

## Decoupling of Diffusion from Structural Relaxation and Spatial Heterogeneity in a Supercooled Simple Liquid

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(Received 22 November 2001; published 16 October 2002)

We report a molecular dynamics simulation of a simple monatomic glass-forming liquid. It is shown that transition to deeper minima in the energy landscape under supercooling results in the formation of icosahedrally structured domains with distinctly slow diffusion which grow with cooling in a low-dimensional manner and percolate around  $T_c$ , the critical temperature of the mode-coupling theory. Simultaneously, a sharp slowing down of the structural relaxation relative to diffusion is observed. It is concluded that this effect cannot be accounted for by the spatial variation in atomic mobility. The low-dimensional clustering is discussed as a possible mechanism of fragility.

DOI: 10.1103/PhysRevLett.89.195701

PACS numbers: 64.70.Pf, 02.70.Ns

Fragile liquids [1], having been cooled below a characteristic temperature  $T_A$ , which is typically close to the melting point, undergo a transition to the supercooled dynamics regime with super-Arrhenius slowing down and stretched-exponential relaxation. Mode-coupling theory [2] appears only to be successful in interpreting early stages of supercooled dynamics. Further cooling results in a fundamental transformation of the liquid state that has not yet been comprehended in terms of theoretical models [3]. This transformation is manifested by three principal phenomena observed in the vicinity of the glass transition point  $T_g$ : (i) the liquid undergoes a structural transformation shifting to the area of its energy landscape with deeper minima [4]; (ii) a long-range slowly relaxing spatial heterogeneity arises [5] that is observed as formation of structurally [6] and dynamically [7] distinct long-lived domains; and (iii) a new type of liquid dynamics develops where the structural relaxation becomes retarded relative to the translational diffusion, thus breaking the Stokes-Einstein relation [8]. It appears sensible to ask whether these three observations represent different aspects of the same phenomenon, and, if so, what its primary mechanism is.

Here, we address these questions in a molecular dynamics simulation examining the structural and dynamical aspects of a simple monatomic liquid in a strongly supercooled equilibrium state. The model comprises 16 000 particles interacting via a pair potential [9] designed to favor icosahedral order in the first coordination shell. In this way, the liquid imitates the structure of simple metallic glass formers [10]. Sufficiently long relaxation under supercooling transforms it into a dodecahedral quasicrystal [11]; but, due to its exceeding complexity, this transformation can be delayed, keeping the liquid in a metastable supercooled state on a time scale that allows us to explore its essential dynamical properties [12]. The potential and all the quantities computed here are expressed in terms of the Lennard-Jones reduced units. We cool the liquid towards the glass tran-

sition at a constant density  $\rho = 0.85$  in a stepwise manner, equilibrating it at each temperature point.

The temperature variation of the self-diffusion coefficient is shown in Fig. 1(a). A clear transition to the supercooled dynamics regime marked by the onset of super-Arrhenius behavior occurs at  $T_A = 0.8$ . This is accompanied by a pronounced stretched-exponential relaxation [12]. We analyze the energy landscape transformation under cooling by performing the steepest descent energy minimization of the instantaneous liquid configurations [13] producing the so-called inherent structure (IS) configurations [14]. In spite of the dramatic drop of diffusivity between  $T = 1$  and  $T = 0.3$ , the respective IS radial distribution functions shown in Fig. 1(b) indicate only a marginal change of the local order. Nevertheless, the IS energy [Fig. 2(a)], remaining almost constant at higher temperatures, decreases as the liquid is cooled below  $T_A$ . A similar effect was observed in a supercooled two-component Lennard-Jones liquid [4].

The principal issue that we address in this study concerns the effect that the energy landscape transformation as indicated by the reduction of IS energy has on the liquid dynamics. In this context, we investigate two dynamical anomalies mentioned above: spatial variation in atomic mobility and breaking the Stokes-Einstein relation. It is intuitively clear that the former must be intimately connected with the structural heterogeneity. It was suggested [15] that a liquid approaching  $T_g$  develops extensive domains of distinct structure based on the energy-favored local order incompatible with periodicity, which is apparently icosahedral in the present case. A detailed investigation of the evolution of icosahedral order in this system under cooling can be found elsewhere [9,13]; its results essential for the present analysis are shown in Fig. 2. The number of icosahedrally coordinated atoms, Fig. 2(b), remains almost temperature independent for  $T > T_A$  and grows rapidly with cooling below  $T_A$ . This clearly correlates with the behavior of the IS energy in Fig. 2(a), indicating that the lower-energy minima in

