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Abstract
We examine structural relaxation in a supercooled glass-forming liquid simulated by
constant-energy constant-volume (*NVE*) molecular dynamics. Time correlations of the total
kinetic energy fluctuations are used as a comprehensive measure of the system's approach to the
ergodic equilibrium. We find that, under cooling, the total structural relaxation becomes delayed
as compared with the decay of the component of the intermediate scattering function
corresponding to the main peak of the structure factor. This observation can be explained by
collective movements of particles preserving many-body structural correlations within compact
three-dimensional (3D) cooperatively rearranging regions.

Understanding the microscopic mechanisms of the super-Arrhenius slowing down in fragile glass-forming liquids [1] remains a major problem in condensed-matter physics [2, 3]. It is understood that below the temperature T_A that marks the crossover to super-Arrhenius behaviour, liquid dynamics is controlled by the topography of the potential energy-landscape (PEL) [4]. The PEL is known to be divided into metabasins—areas of PEL confining sets of mutually well-connected local energy minima [5]. Inter-metabasin transitions, mediating the (primary) α-relaxation, involve uncorrelated movements of large groups of particles [6]. On a shorter timescale, confinement to a metabasin imposes structural constraints upon the atomic motions, reducing the number of accessible degrees of freedom. This renders intra-metabasin dynamics highly collective, in accordance with the Adam–Gibbs concept of independent cooperatively rearranging regions (CRR) [7].

The geometry and dynamics of CRR remain elusive. By definition [7], a CRR is a minimum-sized region of structure possessing a relaxational degree of freedom independent of the region's environment. It was suggested [8] that this degree of freedom can be associated with a coherent linear translation of a string-like cluster of particles within a slowly changing structural environment [9]. On the other hand, the random first-order transition theory of glasses [10] predicts a transition, at some stage of the liquid's cooling, from a string-like shape of CRR to a compact one. The concept of a compact CRR presumes that there exists a relaxational degree of freedom that makes it possible for a 3D configuration of particles confined to that CRR to perform a cooperative movement that would preserve some of the many-body structural correlations constraining the configuration.

A distinctive aspect of the relaxation dynamics associated with compact CRR is that the described cooperative 3D movements of particles are expected to result in decorrelation of the density fluctuations while preserving slower-decaying many-body structural correlations. The relaxation of the density fluctuations is described by the intermediate scattering function $F(Q, t)$ [11]. Its slowest-decaying component (within the relevant range of Q) corresponds to Q_m—the position of the main maximum of the structure factor $S(Q)$. In the case of cooperative 3D particle movements within compact CRR, $F(Q_m, t)$ is expected to decay well before the total liquid's structural relaxation has been accomplished. This can be understood using the following simple model. Consider slowly relaxing structural domains (clusters) immersed in a faster relaxing liquid. Let the clusters perform uncorrelated rotational and translational movements. It is easy to see that $F(Q_m, t)$ for such a model would decay well before the clusters dissipate as structural entities.

Detecting the described effect requires the use of a comprehensive measure of the structural relaxation that would be independent of the dissipation of density fluctuations. In this paper, we report a molecular dynamics (MD) simulation of a fragile glass-forming liquid where the structural relaxation is measured by the time correlations of the fluctuations of the system's total kinetic energy. We find that, as the liquid is cooled sufficiently close to the mode-coupling theory (MCT) [12] critical temperature T_c, its total structural relaxation becomes delayed as compared with the respective decay of $F(Q_m, t)$. This anomaly can be interpreted as an indication of the existence of slowly dissipating many-body correlations constraining the movements of cooperatively rearranging 3D groups of particles. These groups can be identified with compact CRR.

The MD simulation we report here explores a fragile simple one-component glass-forming liquid demonstrating a pronounced tendency for icosahedral clustering [13] (named Z2 in that reference), with the estimated $T_c = 0.65$, fragility index $B = 4.5$, and $T_A = 1.1$. For each temperature, an equilibrium simulation in an NVE ensemble was performed using a system of 16 384 particles. A system of 128 000 particles was also tried, and no size-dependent effects have been observed.

