From cage–jump motion to macroscopic diffusion in supercooled liquids

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The evaluation of the long term stability of a material requires the estimation of its long–time dynamics. For amorphous materials such as structural glasses, it has proven difficult to predict the long–time dynamics starting from static measurements. Here we consider how long one needs to monitor the dynamics of a structural glass to predict its long–time features. We present a detailed characterization of the statistical features of the single–particle intermittent motion of structural glasses, and show that single–particle jumps are the irreversible events leading to the relaxation of the system. This allows to evaluate the diffusion constant on the time–scale of the jump duration, which is small and temperature independent, well before the system enters the diffusive regime. The prediction is obtained by analyzing the particle trajectories via a parameter–free algorithm.

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INTRODUCTION

The glass transition is a liquid to solid transition that occurs on cooling in molecular and colloidal systems. The transition is characterized by a slowing down of the dynamics which is more pronounced than that occurring in critical phenomena, and that takes place without appreciable structural changes. Understanding the origin of this slowdown is a major unsolved problem in condensed matter [1, 2], that has been tackled developing different competing theories that try to describe the observed phenomenology from a thermodynamic or from a kinetic viewpoint. See Ref. [3, 4] for recent reviews. From a practical viewpoint, solving the glass transition problem is of interest as this would allow to estimate the long term stability of glassy materials, e.g. drugs and plastic materials such as organic solar cells [5]. In this respect, since we are not yet able to fully predict the long term dynamics of a glassy system from its static properties, it becomes of interest to consider how long we need to observe a system before we can predict its dynamical features. This is a promising but still poorly investigated research direction.

Since the relaxation process occurs through a sequence of irreversible events, in this line of research it is of interest to identify these events and to determine their statistical features. For instance, by identifying the irreversible events with transitions between (meta)basins of the energy landscape [6–8], that can only be detected in small enough systems ($N \lesssim 100$), it is possible to predict the diffusivity from a short time measurement. Similarly, the diffusivity can also be predicted if the irreversible events are associated to many–particles rearrangements [9–14], that are identified via algorithms involving many parameters. We approach this problem considering that in glassy systems particles spend most of their time confined within the cages formed by their neighbors, and seldom make a jump to a different cage [15], as illustrated in Fig. 1 inset). This cage–jump motion is characterized by the waiting time before escaping a cage, by the typical cage size, and by the type of walk resulting from subsequent jumps. Previous experiments and numerical studies have investigated some of these features [9–11, 16–23], as their temperature dependence gives insight into the microscopic origin of the glassy dynamics. Here we show that single–particle jumps are the irreversible events leading to the relaxation of the system and clarify that the typical jump duration ($\Delta t_j$) is small and temperature independent: this allows to estimate the single particle diffusion constant resulting from a sequence of jumps, $D_j$, and the density of jumps, $\rho_j$, on the time scale of $\langle \Delta t_j \rangle$, if the size of the system is large enough. These estimates lead to an extremely simple short time prediction of the diffusivity of the system

$$D(T) = D_j(T)\rho_j(T),$$

that can be simply exploited by investigating the particle trajectories via a parameter–free algorithm.

METHODS

We have obtained these results via NVT molecular dynamics simulations [24] of a model glass former, a 50:50 binary mixture of $N = 10^3$ disks in two dimensions, with a diameter ratio $\sigma_L/\sigma_S = 1.4$ known to inhibit crystallization, at a fixed area fraction $\phi = 1$. Two particles $i$ and $j$, of average diameter $\sigma_{ij}$, interact via an Harmonic potential, $V(r_{ij}) = \epsilon ((\sigma_{ij} - r_{ij})/\sigma_L)^2$, if in contact, $r_{ij} < \sigma_{ij}$. This interaction is suitable to model soft colloidal particles [25, 26]. Units are reduced so that $\sigma_L = m = \epsilon = k_B = 1$, where $m$ is the mass of both particle species and $k_B$ the Boltzmann’s constant. In the following, we focus on results concerning the small particles, but analogous ones hold for both species. Our results rely on the introduction of a novel algorithm to identify in the particle trajectories both the cages, as in previous studies, as well as the jumps, whose features are here studied for the first time. The algorithm is based on the consid-
We have divided the trajectory of each particle in a sequence of periods during which the particle is caged, of duration $t_w$, separated by periods during which the particle is jumping, of duration $\Delta t_J$. The waiting time distribution within a cage, $P(t_w)$, illustrated in Fig. 2, is well described by a by power law with an exponential cutoff,