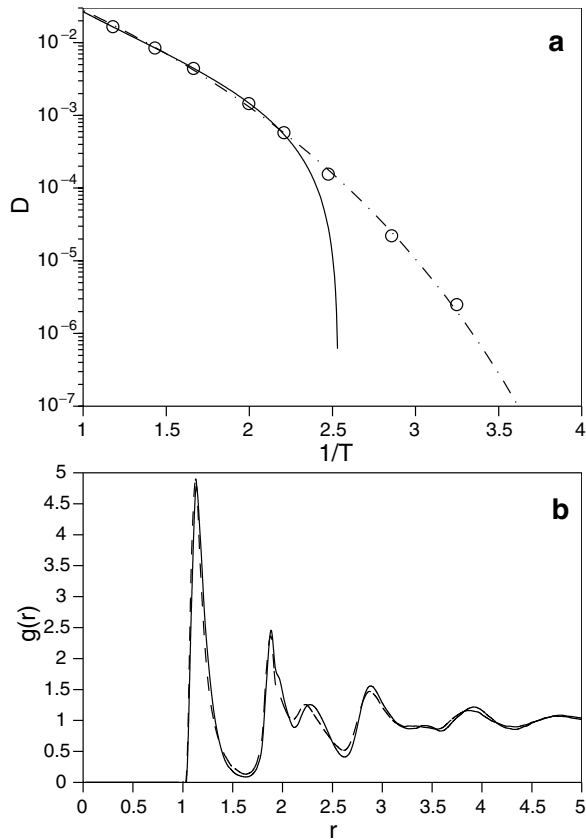


FIG. 1. (a) Circles: temperature variation of the diffusion coefficient  $D$ . Solid line is a fit of the equation:  $D = A(T - T_c)^\gamma$ , yielding the mode-coupling theory critical temperature  $T_c = 0.39$ . Chain-dashed line is the fit of Vogel-Fulcher-Tammann law:  $D = D_0 \exp[BT_0/(T - T_0)]$ , with  $T_0 = 0.17$  and  $B = 9.14$ . (b) Radial distribution functions for two IS configurations. Solid line:  $T = 0.3$ ; dashed line:  $T = 1.0$ .

the energy landscape that the liquid occupies in the supercooled state are associated with icosahedral order.

Figure 2(c) shows the temperature variation of the maximum size of continuous aggregations of connected icosahedra (it is assumed that two icosahedra sharing at least three atoms are connected). These low-energy configurations possess a higher mechanical stability than other configurations arising in the liquid. The pattern in Fig. 2(c) is consistent with those shown in Figs. 2(a) and 2(b). The cluster size remains temperature independent above  $T_A$  and grows rapidly with cooling below  $T_A$ , diverging around  $T_c$  where connected icosahedra form a percolating network. We also note that the onset of percolation reduces the temperature variations of both the number of icosahedra and the IS energy.

The growth of a continuous bulk aggregation of icosahedrally coordinated atoms in a flat 3D space is limited by the rapidly increasing strain energy caused by geometric frustration. Here, the unlimited size of the icosahedral clusters is a result of low-dimensional growth. An example demonstrating this tendency—a cluster of 716 atoms detected at  $T = 0.45$ —is shown in

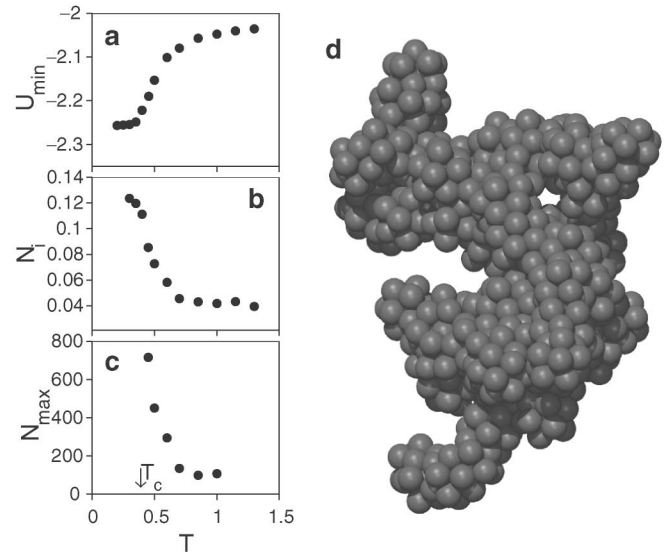


FIG. 2. (a) Temperature variation of the IS energy, per atom. (b) Temperature variation of the relative number of atoms with icosahedral coordination (we assume two atoms separated by a distance of less than 1.5 to be neighbors). (c) Temperature variation of the maximum size of the icosahedral cluster. The error bars, as estimated from three independent runs, are within the dots size. (d) An icosahedral cluster of 716 atoms detected at  $T = 0.45$ . Note that its size exceeds the range of structural correlations, Fig. 1(b).