Consider a system of N particles in an NVE ensemble. Using the expression for the isometric heat capacity [14, 15], its entropy s can be linked to the variance of the kinetic energy k (both per particle):

$$c_v^{-1} = \frac{1}{T}\left(\frac{\partial s}{\partial T}\right)_V^{-1} = \frac{2}{3} - N\frac{\langle k^2 \rangle - \langle k \rangle^2}{\langle k \rangle^2}. \quad (1)$$

The respective expression for the entropy explored by the system within the time interval t, $s(t)$, [16], will be:

$$\frac{1}{T}\left(\frac{\partial s(t)}{\partial T}\right)_V^{-1} = \frac{2}{3} - N\frac{\langle \langle k^2 \rangle_t - \langle k \rangle_t^2 \rangle}{\langle k \rangle^2} \quad (2)$$

where $\langle \ \rangle_t$ denotes averaging over the time interval t. The system's approach to the ergodic equilibrium can be comprehensively assessed as the difference between the two quantities [17]:

$$\Omega(t) = \frac{1}{T}\left[\left(\frac{\partial s}{\partial T}\right)_V^{-1} - \left(\frac{\partial s(t)}{\partial T}\right)_V^{-1}\right] = N\frac{\langle k \rangle^2 - \langle \langle k \rangle_t^2 \rangle}{\langle k \rangle^2}. \quad (3)$$

Note that $\Omega(t)$ is a formal analogue of an earlier suggested measure of ergodic convergence [18] calculated from the time-dependent variance of the *single* particle energy. Following the arguments presented in that work, it is also possible to conclude that the large-t asymptotic behaviour of $\Omega(t)$ can be described as

$$\Omega(t)/\Omega(0) = \frac{\langle k \rangle^2 - \langle \langle k \rangle_t^2 \rangle}{\langle k \rangle^2 - \langle k^2 \rangle} \longrightarrow \frac{\tau}{t}, \qquad t \to \infty \quad (4)$$

where

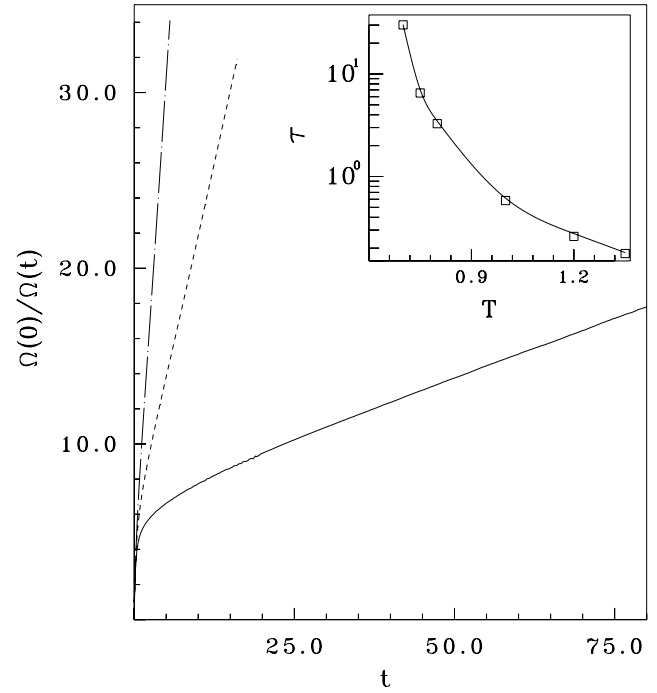$$\tau = 2\int_0^\infty \mathrm{d}t \, c(t)/c(0) \quad (5)$$

Figure 1. Asymptotic behaviour of $\Omega(t)$ as predicted by equation (4). Solid line, $T = 0.75$; dashed line, $T = 1$; chain-dotted line, $T = 1.35$. Inset: solid line, τ as evaluated from the asymptotic slope of $\Omega(0)/\Omega(t)$, defined in equation (4); boxes, τ calculated by integrating $c(t)$, defined in equation (5).

and $c(t)$ is the time correlation function for the system's total kinetic energy fluctuations:

$$c(t) = \langle \delta k(t)\delta k(0)\rangle \quad (6)$$

with $\delta k(t) = k(t) - \langle k \rangle$. This asymptotic behaviour of $\Omega(t)$ is indeed observed in our MD simulations, both above and below T_A, see figure 1. The inset of that figure demonstrates the agreement between τ as evaluated from the asymptotic slope of $\Omega(0)/\Omega(t)$ (equation (4)), and that obtained by direct integration of the correlation function $c(t)$ (equation (5)).

Thus, the system's relaxation, as measured by $\Omega(t)$, is ultimately controlled by the decay of $c(t)$. The general structure of this correlation function is shown in figure 2. Its short-time behaviour (shown in the inset) is dominated by large-scale oscillations. The latter are evidently caused by particles' vibrations within the cages of their immediate neighbours, the frequency being determined by the mean-square force [19] with weak temperature dependence.

