Connected Network of Minima as a Model Glass: Long Time Dynamics

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A simple model to investigate the long time dynamics of glass formers is presented and applied to study a Lennard-Jones system in supercooled and glassy phases. According to our model, the point representing the system in the configurational phase space performs harmonic vibrations around (and activated jumps between) minima pertaining to a connected network. Exploiting the model, in agreement with the experimental results, we find evidence for (i) stretched relaxational dynamics, (ii) a strong T dependence of the stretching parameter, and (iii) breakdown of the Stokes-Einstein law. [S0031-9007(98)07786-2]

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In recent years many efforts were devoted to the understanding of the phase space landscape in supercooled liquids and structural glasses, and, in particular, to the identification of those landscape details that are responsible for the structural arrest taking place at the glass transition temperature T_g [1,2]. It has been recently speculated [3] that the free energy landscape of structural glasses is similar to that of some generalized spin glass models. It was shown that in these systems there exists a dynamical temperature T_D (which is well defined in mean field approximation and becomes a crossover region in real systems) at which the spin dynamics is subject to a critical slowing down. Below T_D the residual, extremely slow, dynamics is dominated by long time activated processes consisting of jumps among different free energy minima. A similar situation holds in the case of structural glasses. Here, according to the mode coupling theory of the glass transition [4], a critical temperature (T_C) exists, which marks the freezing of the local molecular structure. Below T_C the hopping processes control the diffusive dynamics. This parallel supports the conjecture that also in structural glasses the description of the dynamics slowing down can be done in term of free energy landscape (FEL).

The numerical investigation of the dynamics of supercooled liquids and glasses, and their link with the FEL, is very hard due to the presence, approaching T_C, of this very slow dynamics. More important, one has to face the frustrating situation that the simple model systems where the theories are well developed [as, for example, the Lennard-Jones (LJ) systems] cannot be undercooled down to T_C because crystallization starts a few degrees below the melting temperature T_M.

In this Letter we introduce an alternative method to study the slow dynamics in glasses and in deeply supercooled liquids; at variance with the usual molecular dynamics (MD) simulation, we describe the dynamics of the system as relaxation taking place in a connected network of potential energy minima. The jumps among minima are described by an appropriate master equation,

and, in this way, (i) we can investigate the long time behavior of a glass in short simulation times since the solution of the master equation is an eigenvalue problem and (ii) we can avoid crystallization as the crystalline minima are eliminated from the network. At variance with previous approaches [5], the characteristics and connectivity of the minima, and other energy-landscape properties entering the determination of the transition probabilities, are inferred from the MD investigation of a small system (one component LJ in the present case). The physical quantities (total energy, pressure, transport coefficient) obtained from the model agree with those derived from MD up to temperatures above the melting point, supporting the jump model even in the liquid phase of LJ fluids. In the low temperature region we find evidence for (i) stretched behavior of the relaxation process, (ii) temperature dependence of the stretching exponent, β_K, which changes from ≈ 1 at high T down to ≈ 0.3 at low T, and (iii) breakdown of the Stokes-Einstein relation. All of these results are in agreement with the experimental findings in non-network forming glasses, and, in particular, in those glasses that are "fragile" according to Angell's definition [6].

In a glass, the atoms are (almost) frozen in some (meta)stable positions. The short time dynamics is dominated by small vibrations around the stable position. This dynamics can be described within the harmonic approximation, and all of the relevant information is obtained by diagonalizing the dynamical matrix [7]. At long times, collective jumps among different stable positions involving many atoms become possible and are controlled by a master equation, whose elements, the transition rates, are determined by minima energies, barrier heights and other topological properties along the path.