$$P(t_w) \propto t_w^{-\beta} \exp \left( -\frac{t_w}{\tau_w} \right),$$

as observed in different systems \[18, 22\]. The exponent $\beta(T)$ increases by lowering the temperature, ranging in the interval $\beta \in [0.4, 0.95]$. Since $\langle t_w(T) \rangle = \tau_w(T)(1 - \beta(T))$, this implies that the average waiting time $\langle t_w \rangle$ grows slower than the exponential cutoff time, $\tau_w(T)$, as illustrated in the inset. The time of flight distribution $P(\Delta t_J)$, illustrated in Fig. 3, decays exponentially. The collapse of the curves corresponding to different temperatures clarifies that, while the average time a particle spends in a cage increases on cooling, the average duration of a jump is temperature independent. We find $\langle \Delta t_J \rangle \approx 100t_b$. We note that the presence of a temperature dependent waiting time and of a temperature independent jump time is readily explained via a two well potential analogy; indeed, the waiting time corresponds to the time of the activated process required to reach the energy maximum, while the jump time is that of the subsequent ballistic motion to the energy minimum. We define the length of a jump $\Delta r_J$, as the distance between the center of mass of adjacent cages, as illustrated in Fig. 1 (inset). Fig. 3 shows that this length is exponentially distributed, with a temperature dependent average value.

Since the average jump length is at least a factor three larger than the cage gyration radius, which is Gaussian distributed (not shown), one can consider each particle as a walker with a temperature dependent step size $\langle \Delta r_J \rangle$, and a temperature independent time of flight $\langle \Delta t_J \rangle$. The features of this walk can be inferred from the mean squared displacement $\langle r^2(\theta_J) \rangle$, illustrated in Fig. 4 (inset), where the average is taken over the ensemble of particles which have performed $\theta_J$ jumps. At all temperatures, the walk is to a good approximation diffusive from the onset. Accordingly, we predict the diffusion constant $D_J$ of the jumpers to be that of a pure random walk with step size $\langle \Delta r_J \rangle$ and time of flight $\langle \Delta t_J \rangle$:

$$D_J = \lim_{\theta_J \to \infty} \frac{\langle r^2(\theta_J) \rangle}{\theta_J(\Delta t_J)} = \frac{\langle \Delta r_J^2 \rangle}{\langle \Delta t_J \rangle}. \quad (3)$$

The validity of this prediction is verified in Fig. 4. This result shows that single-particle jumps are the intrinsic feature of glassy systems.
reversible events leading to the relaxation of the system, and suggests that they are the elementary units of both local irreversible many–particle rearrangements \[12\] \[11\], as well as of global irreversible events, such as transitions between basins in the energy landscape \[6\] \[36\] \[37\]. In addition, Eq. 3 allows to estimate a long time quantity, the jumper’s diffusion constant, \(D_J\), from properties of the cage–jump motion estimated at short times, of the order of \(\langle \Delta t_J \rangle\). Since the time of flight \(\langle \Delta t_J \rangle\) is temperature independent, Eq. 3 also clarifies that the decrease of \(D_J\) on cooling is due to that of \(\langle \Delta r_J^2 \rangle\). As an aside, we note that these results support the speculation of Ref. 23 that rationalized data from different glass formers in the Continuous Time Random Walk paradigm \[34\], postulating a simple form for the waiting time and jump distributions. Here, we have explicitly measured the cage–jump statistical properties.

The increase of the average waiting time on cooling leads to a decrease of the density of jumps, whose temperature dependence is illustrated in Fig. 4. Indeed, these two quantities are related as \(\rho_J\) is to good approximation equal to the fraction of the total time particles spend jumping,

\[
\rho_J = \frac{\langle \Delta t_J \rangle}{\langle t_w \rangle + \langle \Delta t_J \rangle}, \tag{4}
\]

as illustrated in Fig. 4a. We note that the r.h.s. of the above equation is computed after having determined the waiting time distribution, i.e. on a temperature dependent timescale of the order of the relaxation time, whereas the l.h.s. is estimated on the small and temperature independent timescale of the order of \(\tau_w\). This is always the case in the investigated temperature range, as we find \(\rho_J N \approx 25\) at the lowest temperature. In general, the time of observation required to measure \(\rho_J\) scales as \(\Delta t = \langle \Delta t_J \rangle / \rho_J N\). This is always much smaller than the relaxation time, as Eq. 4 leads to \(\Delta t \approx (\langle t_w \rangle + \langle \Delta t_J \rangle)/N \ll \langle t_w \rangle \ll \tau_w\).