The described short-time behaviour of $c(t)$ obviously excludes the possibility of using its normalized integral τ, equation (5), which determines the decay rate of $\Omega(t)$, as an unambiguous measure of the liquid's relaxation rate. However, the initial oscillatory regime of $c(t)$ is distinct in time, and decoupled from the relaxational regime that follows it. The structural relaxation in the asymptotic α-regime can therefore be adequately measured by the long-time decay of $c(t)$. We remark that, above T_A, this longer-time relaxational evolution of $c(t)$, when presented as a function of the mean-square displacement, figure 2, demonstrates the standard
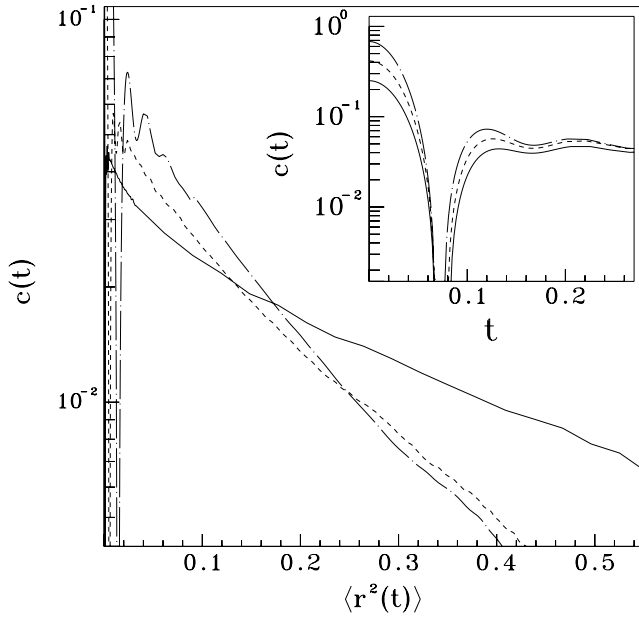
Figure 2. Evolution of the correlation function $c(t)$, as defined by equation (6), shown as a function of the mean-square displacement. Solid line, $T = 0.75$; dashed line, $T = 1.00$; chain-dotted line, $T = 1.35$. Inset: the short-time behaviour of the same curves. Note that in the inset they are shown as a function of time.

Figure 3. Structural relaxation in the temperature domain of supercooled liquid dynamics. Solid lines, $c(t)$; dashed lines, $F(Q_m, t)$; left and right curves, respectively, correspond to $T = 0.75$ and $T = 0.7$. Dots: the fits of the KWW stretched exponential approximation $A \exp[-(t/\tau)^\beta]$. The values of the fitting parameters are presented in table 1. All sets of data presented in the plot are scaled by the respective values of A.

Table 1. Parameters' values for the stretched exponential KWW fits to the relaxation functions shown in figure 3.

	T	A	$6D\tau$	β
$c(t)$	0.75	0.0393	0.71	0.96
$F(Q_m, t)$	0.75	0.72	0.71	0.96
$c(t)$	0.7	0.0557	1.02	0.75
$F(Q_m, t)$	0.7	0.72	1.02	0.865

liquid universality of the diffusion–relaxation relation. This universality evidently breaks below T_A.