In order to set up the connected network of minima and determine the transition rates, we need the topology of the multidimensional potential energy hypersurface of the system. To this end, we numerically analyze the potential energy landscape (PEL) of small ($N = 11-29$ atoms) LJ

systems with periodic boundary conditions. The small size of the system allows an exhaustive investigation of the landscape and, at the same time, exhibits complex enough features and behavior to capture the physics of the system. The atoms interact via the 6–12 LJ potential $V_{LJ}(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6]$, with $\epsilon/k_B = 125.2$ K (k_B, Boltzmann constant) and $\sigma = 0.3405$ nm, appropriate for argon. The simulated density is $\rho = 42 \times 10^{-3}$ mol/cm^3.

The first step is to search for the potential energy minima. We use a modified steepest descent method [8], starting from high temperature MD configurations to find the inherent configurations corresponding to local minima which are often crystallinelike. In order to establish whether a minimum corresponds to a glassy structure, we use the static structure factor $S(\vec{q}) = N^{-1}|\sum_j e^{i\vec{q}\cdot\vec{r}_j}|^2$. For a pure crystalline configuration of N particles, $S(q)$ is made up of "Bragg" peaks and its value at the peaks is $S_{max} = N$, whereas for a glass one usually finds $S_{max} \approx 2$–3. In small size samples there are obviously intermediate situations, and for a minimum to be "glassy" we adopt the criterion $S_{max} \leq N/2$.

As a second step, for each pair of minima a and b with energy E_a and E_b, respectively, we first determine the mutual distance $d_{a,b} = \min(|\underline{r}_a - \underline{r}_b|)$, where $\underline{r}_a$ is the position vector of the minima in the $3N$ dimension configurational space, and min indicates the minimization with respect to all symmetry operations: continuous translations, permutations of particles, and the 48 symmetry operations of the cubic group. We then analyze the potential energy profile experienced by the system in traveling from one minimum to another and determine the potential energy barrier. Among the different paths joining a and b, we assume [8] that the system follows that with the least action. The action integral is defined as $S(\ell) = \int_\ell ds\sqrt{V(\underline{r}(s)) - V_0}$, where ℓ indicates a generic path, s is the curvilinear coordinate, and $V_0 = \min\{E_a, E_b\}$. The minimization of $S(\ell)$ is performed by dividing the path into $n = 16$ intervals and minimizing the action function with respect to the extrema of the n segments constrained to move in hyperplanes perpendicular to the straight path. The highest energy value, V_{ab}, along the least action path (LAP) determines the saddle point of the path. Not all of the pairs of minima are directly connected, since, sometimes, the LAP joining them crosses a third minimum. Therefore, there is a nontrivially connected network of minima. Next, we measure the curvature, defined as the determinant of the Hessian of potential energy function, in each minimum $a(\det\{V_a''\})$, and a-b saddle point $(\det\{V_{ab}''\})$. Also important is the absolute value of the negative curvature on the saddle point, $\tilde{\omega}_{ab}$.

In order to give a full statistical description of the PEL, we study the distributions, $P(x)$, of the relevant quantities x (here x represents E_a, $\Delta E_{ab} = E_a - E_b$, d_{ab}, V_{ab}, $\det\{V_a''\}$, $\det\{V_{ab}''\}$, or $\tilde{\omega}_{ab}$) and their cross correlations, $P(x_1, x_2)$. Cross correlations among the measured quantities are observed. The most evident is a linear correlation in double log scale between the distance and the barrier height along the LAP between two minima. A rather weak correlation is also observed between the energy and curvature of extrema points of PEL.

The model we introduce is a connected network of potential energy minima with a jump dynamics described by an appropriate master equation

$$\dot{p}_a(t) = \Sigma_c W_{ac} p_c(t), \qquad (1)$$

where $p_a(t)$ is the probability that the system is in minimum a at time t [actually, $p_a(t) \equiv p_a(t\,|\,b)$, indicating that at $t = 0$ the system was in minimum b] and the nondiagonal elements of the transition matrix, the transition rates W_{ab}, are determined from the energetic and topological properties of the PEL. In order to satisfy the equilibrium condition, $p_a^o \equiv p_a(t \to \infty) \propto (\det V_a'')^{-1/2}e^{-\beta E_a}$, with $\beta = (k_B T)^{-1}$, W_{ab} must obey the detailed balance $W_{ab} p_b^o = W_{ba} p_a^o$. Following [9] we make the ansatz