The features of the cage–jump motion allow to predict the macroscopic diffusion via Eq. 4 \(D = \rho_J D_J\). This
Eq. 1 can also be expressed as

$$D = \lim_{t \to \infty} \frac{1}{Nt} \sum_{p=1}^{N} [r_p(t) - r_p(0)]^2 = \frac{1}{Nt} \sum_{p=1}^{N} \theta^{(p)}(t) D_J \langle \Delta t_J \rangle,$$

where the last equality is obtained considering that, at time $t$, the contribution of particle $p$ to the overall square displacement is due to $\theta^{(p)}(t)$ jumps of average size $D_J \langle \Delta t_J \rangle$. Eq. 4 follows as

$$\langle \theta_J(t) \rangle = \frac{1}{\langle \Delta t_J \rangle + \langle \tau_w \rangle},$$
a quantity related to $\rho_J$ by Eq. 4. Eq. 1 can also be expressed as

$$D = \rho_J \langle \Delta r_J^2 \rangle \langle \Delta t_J \rangle.$$

through Eq. 3. Our numerical results are consistent with this prediction, as we find $D = m \rho_J \langle \Delta r_J^2 \rangle$, with $m \approx 0.75$, as illustrated in Fig. 5. We explain the value $m < 1$ considering that the time of flight, $\Delta t_J$, is a slightly underestimation of the time required to move by $\Delta r_J$, as after jumping a particle rattles in the cage before reaching its center of mass. Eq. 3 has two important merits. First, it connects a macroscopic property, the diffusion coefficient, to properties of the cage-jump motion. Second, it connects a quantity evaluated in the experimental viewpoint, to the over-}

FIG. 5. Linear dependence of the diffusion constant on features of the cage-jump motion. Open circles and the solid line are measured data and the prediction from Eq. 3, respectively. We stress that $D$ is estimated at long times, while $\rho_J \langle \Delta r_J^2 \rangle$ is estimated at short times, well before the system enters the diffusive regime. The solid line has slope $m \approx 0.75$. Inset: the persistence relaxation time, $\tau_p$, is proportional to the ratio, $(\langle t_{mb}^2 \rangle / \langle t_w \rangle)$, of the moments of the waiting time distribution. The solid line is a power law with exponent 1.

the average waiting time $\langle t_w \rangle$. This is explained considering the spatial heterogeneity of the dynamics. Indeed, in the system there are mobile regions that last a time of the order of the relaxation time $\tau_w$ [10, 23, 32, 41], where the typical waiting time is smaller than the average. The subsequent jumps of particles of these regions influence the average waiting time $\langle t_w \rangle$ but do not contribute to the decay of the persistence correlation function, which is therefore controlled by the decay time of the waiting time distribution, $\tau_p \propto \tau_w$. It is also possible to relate $\tau_p$ to the first two moments of $P(t_w)$, as due to Eq. 2 $\tau_w \propto \langle t_w^2 \rangle / \langle t_w \rangle (2 - \beta) \approx \langle t_{mb}^2 \rangle / \langle t_w \rangle$ (see Fig. 5 inset). This expression for the relaxation time, and Eq. 4 for the diffusion coefficient, are formally analogous to those suggested by trap models [33], that interpret the relaxation as originating from a sequence of jumps between metabasins of the energy landscape [33, 36, 37]. Indeed, trap models predict the diffusion coefficient and the persistence relaxation time [33, 40] to vary as $D \propto a^2 / \langle t_{mb}^2 \rangle$, and as $\tau_p \propto \langle t_{mb}^2 \rangle / \langle t_{mb} \rangle^2$. Here $t_{mb}$ is the waiting time within a metabasin, and $a$ the typical distance between two adjacent metabasins in configuration space. It is therefore worth stressing that, since our results concern the single particle intermittent motion, they have a different interpretation and a different range of applicability. In particular, since $\langle t_{mb}^2 \rangle$ varies with system size as $O(1/N)$, transitions between metabasins can only be revealed investigating the inherent landscape dynamics of small ($\sim 100$ particles) systems [32], and models to infer
the dynamics in the thermodynamic limit need to be developed. Conversely, our prediction for the diffusion coefficient lacks any system size dependence and works at short times, as previously discussed. These results support a physical interpretation of the relaxation in terms of trap models, but clarify that it is convenient to focus on single particle traps, rather than on traps in phase space, at least as long as the relaxation process occurs via short-lasting jumps.

**DISCUSSION**

We have shown that the diffusion coefficient of a glass former can be estimated on a small timescale, which is of the order of the jump duration and much smaller that former can be estimated on a small timescale, which is via short-lasting jumps.

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**DISCUSSION**

We have shown that the diffusion coefficient of a glass former can be estimated on a small timescale, which is of the order of the jump duration and much smaller that former can be estimated on a small timescale, which is via short-lasting jumps. This prediction requires the identification of cages and jumps in the particle trajectories, we have show to be easily determined via a parameter-free algorithm if cages and jumps are characterized by well separated time scales. This result is expected to be relevant in real world applications in which one is interested in predicting the diffusivity of systems that are in equilibrium or in a stationary state. It can also be relevant to quickly determine an upper bound for the diffusivity of supercooled out-of-equilibrium systems.

Open questions ahead concern the emergence of correlations between jumps of a same particle closer to the transition of structural arrest, and the presence of spatio-temporal correlations between jumps of different particles. In addition, we note that persistence correlation function behaves analogously to a self-scattering correlation function at a wavevector of the order of the inverse cage–jump motion, and the relaxation time at different wave vectors.

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