We now exploit $c(t)$ for a detailed analysis of the α-relaxation process in the supercooled dynamics regime. In figure 3, the asymptotic behaviour of $c(t)$ is compared with that of $F(Q_m, t)$, for two temperatures below T_A. For convenience, both are plotted as a function of the mean-square displacement. To facilitate the comparative quantitative analysis, the correlation functions presented in figure 3 have been fitted, within the relevant domains of time, with the Kohlrausch–Williams–Watts (KWW) stretched exponential function $A \exp[-(t/\tau)^\beta]$ which we use here in the equivalent form $A \exp\{-[\langle r^2(t)\rangle/6D\tau]^\beta\}$, D being the diffusion coefficient. The parameters' values for the fits are compiled in table 1. Furthermore, to make it possible to compare the two kinds of correlation functions on an equal footing, each function has been scaled by the respective value of the KWW parameter A. Both $F(Q_m, t)$ and $c(t)$ appear to be well described by the KWW approximation within the α-relaxation time domain. The latter follows the initial stage of the relaxation process, confined to $\langle r^2(t)\rangle < 1$, that corresponds to conformational rearrangements of particles within the cage of the first neighbours.
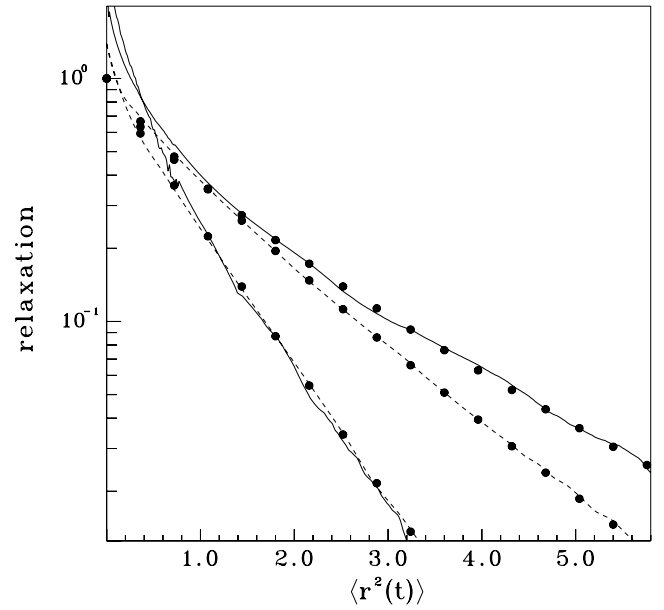
For $T = 0.75$, the asymptotic behaviour of the two correlation functions is indistinguishable, within the accuracy of the KWW fit[3]. However, as the liquid is cooled to $T = 0.7$, the asymptotic decay of $c(t)$ becomes considerably delayed as compared with the respective decay of $F(Q_m, t)$. We also note that the observed delayed decay of $c(t)$ is accounted for by a measurable reduction of the respective KWW stretching parameter β (table 1). The relaxation stretching, arising under cooling below T_A, is commonly viewed as a result of superposition of relaxation processes with an extended range of relaxation times. Thus, the additional relaxation stretching detected using $c(t)$ indicates an additional slow relaxation process not captured by $F(Q_m, t)$.

We remark that a system with a finite configurational entropy possesses a finite range of structural correlations. Therefore, the ergodicity-restoring structural relaxation in a liquid is a strictly local process. In the case of pair correlations, the correlation range r_c corresponds to a vanishing radial distribution function $g(r)$. Respectively, if relaxation of the pair correlations is considered in terms of $F(Q, t)$, the lowest Q relevant for the structural relaxation can be estimated as $Q_{min} = 2\pi/r_c$. The Q-dependent relaxation time of $F(Q, t)$ can be estimated from the structure factor $S(Q)$ [20] as $\tau(Q) = S(Q)/Q^2$. In a typical dense simple liquid [11] $S(Q_m)/S(Q_{min}) > (Q_m/Q_{min})^2$, and, therefore, $\tau(Q_m)$ is expected to exceed $\tau(Q_{min})$. In figure 4, we test this conjecture for the simulated liquid at $T = 0.7$. The figure shows that $g(r)$ apparently vanishes beyond $r_c = 10$, from which we estimate

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[3] The statistical accuracy of the correlation function $c(t)$ as shown in figure 4 required the averaging over the total simulation run of 10^9 timesteps.
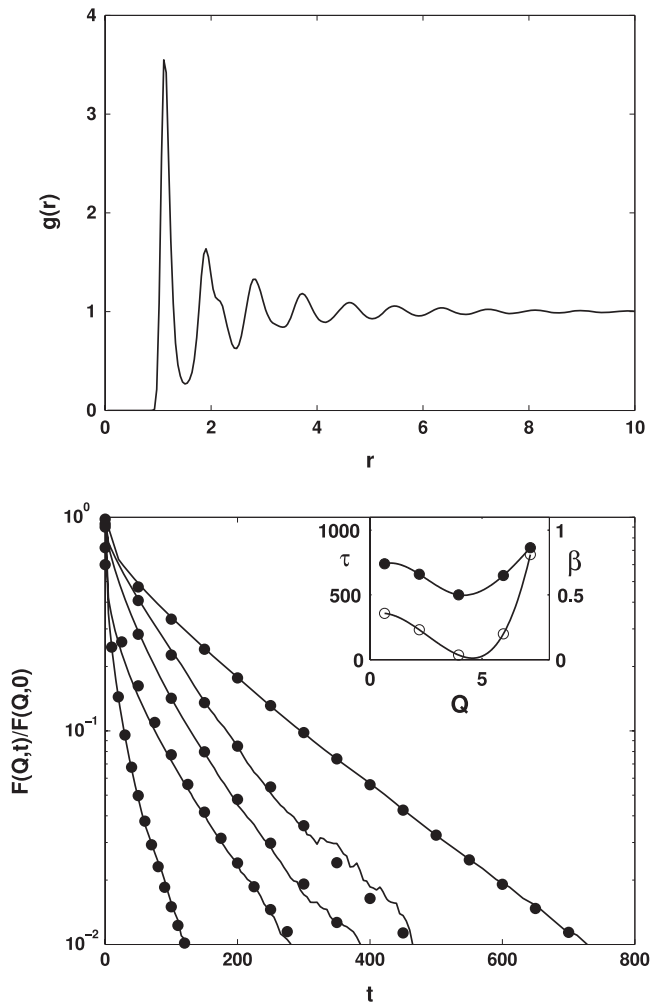
Figure 4. Top panel: radial distribution function for the simulated liquid at $T = 0.7$. Bottom panel: $F(Q, t)$. From left to right: $Q = 4, 6, 2, 0.6, 7.2$. Dots correspond to the fits of KWW. Inset shows the KWW parameters derived from the fitting. Open circles: τ (left-hand scale); dots: β (right-hand scale).

