Anomalous diffusion in supercooled liquids: a long-range localisation in particle trajectories

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A statistical analysis of the geometries of particle trajectories in the supercooled liquid state is reported. We examine two structurally different fragile glass-forming liquids simulated by molecular dynamics. In both liquids, the trajectories are found to exhibit a long-range localisation distinct from the short-range localisation within the cage of nearest neighbours. This novel diffusion anomaly is interpreted as a result of the potential-energy landscape topography of fragile glass-formers where the local energy minima coalesce into metabasins - compact domains with low escape probability.

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It is generally understood that the non-Arrhenius behaviour and other dynamical anomalies observed in fragile\textsuperscript{1} glass-forming liquids are caused by a particular topology of the potential energy-landscape (PEL)\textsuperscript{2,3}. Having been cooled below the cross-over temperature $T_\alpha$, the liquid stays within the basins of attraction of local PEL minima long enough for the velocities to decorrelate, and its structural relaxation is controlled by the inter-basin connectivity network. A distinctive feature of the PEL of a fragile liquid is that the basins are geometrically organised into a two-scale pattern whereby compact sets of contiguous basins (metabasins)\textsuperscript{4,5} are separated by barriers with higher activation energy than those for elementary interbasin transitions.

The impact of this PEL pattern upon the supercooled liquid dynamics can be understood as follows. In a multidimensional space, a boundary is close to almost every point of the domain it confines\textsuperscript{6}. Therefore, almost every PEL minimum in a metabasin is separated by the metabasin’s boundary from some of its Euclidean neighbour minima\textsuperscript{7,8}. The resulting reduction in the number of accessible relaxational degrees of freedom slows down the relaxation and renders elementary interbasin transitions increasingly collective\textsuperscript{9,10}, in accordance with the Adam-Gibbs conjecture\textsuperscript{11}. At a larger time scale, the system’s confinement to a metabasin is expected to produce a localisation effect in its configuration-space trajectory. It is assumed that the intra-metabasin dynamics correspond to $\beta$-relaxation, whereas irreversible $\alpha$-relaxation, and the respective decorrelation of the system’s configuration-space trajectory, occur by virtue of the inter-metabasin transitions\textsuperscript{4}. In contrast to collective intra-metabasin dynamics, relaxation beyond the metabasin boundaries is concluded to be mediated by uncorrelated movements of particles\textsuperscript{12}.

The configuration-space trajectory of a liquid can be investigated by means of statistical analysis of its 3D-space projection - a trajectory of a single particle. Based on the above arguments, we can discriminate three distinct regimes in the particle trajectory of a supercooled liquid (following the initial ballistic regime). (i) Short-range localisation of a particle within the cage of its neighbours; (ii) Persistent diffusion due to the collective intra-metabasin dynamics\textsuperscript{13}; (iii) Long-range localisation produced by the system’s long-time confinement to a metabasin. These anomalies can be detected as the respective deviations of Hausdorff measure from its value for the Brownian diffusion\textsuperscript{14}. Regimes (i) and (ii) have been observed in molecular-dynamics simulations\textsuperscript{13}; the third one has not been reported so far.

In this Letter, we analyse the statistical geometry of particle trajectories in the supercooled liquid state. We examine two structurally distinct fragile glass-forming liquids simulated by molecular dynamics. Evidence is presented for the long range localisation in the particles diffusion conjectured above as regime (iii). The observed effect can be regarded as direct evidence for the presence of metabasins in the PEL topography of fragile liquids. It also makes it possible to assess the spatial extent of a metabasin. We discuss the impact of the metabasin confinement on the relation between relaxation and diffusion.

