r^4(t)\rangle/5\langle r^2(t)\rangle^2-1$, 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 [5,8]. This quantity is located at the end of the β beginning of the α relaxation (the crossover from the caging to the diffusive regime in the mean squared displacement plot) and constitutes the characteristic time for dynamical heterogeneities. Additionally, t^* depends strongly on temperature and grows quickly as we move towards T_c [5,8]. However, not all the mobile particles within a t^* time span contribute decisively to the α relaxation, as we have recently demonstrated [7]. Instead, the α relaxation is driven by a series of a few MB transitions [6,7,13–15] which are triggered by the occurrence of large compact clusters of medium-range mobile particles called democratic motions [7]. These clusters tend to be richer in *A* particles, but a deeper study is needed to completely elucidate their nature. Additionally, the mean residence time in a MB has been estimated to be close to t^* [7].

B. Isoconfigurational method

We now outline the isoconfigurational (IC) method introduced in [16]. In it one performs a series of equal length MD runs (trajectories) 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 (that is, one builds an IC ensemble). For times when the system is dynamically heterogeneous, each run or trajectory 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 [16]. Propensity of a particle for motion in the initial configuration for a fixed time interval of length t has been defined as [16] $\langle \Delta \mathbf{r}_i^2 \rangle_{\mathrm{IC}}$, (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 of the sample [16,17]. 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 [16]. By applying this method to the 3D LJ2 system [17] we followed 1200 IC trajectories and calculated propensities as $\langle \Delta \mathbf{r}_i^2 \rangle_{\mathrm{IC}}=\langle \Delta \mathbf{r}_i^2(0) \rangle_{\mathrm{IC}}=\langle [\mathbf{r}_i(t^*)-\mathbf{r}_i(0)]^2 \rangle_{\mathrm{IC}}$. In so doing [17], we found that propensities are not uniform but vary from particle to particle and a few ones display high values (more than three times higher than the mean value). Additionally, as in [16] we found that these high propensity particles are confined to certain regions of the sample. It is interesting to stress that in a single IC trajectory (which represents a particular realization of the dynamics) we can find that many of these high propensity particles are not mobile. Thus a single trajectory exploration is not able to determine unjammed regions.

The fact that the spatial distribution of propensity for the time interval $[0,t^*]$ is determined by the initial configuration indicates 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 $t<t^*$, 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).

In [17] we defined a time-dependent propensity for a fixed time interval. That is, we calculated propensities for a t^* length time interval, but we left the origin of the time interval as a variable. On other words, we started 1200 IC runs at $t=0$ but calculated propensities as $\langle \Delta \mathbf{r}_i^2(t) \rangle_{\mathrm{IC}}=\langle [\mathbf{r}_i(t+t^*)-\mathbf{r}_i(t)]^2 \rangle_{\mathrm{IC}}$. 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 and that this procedure is apt to study the persistence on the propensities of the memory of the initial configuration. With this method we found that particle propensities clearly become uniform very quickly (they quench and fluctuate smoothly around the mean value) for times slightly greater than t^*, much before the time for the α relaxation (τ_α is an order of magnitude greater than t^*) [17]. Hence a main conclusion emerged [17]: The influence of structure on dynamics is only local in time which concerns the propensity for motion, thus being influential for the β but not for the α relaxation.

C. The distance matrix method

We now describe briefly the distance matrix method to study MB dynamics [7,17]: For a given single IC trajectory we record equally spaced configurations (for example, 100 configurations, as in [7,17]) for a total run time close to the α relaxation (thus consecutively recorded configurations are separated by a 10 percent t^* time interval) and build the following distance matrix [7,19–22], (DM): $\Delta^2(t',t'') = (1/N)\Sigma_{i=1}^{N} |\mathbf{r}_i(t') - \mathbf{r}_i(t'')|^2$, 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 [6,7,13–15,22]), we must investigate small systems, since for large systems the results originated from different subsystems would obscure the conclusions [6,7,13–15,22]. 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 (we repeated the study for subsystems of 150 particles within a large system of 8000 particles; that is, we focused only on a portion of the large system). Figures 1(a) and 1(b) show two examples which display the typical behavior for runs with $T=0.5$ (each matrix corresponds to a different trajectory, both belonging to the same IC). In this figure time in measured in reduced units. The gray level of the squares in the DM depicts the distance between the corresponding configurations, the darker the shading 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^*. 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 five times higher than the mean squared