$Q_{min} \approx 0.6$. Relaxation of $F(Q, t)$ is analysed within the relevant range of Q bounded by Q_{min} and Q_m. For each value of Q, the decay of $F(Q, t)$ is quantified by the KWW fit; the Q variations of the resulting KWW parameters are shown in the inset. Evidently, $\tau(Q_m)$ is a pronounced absolute maximum within the explored range of Q, whereas β does not change significantly. Therefore, structural relaxation in our liquid at $T = 0.7$, in the pair approximation, is entirely controlled by $F(Q_m, t)$. This leads to the conclusion that the observed delay of the total structural relaxation relative to the decay of $F(Q_m, t)$ is due to the delay of the relaxation of higher-order correlations relative to that of pair correlations.

The main peak of $S(Q)$ is linked to the local order (cages of nearest neighbours). Therefore, one reason for the decay of $F(Q_m, t)$ can be a comprehensive dissipation of the local order due to uncorrelated particle motions. But it can also be caused by collective particle movements preserving the higher-order structural correlations. This will delay the total structural relaxation relative to the decay of $F(Q_m, t)$ as we observe for $T = 0.7$. The increase in the life-time of these structural

correlations can be attributed to a rapid buildup of locally preferred structure that is expected upon cooling the liquid towards T_c. This transformation in the relaxation dynamics can be interpreted as a crossover to the regime of compact CRR as conjectured in [10].

The locally preferred structure in this system is icosahedral. Like an earlier studied liquid with a similar structure [21, 22], it demonstrates a strong tendency for a low-dimensional icosahedral aggregation [13] growing towards percolation as $T \rightarrow T_c$. Relative mobility of these structural elements can be conjectured as a conceivable reason for the decoupling between $c(t)$ and $F(Q_m, t)$. As a corroborating observation, the anomalous decay of $F(Q_m, t)$ reported here can be compared with a related Q-dependent anomaly in the non-ergodicity parameter in a supercooled low-density liquid approaching gelation transition [23] caused by a percolating cluster network. Compact 3D CRR were also found below T_c in the binary Lennard-Jones (BLJ) system [24] and NiZr [25], and bond-preserving movements of structural domains were observed at a saddle point crossing of the BLJ system [26]. On the other hand, a study of the frequency-dependent specific heat in silica [27], also based on the analysis of the kinetic energy fluctuations, showed no discrepancy between the relaxation of these fluctuations and the decay of the *self part* of $F(Q, t)$.

We note that, because of the particles' indistinguishability, the structural correlations can survive particles' exchange induced by vacancy hopping. Therefore, the slow energy fluctuations we report here cannot be necessarily associated with breaking bonds connecting the nearest neighbours. The vacancy-assisted particle hopping, common in supercooled liquids, significantly complicates the problem of identifying the groups of particles involved in the conjectured compact CRR dynamics.

One of the consequences of compact CRR concerns the relaxation of shear stress. The liquid can possibly accommodate the shear strain and relax the induced stress by a mutual rearrangement of slowly relaxing clusters [28] before their internal structure has dissipated. Thus, shear stress relaxation in a supercooled liquid, like the dissipation of the local density fluctuations as measured by $F(Q_m, t)$, does not necessarily imply structural relaxation.

In summary, we found a novel aspect of the supercooled liquid dynamics manifested by the advanced decay of $F(Q_m, t)$ relative to the actual structural relaxation. The latter has been assessed from the decay of the time correlations of the system's total kinetic energy fluctuations. The observed effect can be interpreted as being caused by the cooperative movements of particles constrained by slowly decaying many-body structural correlations within compact CRR which appear as the liquid is cooled close to T_c. The observed transformation in the relaxation mechanism can be regarded as a result of the metabasin topography of the PEL of our model.

Acknowledgments

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