Role of Unstable Directions in the Equilibrium and Aging Dynamics of Supercooled Liquids

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The connectivity of the potential energy landscape in supercooled atomic liquids is investigated through a calculation of the instantaneous normal modes spectrum and a detailed analysis of the unstable directions in configuration space. We confirm the hypothesis that the mode-coupling critical temperature is the T at which the dynamics crosses over from free to activated exploration of configuration space. We also observe changes in the local connectivity of configuration space sampled during aging, following a temperature jump from a liquid to a glassy state.

Understanding the microscopic mechanism for the incredible slowing down of the dynamics in supercooled glass forming liquids is one of the hot topics in condensed matter physics. In recent years, the combined effort of high level experimental techniques [1], computational analysis [2,3], and sophisticated theoretical approaches [4–6] has provided an enormous amount of novel information. In particular, it appears more and more clearly that in addition to the melting temperature and the calorimetric glass transition temperature, T_g, another temperature plays a relevant role. This temperature, located between 1.2 and 2 T_g depending on the fragility of the liquid, signals a definitive change in the microscopic processes leading to structural relaxation. Mode coupling theory (MCT) [4] was first in identifying the role of this crossover temperature, T_c. According to MCT, for $T \geq T_c$ the molecular dynamics is controlled by the statistics of the orbits in phase space [4,7], while below T_c, the dynamics becomes controlled by phonon assisted processes [4]. Studies based on disordered mean field p-spin models have also stressed the role of such a crossover temperature [8].

Computer simulation studies of realistic models of liquids have addressed the issue of the structure of configuration space in supercooled states [3]. Two different techniques have provided relevant information on phase space structure: the instantaneous normal mode approach (INM) [9], which focuses on the properties of the finite temperature Hessian, allowing the calculation of the curvature of the potential energy surface (PES) along $3N$ independent directions, and (ii) the inherent structure (IS) approach [10], which focuses on the local minima of the potential energy. Different from mean field models, computer simulation analysis provides a description based on the system's potential energy, the free energy entering only via the equilibrium set of analyzed configurations.

In principle, the INM approach should be well suited for detecting a change in the structure of the PES visited above and below T_c. A plot of the T dependence of the fraction of directions in configuration space with negative (unstable) curvature, f_u, should reveal the presence of T_c. Unfortunately, as it was soon found out [11], anharmonic effects play a non-negligible role and several of the negative curvature directions are observed even in crystalline states, where diffusivity is negligible. A similar situation is seen in p-spin models, where the number of negative eigenvalues of the Hessian is not zero at T_c [12]. Bembenek and Laird [13] suggested inspecting the energy profile along the unstable directions to partition the negative eigenmodes in shoulder modes (sh) (i.e., anharmonic effects) and double-well (dw) modes (i.e., directions connecting different basins). While for a particular molecular system the fraction of double-well modes f_{dw} has been shown to go to zero close to T_c [14], for atomic system, f_{dw} is significantly different from zero even in crystalline and glassy states [13]. The existence of dw directions in thermodynamic conditions where the diffusivity is zero, i.e., in situations where the system is constrained in a well-defined basin, strongly suggests that the two minima joined by the unstable double-well directions may lead to the same inherent structure IS. Such a possibility has been demonstrated very clearly in Ref. [15].

The aim of this Letter is to present a detailed evaluation of: (i) the number of escape directions, N_{escape}, leading to a basin *different* from the starting one; (ii) the number of distinct basins, N_{distinct}, which are connected on average to each configuration via a dw direction. This analysis, based on a computationally demanding procedure, shows that indeed the PES regions visited in thermal equilibrium above and below T_c are clearly different. We also study the evolution of the sampled PES as a function of time following a quench from above to below T_c. We show that, in analogy with the equilibrium case, two qualitatively different dynamical regimes exist during aging, related to different properties of the sampled PES.

The system we study is composed of a binary (80:20) mixture of $N = 1000$ Lennard Jones atoms [16]. The dynamics of this system is well described by MCT, with a critical temperature T_c equal to 0.435 [17].

We begin by considering the equilibrium case. At each T, for each of the 50 analyzed configurations, we calculate the INM spectrum and—by rebuilding the potential energy profile along straight paths following directions

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with negative curvature—we classify the unstable modes into dw and sh. It is important to notice that the classification is done by studying the shape of the PES along one eigenvector, i.e., beyond the point in configuration space where the eigenvector was calculated. In principle, to identify a dw or a sh mode, one should follow a curvilinear path. Indeed, the use of straight paths guarantees only the identification of the dw modes whose one-dimensional saddle energy is close to the potential energy of the system. As discussed in more length in [18] those dw modes are the ones relevant for describing motion in configuration space.