$$W_{ab} = \frac{\tilde{\omega}_{ab}^2}{\gamma}\left(\frac{\det V_b''}{|\det V_{ab}''|}\right)^{1/2} e^{-\beta(E_{ab} - E_b)}, \qquad (2)$$

where γ is a friction constant which determines the time scale. This choice of the transition matrix is based on the approximation of the problem of escape from a metastable state as a Markovian-Brownian d-dimensional motion in the overdamped friction regime [9].

To set up our model minima network, we proceed in the following way. Having fixed the number of minima ($M = 400$ in the present case), we extract the energy of these minima and their curvatures from the previously found bivariate distribution. For each minimum we randomly extract 20 minima connected to it and define a connection matrix c_{ab} that contains the number of steps required to go from a to b. We then define the distance d_{ab} as c_{ab} times the value extracted from the distribution of the distances $P(d_{ab})$, and from these the energies of saddle points. The further statistical features of saddle points (curvatures) and minima (transverse component of the microscopic stress tensor; see below) are determined from bivariate (correlation curvature-saddle-point energy) and simple extractions, respectively.

To check the reliability of the model, we first concentrate on the static properties. Following our model, the partition function is approximated by a sum over the minima and the harmonic vibrations around them:

$$\mathcal{Z}(\beta) = \beta^{-3N/2}\Sigma_a(\det V_a'')^{-1/2}e^{-\beta E_a}. \qquad (3)$$

In Fig. 1 we show the potential energy of a LJ system with $N = 29$ particles as obtained through MD and as calculated from (3) by taking into account either all minima (dotted line) or only the glassy ones (solid line). The MD data are obtained by progressively heating the glass (○) up to the liquid phase, and then cooling the system slowly (●), to obtain crystallization. We observe
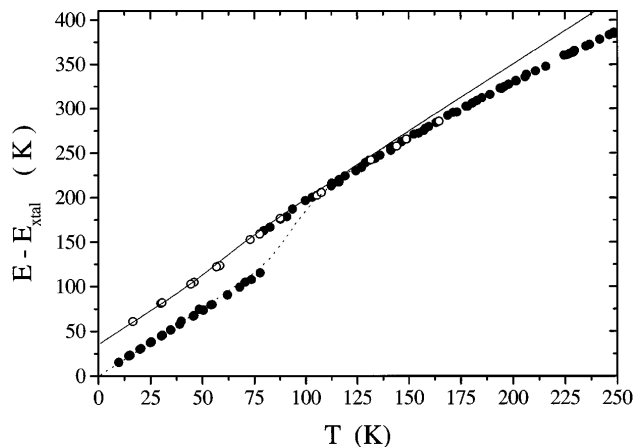
FIG. 1. Potential energy of the LJ system as determined from MD heating the glass (○) and cooling the liquid (●), and from the present model using all of the minima (dotted line) or only the glassy minima (solid line).
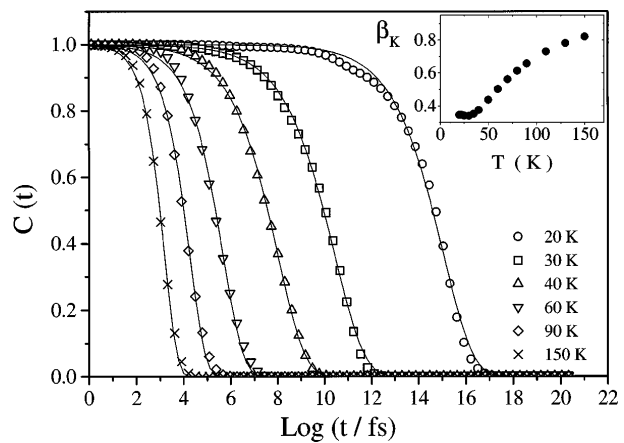

FIG. 2. Normalized autocorrelation functions of the off-diagonal elements of the stress tensor at the indicated temperatures as determined from the model (open symbols). The lines represent the best fits to the data with a stretched exponential time decay. The inset shows the T dependence of the stretching parameter β_K.

a quantitative agreement between the MD data and the model up to $T \approx 150$ K, a temperature well above the melting point ($T_m \approx 80$ K). At higher temperature the simple local-vibration/collective-jumps model fails.