The MD simulations we report here explore two simple fragile glass-formers. One is the Z2 model\textsuperscript{15} demonstrating a pronounced tendency for icosahedral clustering. This liquid was simulated at the number density $\rho=0.85$. At that density, its estimated mode-coupling theory\textsuperscript{16} critical temperature $T_c=0.65$, fragility index $B=4.5$ and $T_A=1.1$. The liquid was simulated at two temperatures: $T=1.2$ and $T=0.7$, above and below $T_A$, respectively. The other glass-forming liquid explored here was the binary Lennard-Jones system (BLJ) commonly used in glass studies\textsuperscript{17,18,19}. The interaction potential was truncated at $r=r_0=3.0036$ using the Stroddard-Ford quadratic cutoff\textsuperscript{20}. The BLJ liquid
was simulated in a supercooled state at \( \rho = 1.19 \) and \( T = 0.451 \). In this model, we analysed the trajectories of the smaller (more mobile) particles. Both models were simulated in the \( NVE \) ensemble with \( N = 16000 \).

Traditionally, statistics of diffusing particles is presented in terms of the distribution of particle displacements at time \( t \), \( G_\varepsilon(r,t) \) \[21\]. In the case of Brownian diffusion, this is a Gaussian, and its second moment, the mean-square displacement, depends on \( t \) as \( \langle r(t)^2 \rangle = 6Dt \), \( D \) being the diffusion coefficient.

Alternatively, the particles’ diffusion can be described in terms of the first-passage time distribution \( P(\varepsilon,t) \) \[22\]. \( P(\varepsilon,t) \) is the probability that a particle’s first crossing of the boundary of a sphere of radius \( \varepsilon \) centered at the particle’s initial position happens within the time interval between \( t \) and \( t + dt \). For Brownian diffusion, the first moment of this distribution, the mean first-passage time \( \tau_\varepsilon \) is equal to \( \tau_\varepsilon = \varepsilon^2/(6D) \) \[22\].

In this study, we analyse the statistical geometry of particle trajectories. It is convenient for this purpose to use the distribution of first passage trajectory lengths (FPL) \( P(\varepsilon,L) \), rather than first passage times. These two distributions are equivalent for the description of liquid diffusion (except for very short times) since, in dense liquids, velocities decorrelate much faster than trajectories. The length of a particle trajectory is defined as the time integral of its instantaneous speed. With good accuracy, the trajectory length within time \( t \) is \( L = vt \), where \( v = \sqrt{8\pi \varepsilon} \) is the mean particle speed \[23\]. We denote the first moment of the FPL as \( L_\varepsilon \). For the trajectory of a Brownian particle we have

\[
L_\varepsilon = \frac{v\varepsilon^2}{6D}
\]

In this study we explore correlations in the system’s configuration-space trajectory and use the decay of the correlations as an indicator of the system’s approach to ergodic equilibrium. The presence of correlation effects in a particle trajectory can be detected from its scaling behaviour. The latter can be quantitatively analyzed in terms of the trajectory’s fractal dimensionality (Hausdorff measure) \[14\]. The Hausdorff measure \( \alpha \) is defined as the logarithmic derivative of \( L_\varepsilon \):

\[
\alpha(\varepsilon) = \frac{d \ln L_\varepsilon}{d \ln \varepsilon}
\]

As it follows from equations \[14\] and \[2\], \( \alpha(\varepsilon) = 2 \) for a particle trajectory in the large-\( \varepsilon \) limit of Brownian diffusion.

Within the intermediate range of \( \varepsilon \), the deviation of \( \alpha(\varepsilon) \) from the indicated Brownian value can be used to discriminate the specific diffusion regimes discussed above. If \( \alpha(\varepsilon) > 2 \), consecutive particle displacements, defined by the scale of \( \varepsilon \), correlate negatively (the diffusion is localised). If \( \alpha(\varepsilon) < 2 \), consecutive particle displacements correlate positively; this is a signature of persistent diffusion.

Fig. 1 shows \( \alpha(\varepsilon) \) for the three liquid states simulated in this study. A common feature in all cases is a pronounced peak located at around \( \varepsilon = 0.3 \) where \( \alpha(\varepsilon) \) exceeds the Brownian value \( \alpha(\varepsilon) = 2 \). The peak, greatly enhanced by cooling below \( T_A \), indicates negative correlations in the particle trajectory within the respective range of \( \varepsilon \). It apparently represents a localisation effect induced by the particle’s confinement to the cage of nearest neighbours. This can be seen as a 3D projection of the configuration-space trajectory localisation within a PEL minimum basin.