Figure 1 shows the T dependence of the unstable and dw modes for the studied system. In agreement with the analogous calculation of Ref. [13], even at the lowest temperature where equilibration is feasible within our computer facilities, f_{dw} is significantly different from zero. To estimate roughly the number of double wells which do not contribute to diffusion, we have calculated the IS associated with the $T = 0.446$ equilibrium configurations, and we have heated them back to various temperatures below T_c. The corresponding f_u and f_{dw} are also shown in Fig. 1. Both of these quantities depend linearly on the temperature. If we extrapolate f_{dw} for the equilibrium and for these nondiffusive cases, we find that the two curves cross close to the MCT critical temperature T_c. Thus T_c seems to be the temperature at which the number of directions leading to different basins goes to zero, leaving only local activated processes as residual channels for structural relaxation [19].

To estimate in a less ambiguous way the number of different basins which can be accessed from each configuration we apply the following procedure: (i) calculate the dw directions via INM calculation; (ii) follow each straight dw direction climbing over the potential energy barrier and down on the other side until a new minimum is found;
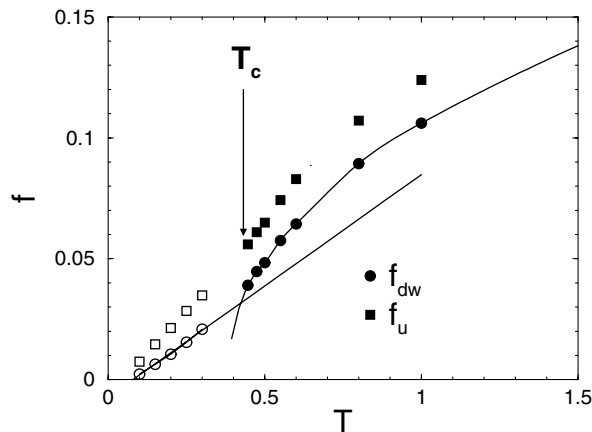

FIG. 1. T dependence of f_u (squares) and f_{dw} (circles). The filled symbols are calculated from equilibrium configurations, the empty symbols from out-of-equilibrium configurations below T_c (see text).

(iii) perform a steepest descent path starting from the new minimum found along the dw direction, as first suggested by Gezelter et al. [15]; (iv) save the resulting IS configuration; (v) repeat (ii)–(iv) for each dw mode. This procedure produces a list of ISs which can be reached from the initial configuration crossing a one-dimensional dw. We note that our procedure guarantees only that the two starting configurations for the quenches are on different sides of the double well, since—as discussed in [18]—there is some arbitrariness in the location of the two minima.

We calculate the relative distance d_{ij}

$$d_{ij} = \sqrt{\frac{1}{N} \sum_{l=1}^{N} (x_l^i - x_l^j)^2 + (y_l^i - y_l^j)^2 + (z_l^i - z_l^j)^2}$$

(1)

between all IS pairs in the list to determine the number of *distinct* basins, $N_{distinct}$, connected to the starting configuration. Here x_m^k, y_m^k, and z_m^k are the coordinates of the mth particle in the kth IS of the list (IS$_k$). We also calculate the distance d_{0i}—where 0 indicates the IS associated to the starting configuration—to enumerate the number of escape directions, N_{escape}, leading to a basin different from the original one (IS$_0$).

In Fig. 2 (upper panel) we show a plot of the distributions of the distances d_{0i} between the starting IS and the minima identified with this procedure for different temperatures. At high temperatures, the distribution has a single peak centered approximately at $d = 0.3$. For lower temperatures, the peak moves to the left and decreases in height. At the same time, a second but distinct peak, centered around $d \approx 10^{-4}$, appears. Since our sample is composed of 1000 particles, an average distance of the order of 10^{-4} means that, also in the case that only one particle has a different position between the two different configurations, this particle has moved less than 0.003 interparticle distance. Thus, we consider the IS i and j as coincident if $d_{ij} < 10^{-2.5}$.

