

Atomistic mechanism of physical ageing in glassy materials

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Abstract – Using molecular simulations, we identify microscopic relaxation events of individual particles in ageing structural glasses, and determine the full distribution of relaxation times. We find that the memory of the waiting time \( t_w \) elapsed since the quench extends only up to the first relaxation event, while the distribution of all subsequent relaxation times (persistence times) follows a power law completely independent of history. Our results are in remarkable agreement with the well-known phenomenological trap model of ageing. A continuous-time random walk (CTRW) parametrized with the atomistic distributions captures the entire bulk diffusion behavior and explains the apparent scaling of the relaxation dynamics with \( t_w \) during ageing, as well as observed deviations from perfect scaling.

The dynamics of glass-forming materials is characterized by slow, spatially heterogeneous and temporally intermittent processes [1–6]. Long periods of caged particle vibrations are interrupted by rapid, localized structural relaxations. Dynamical heterogeneity near the glass transition leads to stretched exponential relaxation of correlation and response functions, as well as subdiffusive, non-Gaussian transport. In the glassy state, configurational degrees of freedom continue to evolve slowly. This phenomenon is called physical ageing [7] and is a defining and universal feature of nonequilibrium glassy dynamics [8]. Structural relaxations become increasingly sluggish with the waiting time \( t_w \) elapsed since vitrification, and almost all material properties change as a result.

Ageing often manifests itself as a simple rescaling of the slow, configurational part of the global correlation functions \( C(t, t_w) = C_{vib}(t) + C_{conf}(t/t_w^{\mu}) \), where \( \mu \) is the ageing exponent. This scaling behaviour has been observed in a wide range of disordered materials [1] and is particularly pronounced in polymer glasses [7], colloidal suspensions [9,10], and physical gels [11]. Recent simulations of structural glasses show that scaling also applies approximately to the distribution of local correlation functions [12] and the distribution of particle displacements (van Hove function) [13], which superimpose when plotted at times of equal mean. Scaling of local correlations can be proved to hold exactly for certain spin glass models whose dynamical action obeys time reparametrization invariance [14]. Despite the apparently universal nature of this phenomenon [15], the physical mechanism behind it remains elusive.

In this letter, we directly observe the atomistic dynamics underlying physical ageing on a single-particle level through molecular-dynamics simulations of two model systems for atomic and polymeric glasses. We consider both the well-known amorphous 80/20 binary Lennard-Jones mixture [16], as well as a bead-spring model for polymer glasses [17,18], where particles interact via the Lennard-Jones potential and are coupled together by stiff springs to form chains of length 10. Twenty thousand particles each are simulated in a periodic simulation box. All results are quoted in Lennard-Jones units. For the polymer (80/20) model, the initial ensemble is equilibrated at \( T = 1.2 (4.0) \) and then quenched under constant volume conditions over 750 LJ time units to \( T = 0.25 (0.33) \) to form a glass \( (T_g \approx 0.35–0.4) \) [19,20]. The initial density of the melt is chosen such that the pressure after the quench is nearly zero. The ageing then proceeds at constant (zero) pressure for various waiting times \( t_w \), and then the dynamics are followed as a function of the measurement time \( t \).

In both models, the effect of ageing can be immediately observed through the one-dimensional mean-squared displacement \( \langle \Delta x^2(t, t_w) \rangle \) shown in fig. 1, which exhibits three regimes: a short-time vibrational regime precedes a

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long plateau characterized by “caged” motion, followed
by a cage escape or α-relaxation regime. The cage escape
time increases with increasing $t_w$, but $\langle \Delta x(t, t_w)^2 \rangle$-curves for
different waiting times can be superimposed in the cage escape
regime by rescaling time with $t_w^\mu$. At long
times $t \gg t_w$, scaling of the mean-squared displacement
fails for both models, and curves for the different ages
merge. Experimental creep compliance curves show the
same behavior, which is a well-known consequence of
subaging ($\mu < 1$) [7].