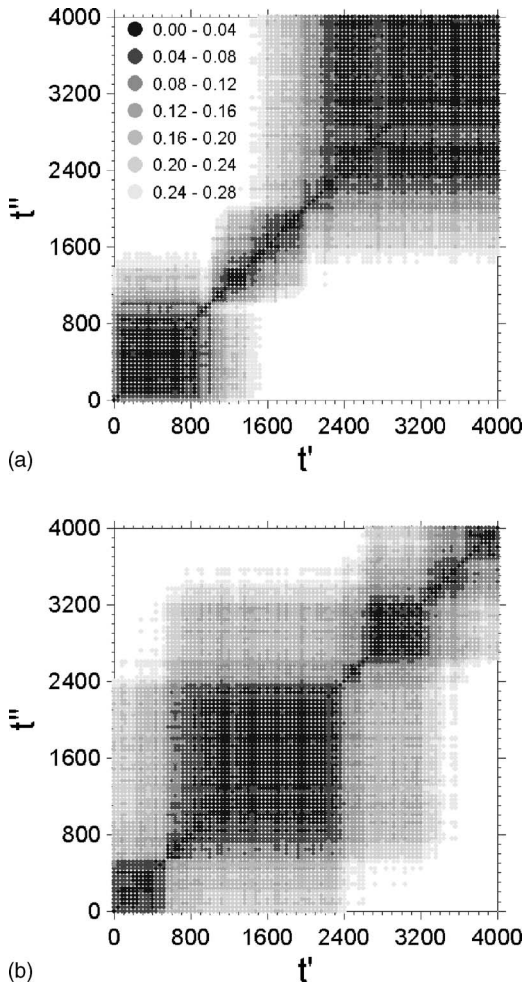

FIG. 1. DM for a pair of IC trajectories.

distance between consecutively recorded structures within a MB and any pair of structures differing by more than 0.2 clearly belong to different MBs [7]. The study of MB transition events has been done previously [7], revealing the decisive role of large compact clusters of mobile 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 [7]. The particles that comprise the d clusters that trigger MB transitions were defined as those whose mobility was greater than 0.3 times the interparticle distance within time intervals around one percent of the α relaxation [7]. Thus, for the system size under study, we found that on the order of 40–60 particles were involved in a d cluster [7]. The two DMs of the graph of Fig. 1 correspond to different trajectories of the same IC, which are confined to the same initial MB. We can see that the two trajectories imply different explorations of the MB, with a different residence time within it. Thus a single trajectory study of the landscape is not able to characterize the local MB. In [17] we studied the topology of the local MB structure of the PES. Our results demonstrated that each MB is connected with a high multiplicity of neighboring MBs such that the probability that a given pair of IC trajectories initiating within a given MB make a transition to the same

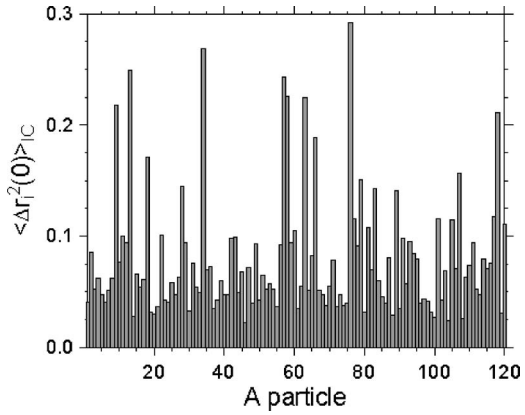

FIG. 2. Propensities for motion for the A particles within time interval $[0,t^*]$, $t^* = 400$.