As for the dynamical properties, the solution of the master equation is found by numerical knowledge of eigenvalues and eigenvectors of the transition matrix, $\lambda(n)$ and $v_a(n)$ respectively ($n = 1, \ldots, M$). In particular,

$$p_a(t \mid b) = (p_b^o)^{-1} \Sigma_n v_a(n) v_b(n) e^{\lambda(n)t}. \quad (4)$$

It is then possible to determine the statistical equilibrium average of a generic observable $O(t)$ from the knowledge of its value O_{ab} calculated at the minima a and b:

$$\langle O(t) \rangle = \Sigma_b p_b^o \Sigma_a O_{ab} p_a(t \mid b). \quad (5)$$

We consider three observables: the mass diffusion coefficient D, the shear viscosity η, and the structural relaxation time τ. In the first case $O_{ab} = |\underline{r}_a - \underline{r}_b|^2$, and $D = \lim_{t \to \infty} \langle O(t) \rangle / 6t$. For the two other cases, we first determine the correlation function of the off-diagonal elements of the stress tensor σ: $C(t) = \langle \sigma^{zx}(0) \sigma^{zx}(t) \rangle$ [10]. In the notation of Eq. (5), $O_{ab} = \sigma_a^{zx} \sigma_b^{zx}$ (where σ_a is the value of the stress tensor calculated at minimum a). The shear viscosity is then calculated as

$$\eta = (k_B T V)^{-1} \int_0^\infty dt\, C(t), \quad (6)$$

and the relaxation time τ is derived from a fit of $C(t)$ to a stretched exponential decay $C(t) = C(0) \exp -(t/\tau)^{\beta_K}$.

We report the values obtained for $M = 400$ and averaged over 50 different extractions of the network parameters. In Fig. 2 we show the normalized correlation functions $C(t)/C(0)$ calculated at different temperatures together with their best fits. In the inset, the T dependence of the stretching parameter β_K is also reported. We reiterate that our model reproduces only the slow dynamics of the glass forming liquids and glasses (the so-called α or structural relaxation process) and does not describe

the fast vibrational dynamics. This explains the presence of only one relaxation step in $C(t)$. We observe that (i) the relaxation dynamics is well represented by a stretched exponential decay, and (ii) the stretching parameter β_K is strongly temperature dependent. The stretching of the α process has been observed by MD in many systems (e.g., in LJ binary mixtures [11] and in more complex molecular liquids such as water [12]). In order to check our model against the "real" (MD) results in LJ fluids, we calculated the stress tensor correlation function $C(t)$ by MD simulation in the accessible T range ($T > 90$ K), and we fitted $C(t)$ to $A \exp(-t/\tau_1) + B \exp[-(t/\tau)^{\beta_K}]$ [the term proportional to A takes into accounts the fast decay of $C(t)$ that is present in the MD simulation]. The values of τ and β_K are consistent with those resulting from the model, and, as expected, τ_1 turns out to be temperature independent. The values of β_K, derived from the model down to 20 K, decrease from 1 at high T (Debye relaxation) down to ≈ 0.35 at low T, a value consistent with experimental findings [13] and theoretical prediction [14] in fragile glass formers.

In Fig. 3a we show the shear viscosity and the relaxation time τ versus inverse temperature. They are almost proportional to each other, strongly increasing in a small temperature range (150–20 K). However, their temperature behavior is well represented by an Arrhenius law, and does not show the dramatic increase expected for fragile glass formers. Whether this unexpected behavior (i) has to be ascribed to a failure of our model, or (ii) is a genuine behavior of LJ liquids at constant density, is still unknown. At those temperature where the direct MD calculation of η is affordable [(○) in Fig. 3a], we found a good agreement between MD and model results, supporting hypothesis (ii).