We proceed to analyze the intermittent dynamics in
these systems by decomposing single-particle trajectories
into discrete hopping events. To investigate the hopping
dynamics, a subset of five thousand particle trajectories
are recorded. A running average of the atom position and
its standard deviation is found for each atom over a
small time window of 400 (40 individual snapshots of
the particle positions)\(^1\). A hop is identified when the
standard deviation $\sigma$ is greater than a threshold of $2(\sigma)$
(see footnote \(^2\)). This method differs from the usual
technique of identifying hops via a threshold in the hop
distance \([5,21,22]\), and effectively captures hops at all
length scales through their increased activity during the
relaxation event. While the correlation factor between
hops is nearly zero, approximately 10\% of hops are either
forward or backward correlated. Removing these hops does
not affect the results.

Figure 2 shows a typical atomic trajectory with the hops
identified using this criterion. The initial hop times $t_1$, the
times between all subsequent hops $\tau$, also called the

\(^1\)The choice of time window affects the width of the resulting
displacement distribution and the normalization constant of the
Persistence time distribution, but the slope of the Persistence time
and the distribution of first hop times are unaffected.

\(^2\)Increasing the threshold broadens both hop time and displacement
distributions; however, thresholds in a range of 1.5 to 2.5
give self-consistent results for the mean-squared displacement in the
continuous-time random walk. A threshold of two was chosen as a
compromise between resolving ageing and reducing noise.

![Figure 1: (Colour on-line) Mean-squared displacement for (a) the
binary Lennard-Jones mixture ($T = 0.33$) and (b) the polymer
model ($T = 0.25$) for waiting times $t_w = 750, 2250, 7500, 22500,$
and 75000 (left to right). From superposition in the cage escape
regime we deduce $\mu = 0.51$ for the Lennard-Jones mixture and
$\mu = 0.62$ for the polymer model. In the polymer model the
terminal slope is smaller due to Rouse dynamics.](image1)

![Figure 2: (Colour on-line) Displacement (red/gray) and standard
deviation (black) from the running average of a typical atomic
trajectory in the polymer model (results are similar for the
Lennard-Jones mixture). The threshold in the standard deviation
used for identifying hops is indicated by a horizontal
dashed line. The times where hops are identified are indicated
by vertical dashed lines.](image2)
In this formulation, $\mathcal{T}$ is either a constant (exponential density of states), or more realistically [23–25], a slowly varying function of time (Gaussian density of states) [26]. We do not observe any curvature in $p(\tau)$, but cannot rule out its existence at longer time scales. While our results clearly show subageing behavior, the ageing exponent in the trap model is strictly unity [26]. However, this holds true only in the limit $t_w \to \infty$. We have observed that depending on the quench conditions, there can be a long-lived transient regime where correlation functions approximately scale with an ageing exponent $\mu < 1$.

To confirm that our analysis captures all important physics, we recompute the ageing dynamics through stochastic realizations of a continuous time random walk (CTRW) using the measured hop distributions $p(t_1, t_w)$, $p(\tau)$ and $p(dx)$ as input. An ensemble of ten thousand random walk trajectories is constructed, where each trajectory is composed of a sequence of hop times and displacements chosen randomly from the measured distributions. The initial displacement is chosen such that the mean-squared displacement coincides with the MD data at the shortest measured relaxation time. This is slightly higher than the actual vibrational amplitude, but accounts for relaxations which occur at times down to the vibrational time scale, but could not be captured otherwise. For the polymer model, a pure random walk is insufficient as the chain connectivity induces subdiffusive Rouse dynamics. The mean-squared displacement of the atoms as a function of the number of hops $n$ is found to be $(\Delta x^2) \sim n^{1/2}$ ($(\Delta x^2) \sim n$ for the binary mixture). In the CTRW, the Rouse behaviour is accounted for by choosing a new particle position from a Gaussian distribution widening as $n^{1/2}$ at every step. This procedure creates the proper displacement statistics.

The full distribution of displacements (van Hove function)
\[
G_s(x, t, t_w) = \langle \delta(x - |x_i(t, t_w) - x_i(0, t_w)|) \rangle
\]
as well as the mean-squared displacements obtained from the CTRW trajectories are compared with MD data in fig. 4 for the polymer model. As time progresses, a Gaussian caged peak at small displacements loses particles to widening exponential tails. The origin of the exponential tails has recently generated intense interest, as they appear to be a universal feature of structural glasses [22,28–31]. The wide distribution of persistence times indicates that relaxation processes occur on all time scales, thus our simulations of the CTRW naturally produce non-Gaussian tails in the van Hove function.