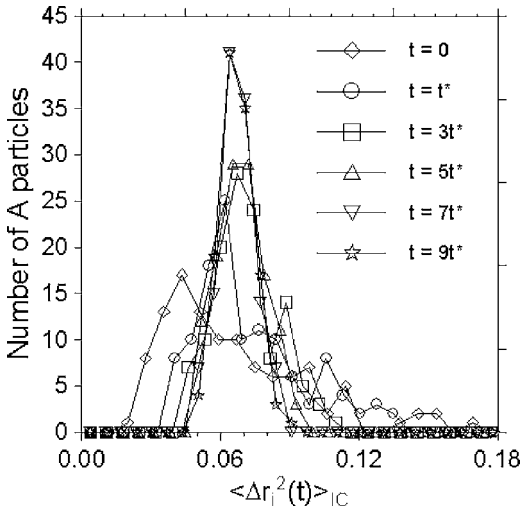

FIG. 3. Distribution of the time dependent particle propensity, $\langle \Delta \mathbf{r}_i^2(t) \rangle_{\mathrm{IC}}$, for time intervals $[t,t+t^*]$, with $t=0,t^*,3t^*,5t^*,7t^*$, and $9t^*$.

MB less than one percent. Thus the MB dynamics is irreproducible and the long time diffusion can be well described as a random walk on MBs. Additionally, contrary to a single trajectory study which can lead to a misleading picture of the local MB, the isoconfigurational method is apt to study different properties of the local MB (for example, the determination of the value of its mean residence time).

III. PARTICLE PROPENSITIES AND UNJAMMED REGIONS

Figure 2 displays the individual particle propensities for the A particles ($\langle \Delta \mathbf{r}_i^2(t=0) \rangle_{\mathrm{IC}}$ for time interval $[0,t^*]$) for an IC of the system at $T=0.5$. Clearly propensities are not uniform but vary from particle to particle and a few ones display high values. This fact reveals the existence of a link between local structure and dynamics. In [17] we already showed that this heterogeneity in particle propensity quickly fades out when we consider the time dependent propensities for times larger than t^*. Thus the influence of structure on dynamics is only local in time. Figure 3 displays the distribution for different times t of the time dependent particle propensities for this system ($\langle \Delta \mathbf{r}_i^2(t) \rangle_{\mathrm{IC}}$ for time intervals $[t,t+t^*]$). We can learn from this figure that at long times the propensity distribution is narrow and peaked around a value close to the mean propensity value of the data of Fig. 2. On the contrary, at very short times (more notably at $t=t^*$) the distribution is broad, presenting a peak at very low values and a shoulder or large tail at a value that exceeds the mean propensity (also including a few cases of very high propensities). Thus, at short times, the propensity is heterogeneous, with both an excess of high propensity and low propensity particles. We shall focus mainly on the particles whose propensity is greater than the mean value (particles with enhanced tendency to mobility which we shall call from now on high propensity particles), but we note that the low propensity ones are also interesting since they represent particles with a very low tendency to move or "frozen."

Figure 4(a) [and also Fig. 4(b)] shows the tridimensional arrangement of high propensity particles [particles whose propensity is higher than the mean value, that is, $\langle \Delta \mathbf{r}_i^2(0) \rangle_{\mathrm{IC}} > 0.078$] for the same IC as that of Figs. 2 and 3. We can see that high propensity particles are not uniformly distributed throughout the sample but confined to certain relatively compact regions. These regions, that are built up by the particles with the highest tendencies to be mobile in the isoconfigurational ensemble, represent less "jammed" (or "active" or "loose") regions of the system. We note that a single trajectory of the IC ensemble is not able to reveal this fact (even when one could show the mobility of a group of these particles). Figure 4(c) shows the case for another IC. The mean propensity value for this other IC is lower than the one for the previous ensemble. Thus, for comparison, we are indicating here high propensity particles as the ones whose propensity for time interval $[0,t^*]$ is greater than the same threshold value as used in Fig. 4(a) [$\langle \Delta \mathbf{r}_i^2(0) \rangle_{\mathrm{IC}} > 0.078$]. We can see that fewer particles are present in this graph compared to the one of Figs. 4(a) and 4(b) (a behavior that will be explained in the next section).

It is noteworthy that the dynamical heterogeneities detected in the past for this system were not compact but consisted of open structures (mainly stringlike) [5]. However, the democratic clusters that trigger the metabasin transitions are in fact compact structures [7]. Moreover, these d clusters are the only events considerably responsible for the structural relaxation (the α relaxation) of the system [7]. Thus it would be interesting to study the relationship between these last clusters and the high propensity regions. Additionally, we remember that in [17] (see also Fig. 3) we have demonstrated that propensities lose their heterogeneous nature quickly after a time commensurate with the MB residence time thus indicating that the influence of structure on dynamics barely survives a MB transition event. These points will be studied in the next section.