The upper panel of Fig. 3 reports the T dependence of the number of dw directions N_{dw}, the number of escape directions, and the number of distinct basins which can be reached by following a dw direction. We find that at high temperature nearly all dw directions lead to a different IS, thus fully contributing to the diffusion process. On lowering the temperature, a large fraction of the directions leads to the same minimum, and, close to T_c, almost all dw directions lead to intrabasin motion. A basin change becomes a rare event. Data in Fig. 3 support the view that T_c is associated to a change in the PES sampled by the system, and, consequently, in the type of dynamics that the system experiences. Above T_c the system can change basins in configuration space by moving freely along an accessible dw direction, while below T_c the thermally driven exploration of configuration space favors the exploration of the interior of the basins. Diffusion in configuration space, i.e., basin changes, requires a local activated process.
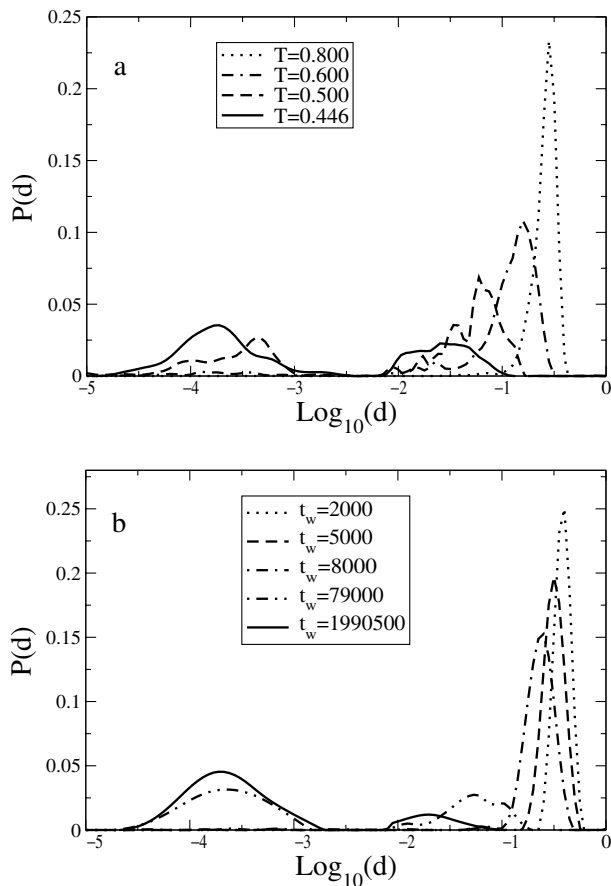
FIG. 2. (a) Distribution of the distances $d \equiv d_{0i}$ between the IS 0 and the ith IS from equilibrium configurations at different temperatures; (b) same quantity for different t_w values during the aging process after a temperature jump from $T_i = 5.0$ to $T_f = 0.2$.
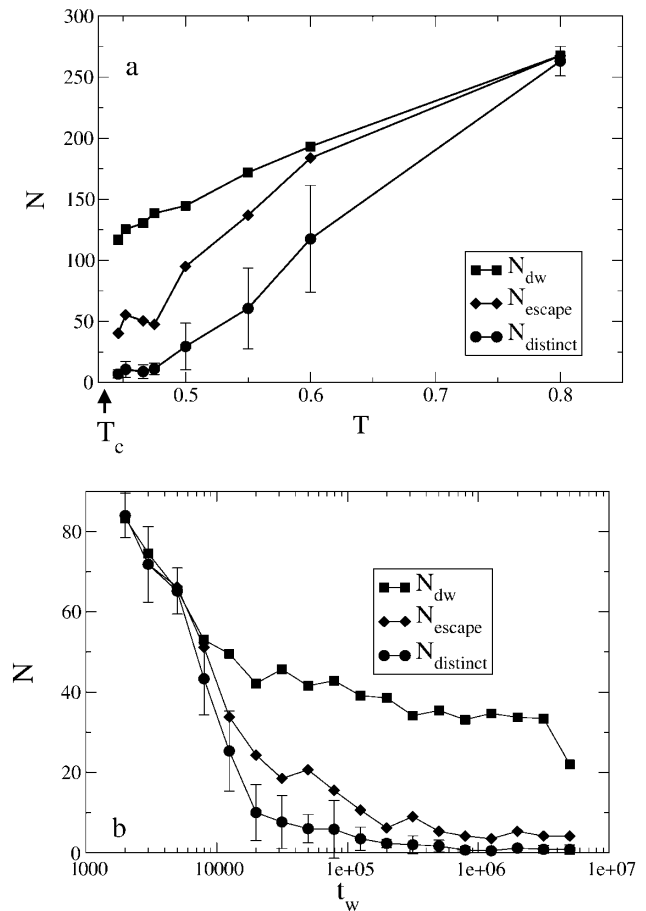

FIG. 3. (a) Number of double wells N_{dw}, of escape directions N_{escape}, and of distinct basins $N_{distinct}$ for equilibrium configurations as a function of T; (b) Same quantities for different t_w values after a temperature jump from $T_i = 5.0$ to $T_f = 0.2$. Time is measured in molecular dynamics steps.