Fig. 2(d). The icosahedral clusters with low-dimensional geometry were observed in the global energy-minima analysis of this system [16]. This analysis also demonstrated that the effect of low-dimensional icosahedral aggregation is destroyed by a variation of the pair potential [17]. It is worth noting that, although icosahedral coordination was found to be ubiquitous for the energy-minima clusters of the Lennard-Jones system [18], in agreement with an earlier study [19], these clusters demonstrate a distinctly bulk pattern of aggregation.

This structural heterogeneity is accompanied by the dynamical heterogeneity. In Fig. 3, the mean-square displacement (MSD) for the atoms initially situated inside the icosahedral domains is compared with that for the initially external atoms with nonicosahedral environments. As the domain size grows under cooling, the latter group of atoms becomes increasingly more mobile than the former one. These results are consistent with earlier observations associating low mobility domains in supercooled liquids with lower energy and higher degree of local ordering [20,21].

Next, we investigate the relation between diffusion and structural relaxation. The rate of ergodicity-restoring structural relaxation can be assessed by comparing the time average of a local variable with its ensemble average [22,23]. If  $u_i$  is the potential energy of atom  $i$ , the respective measure for a system of  $N$  atoms is

$$\Omega_u(t) = \frac{1}{N} \sum_{i=1}^N \left[ \frac{1}{t} \int_0^t u_i(s) ds - \langle u_i \rangle \right]^2, \quad (1)$$

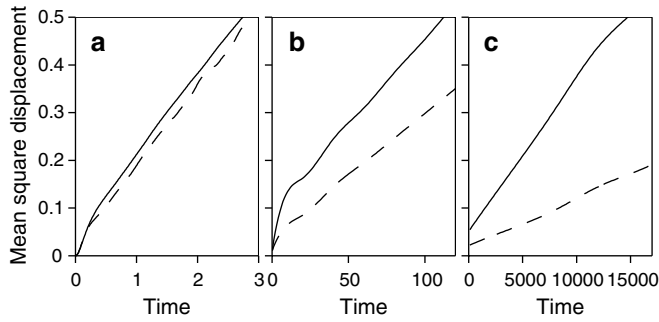


FIG. 3. The impact of the structural heterogeneity on diffusion. Dashed lines and solid lines, respectively: MSD for the atoms that initially had icosahedral coordination and that for the rest of the system. (a)  $T = 1.0$ , (b)  $T = 0.45$ , and (c)  $T = 0.3$ .

where  $\langle \rangle$  denotes the ensemble average. This measure decays with time [23] as:

$$\Omega_u(t) = \Omega_0/D_u t, \quad (2)$$

where  $D_u$  is a constant, and  $\tau = D_u^{-1}$  can be regarded as characteristic relaxation time. Figure 4(b) shows the temperature variation of  $D_u/D$  [the latter was estimated from the slope of asymptotically linear variation of  $\Omega_u^{-1}$  as a function of MSD, Fig. 4(a)]. It remains constant in the stable liquid domain and decreases rapidly as the liquid is cooled below  $T_A$ . The steepest variation of  $D_u/D$  occurs around  $T_c$ ; a tendency for saturation observed in the  $T_g$  area possibly indicates that the system remains nonequibrated. This pattern is thus perfectly consistent with the temperature variations of the IS energy and the domain structure shown in Fig. 2.

Two distinct aspects of dynamical heterogeneity are commonly discussed in relation with breaking the Stokes-Einstein relation [24]. One model [25] explains the latter anomaly as a direct result of the existence of spatial domains with distinctly different rate of atomic mobility. It conjectures that the translational diffusion is mostly confined to the “fast” domains, while the structural relaxation (viscosity) is controlled by the reduced mobility in the “slow” domains; at the same time, the dynamics in each separate domain is assumed to be adequately described by the Stokes-Einstein relation [8]. We note that, although the spatial variation in atomic mobility is found in the present study, Fig. 3, the scale of this effect is by more than an order of magnitude smaller than that of the relaxation-diffusion decoupling in Fig. 4. This observation clearly demonstrates that, even in the domains with lowest atomic mobility, diffusion becomes strongly enhanced with respect to structural relaxation, which is obviously inconsistent with the above model.