IV. RELATIONSHIP BETWEEN STRUCTURAL JAMMING, LOCAL MB FEATURES, AND DEMOCRATIC CLUSTERS

This section is devoted to linking the local structural features of the system, as revealed by the size of the unjammed

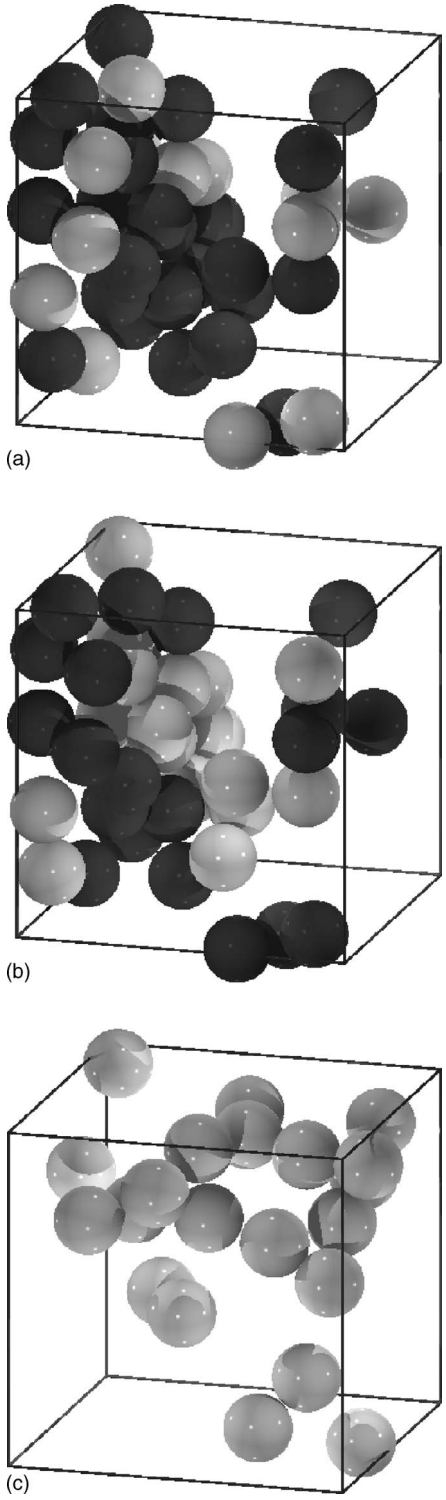

FIG. 4. (a) High propensity A particles for the IC of Figs. 2 and 3. All the particles drawn (gray and black particles) are particles whose propensity is larger than the mean propensity value $[\langle \Delta \mathbf{r}_i^2(0) \rangle_{\mathrm{IC}} > 0.078]$. We indicate in black the high propensity particles that in a given trajectory will take part in the d cluster bringing the system outside the first MB. Such a trajectory corresponds to that of Fig. 1(a). (b) Idem to (a) but indicating in black the high propensity particles that are also part of the first d cluster in another trajectory of the same IC, namely that of Fig. 1(b). (c) High propensity particles $[\langle \Delta \mathbf{r}_i^2(0) \rangle_{\mathrm{IC}} > 0.078]$ for another IC ensemble.