We next turn to the study of out-of-equilibrium dynamics. Configurations are equilibrated at high temperature ($T = 5.0$) and at time $t_w = 0$ are brought to low temperature $T_f = 0.2$ by instantaneously changing the control temperature of the thermostat. Within 100 molecular dynamics steps, the kinetic energy of the system reaches the value corresponding to T_f. Configurations are recorded for different waiting times t_w after the quench. We then repeat the same analysis done for the equilibrium configurations, as described before.

Figure 2 (lower panel) shows the distribution of the distances d_{0i} between the minima IS_0 and IS_i. For short t_w the distribution has a single peak centered approximately at $d_{0i} = 0.3$, as found in the equilibrium configurations at high temperature. As the system ages, the peak shifts to smaller distances and a second distinct broad peak centered at approximately $d_{0i} = 5 \times 10^{-4}$ appears. The observed behavior is similar to the equilibrium one, on substituting T with t_w.

The lower panel of Fig. 3 shows N_{dw}, N_{escape}, and $N_{distinct}$ as functions of t_w. At small t_w, following a double well direction always brings to a basin that is dis-

tinct from the original one, while at long times all dw directions lead to intrabasin motion. Again, the behavior is very reminiscent of the equilibrium one, on substituting T with t_w. From these results, we suggest that two qualitatively different dynamical processes control the aging processes, respectively, for short and long t_w [20]. For short waiting times the system is always close to saddle points that allow it to move from one basin to a distinct one. As the system ages, it is confined to wells that are deeper and deeper, and the number of basins that it can visit by following a dw direction decays to zero. Thus, for long t_w the dynamics of aging proceeds through local activated processes that allow the system to pass over potential energy barriers. As shown in Fig. 3, beyond $t_w = 10^5$ the number of distinct basins is almost zero, which, in analogy with the equilibrium results, supports the view that a crossover from MCT-like dynamics to hopping dynamics may take place at a crossover time during the aging process.

In summary, this Letter confirms the hypothesis that T_c can be considered as the T at which dynamics crosses over

from the free exploration to the locally activated exploration of configuration space. In this respect, the analogy between the slowing down of dynamics of liquids and the slowing down of the dynamics in mean field p-spin model is strengthened. This Letter also shows that changes in dynamical processes associated with changes in the explored local connectivity of configuration space are observed even during the aging process, in the time window accessed by molecular dynamics experiments. MCT-based models of aging [21] could be able to describe the early part of the aging process—i.e., the saddle-dominated dynamics—but may not be adequate for describing the locally activated dynamical region.

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[18] Motion along a straight direction in configuration space will always be associated with a fast rise of the energy profile, since every direction will always describe pairs of atoms moving close enough to probe the repulsive part of the pair potentials [11]. In systems with steep repulsive potentials, such an unphysical rise of the potential energy profile along the straight eigenmode direction sets in very early. In other words, the eigenvector direction changes very rapidly as the system moves in configuration space and very soon the energy profile differs from the profile evaluated along the straight eigenvector approximation. The major effects of such an artificial rise in energy are [11] (i) the transformation of dw direction in sh directions and (ii) the arbitrary location of the two minima along the dw direction and the extremely low value of the one-dimensional barriers along the dw. In particular, effect (i) sets in when, in the studied direction, the system is located far from the saddle and effect (ii) sets in when the system is located close to the saddle point [T. Keyes and W.-X. Li, J. Chem. Phys. **111**, 5503 (1999)]. Notwithstanding these potential pitfalls in the classification procedure, the classification helps in understanding the dynamical changes taking place in the liquid as a function of T and ρ. Indeed the only saddles which are relevant for the dynamical behavior of the system are the ones which are explored by the system, i.e., the ones located in a potential energy range $V \pm \Delta V$—where V is the average potential energy of the system and ΔV is a measure of the potential energy fluctuations. The accessed saddles are included in the type (ii) classification in the above list. As a result, the classification performed along straight directions retains its validity, even if no physical meaning can be attributed to the calculated one-dimensional energy profile. Of course, it would be more appropriate to recalculate the eigenvectors at each step and follow the curved one-dimensional energy profile. Such a procedure could still suffer from the frequent mode-crossing events which are known to characterize the liquid dynamics [M. Buchener and T. Dorfmüller, J. Mol. Liq. **65/66**, 157 (1995)].

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