Another aspect of dynamical heterogeneity that has been conjectured to explain the Stokes-Einstein breaking is dynamical cooperativity [26]. We present here some arguments in favor of this conjecture. First, we have to understand why diffusivity and the rate of structural re-

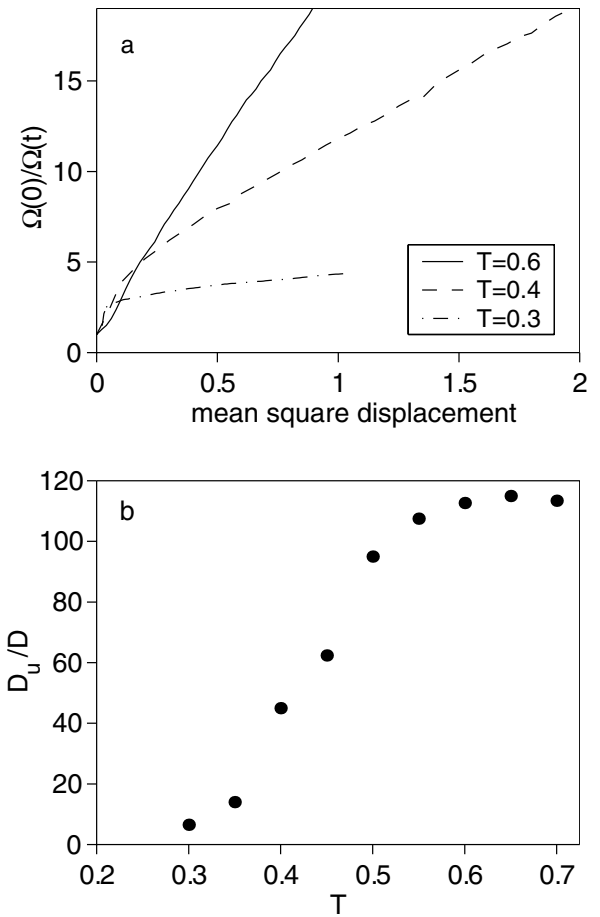


FIG. 4. (a)  $\Omega_u^{-1}$  as a function of MSD. (b) Temperature variation of  $D_u/D$ . The latter is obtained as the slope of asymptotically linear variation of  $\Omega_u^{-1}$  as a function of MSD. Note that at  $T = 0.3$  the system is apparently nonequibrated.

laxation remain universally connected in the stable liquid state. Let us consider a coarse-grained configuration-space trajectory of a liquid system with a certain finite value of MSD per an elementary step. We assume that the relaxation process of a stable liquid represents a random walk in the configuration space constrained by the ensemble-averaged structural correlations. This assumption implies that as a result of an elementary step the system can, with equal probability, be found in any available configuration-space point within the indicated MSD range from its initial position (availability implies that the configuration is allowed by the equilibrium ensemble-averaged structural correlations) [27]. It is clear that the ratio of the average number of available configurations that the system can access in a relaxation step with a fixed MSD to the total number of available configurations remains constant within the domain of stable liquid state where the above assumption is assumed to be valid. On the other hand, this ratio can be regarded as a measure of the relaxation rate if time is expressed in terms of MSD.

Next, we assume that the relaxation process is additionally constrained by time-limited correlations complementary to the ensemble-average equilibrium

structural correlations. These additional correlations are characteristic of the supercooled liquid state; they can be observed both as positional correlations in the form of a transient domain structure discussed above and as a long-range dynamical cooperativity [28]. In this case, the system in its elementary relaxation step cannot access all the available configuration points within the respective MSD range. As a result, diffusion becomes enhanced with respect to the structural relaxation. The magnitude of this effect is apparently controlled by the scale of the described time-limited complementary correlations. Indeed, the dramatic decrease of  $D_u/D$  in Fig. 4 clearly correlates with the divergence of the correlation length associated with cluster percolation at  $T = T_c$  [Fig. 2(c)].

In conclusion, the results presented here connect the profound change in the liquid's behavior at  $1.2T_g \approx T_c$  to the transformation of its residence area on the energy landscape. The coherently structured domains associated with low-energy minima which are occupied in the supercooled regime represent free-energy barriers dividing the phase space into components [29]. In this landscape, the ergodicity-restoring relaxation is facilitated by strongly correlated atomic motions [30] which, as we have shown, are inefficient in exploring the configuration space. We note that the percolation of icosahedral order observed here resembles the picture of rigidity percolation in bonded glass formers [31]. An interesting question that can be addressed in a separate study is whether this percolation occurs at the same temperature as the percolation transition for the higher-mobility domains which too was found around  $T_c$  [20]. Another remark concerns a possible connection between the domain geometry and fragility. The latter is related to the steepness of the slowing down of structural relaxation relative to diffusion shown in Fig. 4 which is concluded to be controlled by the domain growth rate. The low-dimensional domain geometry avoids the inherent geometric frustration that limits the bulk growth of domain structure and, in this way, facilitates rapid increase of the domain size. Therefore, it could conceivably be regarded as a generic feature of the fragile glass formers. Indeed, structurally and dynamically distinct low-dimensional domains have been found in a supercooled two-component Lennard-Jones liquid [7,19].

We thank C. A. Angell, S. R. Elliott, and D. J. Wales for valuable comments. We used VMD software [32]. This study was supported by Swedish Research Council (VR).

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