The CTRW reproduces the true ageing dynamics exceedingly well, with no fit parameters. The same conclusion holds for the binary mixture. As in the trap model, the power law form of $p(\tau)$ is sufficient to generate ageing. Distributions $p(t_1, t_w)$ evolved via the CTRW from the shortest waiting time alone closely track measured distributions. Ageing emerges here as a self-generating,
functions display the same behavior reported in ref. [12]. The superposition of the van Hove and van Hove functions are dominated by the distribution of hop times and displacements. Inset shows the agreement between the mean-squared displacement from MD (lines) and CTRW (symbols) at $t_w = 750$, 7500, and 75000 (left to right).

Fig. 4: (Colour on-line) Van Hove function for the polymer model at $t_w = 75000$, and times of 400, 4000, 40000, 40000 (left to right). Solid lines are molecular-dynamics data and symbols are the results of the CTRW parameterized with the measured distributions. Inset shows the agreement between the mean-squared displacement from MD (lines) and CTRW (symbols) at $t_w = 750$, 7500, and 75000 (left to right).

A dynamical phenomenon, resulting from the fact that the mean persistence time is infinite in the thermodynamic limit. Another consequence of the wide distribution of $p(\tau)$ is anomalous, subdiffusive behavior at long times (see fig. 1) [32].

Our results clearly show that there are two relevant time scales in the relaxation dynamics of the glass: the first hop time which experiences ageing, and the subsequent hop times which are $t_w$ independent. This would seem to refute the hypothesis that the dynamics are universally reparameterized with waiting time as has been suggested for spin glasses [12], and may serve to explain some deviations from local dynamical scaling that have been observed. In ref. [12], the authors note that the distribution of spatially coarse-grained (local) incoherent scattering functions of a binary Lennard-Jones glass superimposes to first order at different waiting times when compared at times where the global correlation function $C_{global}(t, t_w)$ (averaged over the entire system) is equal. However, good collapse was found only for large and small global correlation with significant deviations for mid-values of $C_{global}$.

We further investigate the local dynamical scaling by using the CTRW model to calculate the van Hove distribution for three waiting times and three different values of the mean-squared displacement in fig. 5. Note that here $p(t_1, t_w)$ is generated by evolving the system directly in the ageing CTRW. The superposition of the van Hove functions displays the same behavior reported in ref. [12]. At short times (large $C$), the van Hove functions closely superimpose at times of equal mean. In this regime, few atoms have hopped and their mean-squared displacement and van Hove function are dominated by the distribution $p(t_1, t_w)$, which scales with $t_w$. For the mid-range of the correlation functions, the overlap of the van Hove functions becomes weaker. The long-waiting-time distributions have a sharper trapped peak and wider tails than the short-$t_w$ function. This is due to the fact that the width of the tails is controlled by $p(\tau)$, whereas the height of the caged peak is controlled by $p(t_1, t_w)$. At very long times $t \gg t_w$ (small $C$), the mean number of hops per atom is much greater than one, and the waiting-time–independent behavior begins to dominate the dynamics. In this case, the mean-squared displacement curves merge and there is trivial superposition of the van Hove functions.

To summarize, we have presented a complete characterization of particle diffusion in ageing structural glasses. We find that on a microscopic level, time is not simply reparameterized during ageing. Only the first hop time depends on the waiting time, and the particle subsequently “forgets” its age. The evolution of the first hop time distributions is remarkably close to that assumed in the trap model with annealed disorder. Although this model is a rather abstract picture of glassy dynamics, our results indicate that it may be closer to physical reality on a single-particle level than previously thought. An explicit mapping of the MD data onto a CTRW with measured distributions of hop times and displacements is able to completely reproduce all dynamical features of the relaxing glass, and provides an explanation for the scaling with $t_w$ and small deviations thereof.

Fig. 5: (Colour on-line) Van Hove functions from ageing CTRWs at three different waiting times 750 (solid), 7500 (dotted), and 75000 (dashed) plotted at times $t$ where $(\Delta x^2) = 0.3, 0.1$, and 3 as indicated by horizontal lines in the inset. For these values, the correlation function $C(t, t_w) = \langle \exp(7.2i[x(t_w + t) - x(t_w))]\rangle \approx 0.65, 0.3, \text{ and } 0.1$. Data is generated from the distributions $p(t_1, t_w = 0) = t_1^{-1.2}$ and $p(\tau) = \tau^{-1.2}$.

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