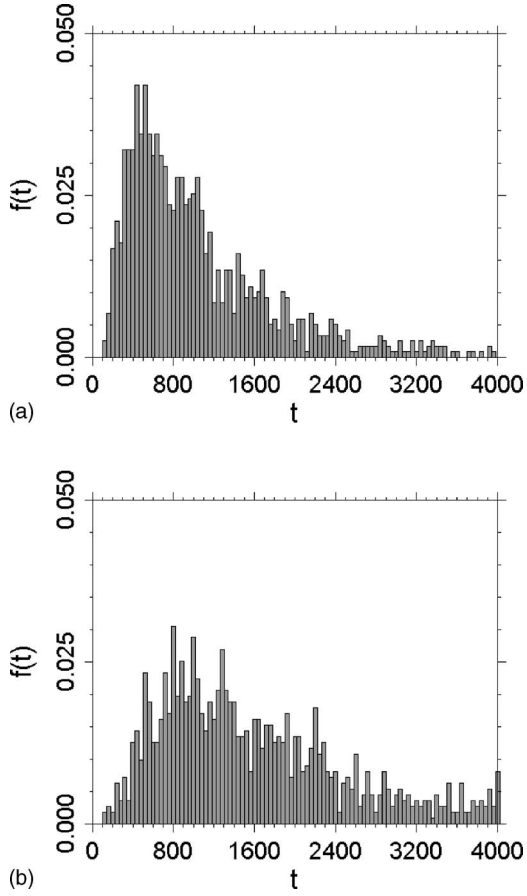

FIG. 5. (a) Distribution of metabasin residence times for the first MB of the IC ensemble of Figs. 4(a) and 4(b); (b) idem for the IC ensemble of Fig. 4(c).

region, to landscape properties, that is, the features of the local MB. Additionally, single dynamical realizations of particle displacements and landscape exploration will be discussed within such context. In this sense, the relation between democratic clusters and high propensity regions will be made explicit.

We performed studies for many isoconfigurational ensembles as previously described. For each IC we recorded 100 equally spaced configurations for each trajectory within an α relaxation time. All these IC trajectories are at first confined to the same MB but each one represents a particular exploration of such MB. The second MBs visited by the different trajectories are different (the probability that any two given trajectories exit to the same second MB is less than one percent [17]). We detected the time of exit from the first MB as the time when the mean squared displacement (MSD) of the particles exceeds 0.15 (for this temperature this threshold guarantees that the system has exited the local MB since MB transition implies sharp jumps of such height in the MSD [17]). Figures 5(a) and 5(b) show the distribution of residence times obtained for the first metabasin of a pair of different IC ensembles at $T=0.5$ [the same as that of Figs. 4(a) and 4(c), respectively]. In such a figure we are plotting the fraction of trajectories, $f(t)$, that leave the first MB at a given time. t^* is close both to the most probable and to the mean residence time [17]. This figure tells us that a single-

trajectory approach is not able to test the confining influence of a MB (we can easily see that some IC trajectories are able to find the exit of the MB quickly while other trajectories of the same IC get trapped within the MB for a long time). By comparing Fig. 5(a) with Fig. 5(b) we can see that the MB residence time is different for them (in fact, there exists a distribution of MBs as classified by their confining strength or residence times for each temperature). We can learn that the MB of Fig. 5(b) is more confining than the one of Fig. 5(a).

In turn, direct comparison of Figs. 4 and 5 shows that the most confining MB [Fig. 5(b)] corresponds to a structure with a smaller high propensity region [Fig. 4(c)]. We recall that in Fig. 4(a) [or Fig. 4(b)] and in Fig. 4(c) we are calculating the degree of jamming of the structure by means of an absolute threshold criterion: Unjammed high propensity particles are those whose propensity for motion is larger than 0.078. As we can note, the IC represented in Fig. 4(c) has fewer unjammed particles which makes its relaxation more constrained. Thus a main result emerges: A low degree of jamming reflects in a large MB residence time while, on the contrary, a structure with a large unjammed region involves an easier short time relaxation and the presence of a less confining local MB. Hence a correlation exists between structural jamming and the local roughness of the PES.

We now study particular single trajectory explorations of a given local MB to determine the *d* clusters that characterize the escapes from it. Different IC trajectories explore the local MB in different ways and exit it by means of different *d* clusters. We studied the same IC ensemble of Figs. 2, 3, 4(a), and 4(b) with the methods of Sec. II to detect *d* clusters [7]. As pointed out before, we have plotted in Fig. 4(a) the high propensity particles that make up the unjammed region of the initial structure of the system for such given IC. In this graph we have also indicated in black the high propensity particles that also belong to the *d* cluster that marks the exit from the initial MB for a given IC trajectory [that of Fig. 1(a)]. Additionally, in Fig. 4(b), we have also plotted the high propensity particles of such IC but indicated in black the particles that take part in the first *d* cluster of another IC trajectory [that of Fig. 1(b)]. A clear connection is evident from these pictures between unjammed regions and *d* clusters: We can note that each *d* cluster involves a considerable subset of the high propensity particles, such that each *d* cluster seems to relax a portion of the unjammed region. In turn, Figs. 6(a) and 6(b) show the corresponding *d* clusters (including all the particles they comprise), also indicating in each case which of their particles are also high propensity particles in the initial structure. We can learn that a significant fraction of the particles of the *d* clusters are unjammed particles within the time scale of the local MB. By studying many different trajectories we found that roughly half the particles of the *d* clusters are high propensity ones.