In Fig. 3b we report the inverse diffusion coefficient D^{-1} versus η/T. The Stokes-Einstein (SE) relation that
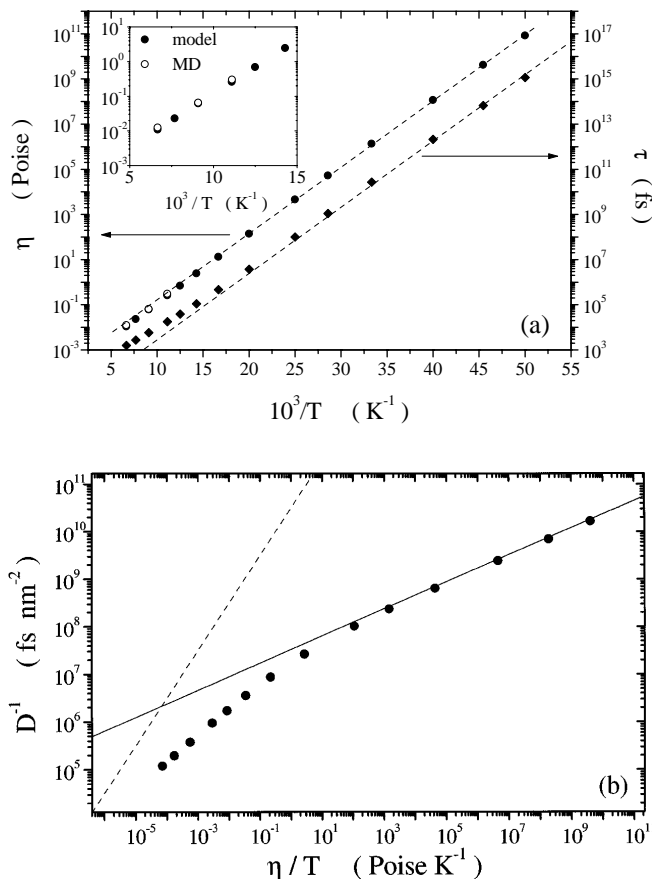
FIG. 3. (a) Shear viscosity and relaxation time versus inverse temperature. In the inset the viscosity data at low temperature are shown on an enlarged scale. (b) Inverse diffusion coefficient D^{-1} versus the ratio η/T. According to the Stokes-Einstein relation, a linear proportionality is expected (dashed line). The solid line, with slope 0.28, is the best fit to the low temperature data.

rigorously describes the diffusive motion of macroscopic objects in fluids and that reproduces also fairly well the diffusion at atomic scale in liquids at high temperatures predicts a direct proportionality, i.e., $D \propto T/\eta$. The dashed line (slope 1) indicates that, at high T, our model asymptotically satisfies the SE relation. Upon decreasing T, the slope ξ decreases down to $\xi \approx 0.28$, indicating a breakdown of the SE relation, as observed in different experiments [15]. In particular, the crossover between the two regimes occurs in the same temperature region where β_K deviates from 1. It is tempting to note that the crossover position at $\eta/T \approx 0.1$ Poise/K and the fractional exponent at low T, $\xi \approx 0.28$, are in fairly good agreement with the experimental results in the fragile glass former o-terphenyl [16,17].

In conclusion, we have presented a simplified model, based on a vibrational local dynamics and on collective jumps among minima, that well describes the structural relaxation features of supercooled liquids and glasses. Exploiting this model we were able to investigate the

long time (low temperature) dynamics. We recover, in the simple LJ system, some important features of a real glass former, in particular, (a) stretching of the relaxational dynamics, (b) temperature dependence of stretching parameter β_K, and (c) breakdown of the Stokes-Einstein relation.

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