For the Z2 liquid at \( T = 1.2 \), representing normal liquid dynamics, the described short-range localisation regime is immediately followed at larger \( \varepsilon \) by convergence to the asymptotic Brownian behaviour. In the case of the supercooled liquid dynamics, both for the Z2 liquid at \( T = 0.7 \) and the BLJ liquid, a broad minimum is observed within \( 0.8 < \varepsilon < 3 \) where \( \alpha(\varepsilon) < 2 \). This effect, indicating positive correlations in a particle trajectory, is characteristic of persistent diffusion (regime (ii) discussed above).

A similar behaviour has already been reported for the BLJ liquid, and concluded to be related to the collective particle motions \[13\].

At still larger values of \( \varepsilon \) we observe, both for the Z2 liquid at \( T = 0.7 \) and the BLJ liquid, another anomaly in the behaviour of \( \alpha(\varepsilon) \). Before eventually converging to the Brownian limit, \( \alpha(\varepsilon) \) in these supercooled liquids exhibits a second maximum located within \( 3 < \varepsilon < 10 \) where \( \alpha(\varepsilon) > 2 \). This feature, shown in the inset in Fig. 1, indicates the presence of a long-range localisation in the particle diffusion that we conjectured above as regime (iii). This interesting novel effect is the central observation of the present study, and we shall discuss it in more detail.

Besides Brownian diffusion, another essential criterion of the ergodic behaviour of a liquid is homogeneity of the diffusion process. In terms of the statistics of the particles’ trajectories, this can be measured by comparing the variance of the FPL distribution: \( \text{Var}[P(\varepsilon,L)] = \langle L(\varepsilon)^2 \rangle/L_\varepsilon^2 - 1 \) with its asymptotic value of \( 2/5 \) expected for Brownian diffusion \[22\]. The evolution of this quantity with respect to \( \varepsilon \) for all three simulated liquid states is shown in Fig. 2. Comparing these data with those in Fig. 1 makes it possible to conclude that the anomalies in the fractal dimensionality observed in the supercooled liquid state, both for Z2 and BLJ, are accompanied by anomalously high levels of variance of the FPL distribution. Excessive variance is observed in both the localisation and the persistent diffusion domains. This observation is consistent with the point of view that the anomalous diffusion in the supercooled liquid state is associated with dynamical heterogeneity.

As we argued above, the localisation regime that we observed as a large-\( \varepsilon \) maximum in \( \alpha(\varepsilon) \) for the super-
FIG. 1: Apparent fractal dimension of a particle trajectory. Solid black line and dashed red line: $Z_2$ liquid for $T = 0.7$ and $T = 1.2$, respectively. Dash-dotted green line, the BLJ liquid. The error bar indicates the estimated standard deviation for the BLJ data.

FIG. 2: The variance of the FPL distribution. Solid black line and dashed red line: $Z_2$ liquid for $T = 0.7$ and $T = 1.2$, respectively. Dash-dotted green line, the BLJ liquid.

cooled liquid state in Fig. 1 can be viewed as a result of the system’s confinement to a configuration-space domain that we associate with a metabasin. In this way, the effect in question is a direct observation of the constraints imposed by the metabasin structure of the PEL upon the liquid diffusion, and its location in terms of $\varepsilon$ makes it possible to conclude the extent of that structure.

It is worth noting that the observed long-range maximum of $\alpha(\varepsilon)$ makes the diffusion at shorter scales faster as compared with the asymptotic Brownian diffusion. To demonstrate this effect, we introduce the $\varepsilon$-dependent diffusion rate $D_\varepsilon$ using Eq. 1:

$$D_\varepsilon = v\varepsilon^2/(6L_\varepsilon)$$  \hspace{1cm} (3)

Fig. 3 displays the ratio of $D_\varepsilon/D$, where $D$ is the Brownian diffusion rate derived from the asymptotic behaviour of the mean-square displacement in the limit of

FIG. 3: Ratio of the $\varepsilon$-dependent diffusion rate (Eq. 3) to the asymptotic Brownian diffusion rate. Solid black line and dashed red line: $Z_2$ liquid for $T = 0.7$ and $T = 1.2$, respectively. Dash-dotted green line, the BLJ liquid.