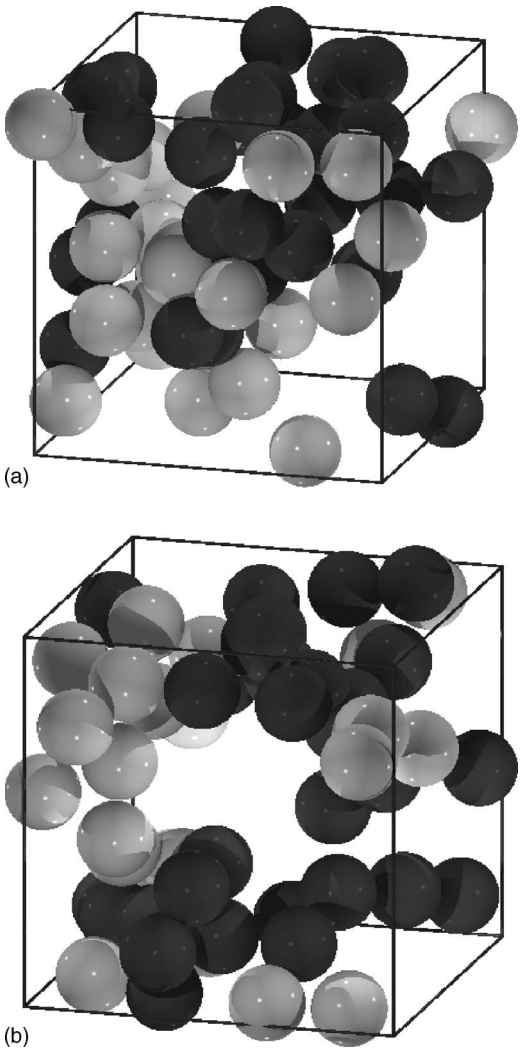

FIG. 6. Democratic clusters (*A* particles) that mark the exit from the first MB for a pair of trajectories within the same IC as that depicted in Figs. 2, 3, 4(a), and 4(b). (a) *d* cluster (particles indicated in black) for one of the trajectories [corresponding to Fig. 4(a)]. The particles of this *d* cluster that are also high propensity particles are indicated in gray. (b) Idem for the other trajectory [corresponding to Fig. 4(b)], again with the particles of the *d* cluster indicated in black and the ones that belong to the *d* cluster and are also high propensity particles indicated in gray.

V. CONCLUSIONS

This work has demonstrated the fact that the heterogeneous nature of the dynamics of supercooled glassy systems stems from the existence of regions of different degrees of jamming throughout the sample at any given time. The degree of jamming is in turn reflected in the confining influence of the local metabasin the system is subject to explore in its potential energy landscape: Particle configurations which present a large unjammed region tend to imply a less confining local metabasin in its potential energy surface and consequently lead to a faster short time dynamics, and vice versa. We have also demonstrated that unjammed regions (high propensity regions) are in fact related to the democratic clusters that trigger MB transitions. Each of these MB transition events represents a step in the structural α relaxation of the system and helps relax the unjammed region. In this regard, we have shown that both kinds of clusters of particles (the high propensity regions and the *d* clusters) are compact objects (unlike other dynamical heterogeneities that have

been found in the past for these systems) and, more importantly, that they share a significant number of particles, thus providing a link between local structure and the relevant events in the structural relaxation of the system. Additionally, we have made evident the fact that different trajectories explore differently the local MB and exit to a distinct MB via a different *d* cluster. And since the local MB connectivity is high, the influence of the initial structure on dynamics is only local in time, thus being irrelevant to the MB dynamics and hence to the long time diffusion of the system.

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