FIG. 4: FPL distribution for the particle trajectories in $Z_2$ liquid for $\varepsilon = 2.424$. $L$ is scaled by $v\varepsilon^2/(6D)$, the $\varepsilon$-dependent mean first passage trajectory length for Brownian diffusion (Eq. 1), $D$ being the asymptotic diffusion rate for the respective $T$. Solid line, $T = 0.7$; dashed red line, $T = 1.2$. The inset depicts, in log-linear scale, the large-$L$ behaviour of the FPL.
large time (in that limit, $D_c$ and $D$ converge). The general behaviour of $D_c/D$ is related to that of $\alpha(\varepsilon)$, Fig. 1, by Eq. 2. The long-range maxima of $\alpha(\varepsilon)$ observed for both supercooled liquids, although appear subtle, obviously result in a measurable reduction of $D_c/D$ within the same range of $\varepsilon$, as can be seen in Fig. 3.

To obtain further insight into this effect, we compare in Fig. 4 two FPL distributions for the Z2 liquid, at $T = 0.7$ and at $T = 1.2$, in both cases for $\varepsilon = 2.424$. As can be seen in Fig. 3, at $T = 0.7$ that value of $\varepsilon$ represents the diffusion enhancement regime, whereas for $T = 1.2$ the diffusion appears to attain Brownian behaviour. In order to compare the distributions on equal ground, we scaled $L$ by $\varepsilon^2/(6D)$, the $\varepsilon$-dependent mean first passage trajectory length for the Brownian diffusion (Eq. 1), $D$ being the asymptotic diffusion rate for the respective $T$. The large-$L$ tails of the distributions (shown in the inset) are practically indistinguishable, and their asymptotic behaviour is apparently exponential. The difference in the first moments of these two distributions arises from a significant extra contribution from shorter-$L$ trajectories in the case of $T = 0.7$ indicating an excessive presence in the supercooled liquid of highly mobile particles. This observation is apparently consistent with both the diffusion enhancement as observed in Fig. 3, and the excess variance in the FPL distribution within the respective range of $\varepsilon$, Fig. 2.

A conceptually interesting aspect of these results concerns the relation between the diffusion and relaxation [24]. How far does a particle of a liquid diffuse before the ergodic equilibrium has been attained? A necessary condition for that is the onset of an equilibrium (Brownian) diffusion regime in the particle trajectories. We see in Figs. 1 and 3 that, in a normal liquid state above $T_\alpha$, Brownian diffusion is reached as soon as a particle leaves the cage of its neighbours. The appearance of two longer-range anomalous diffusion regimes in the supercooled liquid state, which we attribute to the confinement to a metabasin, extends the spatial scale of the non-equilibrium diffusion process, thereby delaying the relaxation relative to the diffusion. In this way, the latter anomaly can also be regarded as an effect of the metabasin topography of the PEL of fragile liquids.

In summary, we find that two physically and structurally different supercooled fragile glass-forming liquids demonstrate a long-range localisation in the particle trajectories. We link this novel effect to the existence of metabasins in the fragile liquids’ PEL topographies. Based on the results of this study, and our arguments presented above, the general impact of the PEL metabasins upon the supercooled liquid dynamics can be described as follows. First, constraints imposed by the metabasin boundary reduce the number of accessible degrees of freedom for the intra-metabasin transitions between the basins of the PEL minima. This induces, within the respective range of distances, collective dynamics and, consequently, persistent diffusion with $\alpha(\varepsilon) < 2$. Second, on a larger spatial scale, the system’s (time-limited) confinement to a compact configuration-space domain defined as a metabasin results in a long-range localisation of the particle trajectories. In this regime, $\alpha(\varepsilon) > 2$. We also show that these anomalies effectively give an intermediate-range diffusion rate that is faster than the asymptotic Brownian diffusion. Finally, the existence of the long-range anomalies in a particle trajectory, delaying its approach to the equilibrium Brownian diffusion, also delays the liquid’s relaxation relative to diffusion.

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