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; iii) breakdown of the Stokes-Einstein relation.

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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, $T_g$. It has been recently speculated [1] that the free energy landscape of structural glasses is similar to that of some generalized spin glasses models, where it was shown that exists a dynamical temperature $T_D$ (which is well defined in mean field approximation and becomes a crossover region in real systems) below which the dynamics is dominated by long time activated processes consisting of jumps among different free energy minima. The parallel between $T_D$ and the critical temperature, $T_C$, of the mode coupling theory (MCT) is natural. If verified, this parallel could lead to a microscopic description of the dynamic slowing down, predicted by MCT, in term of free energy landscape. Approaching $T_C$ (or $T_D$), however, the presence of this very slow dynamics makes the numerical investigation of structural glasses very hard. To our knowledge, only few attempts were made in this direction.

In this letter we introduce a new 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 relaxations 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, we can investigate the long time behaviour of a glass in short simulation times as the solution of the master equation is an eigenvalue problem. 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 Lennard-Jones in the present case).

The physical quantities (total energy, pressure, transport coefficient) obtained from the model agree with those derived from MD up to temperature above the melting point, supporting the jump model even in the liquid phase of Lennard-Jones fluids. In the low temperature region we found evidence for: i) stretched behaviour of the relaxation process; ii) temperature dependence of the stretching exponent, $\beta_K$, which changes from $\approx 1$ at high $T$ down to $\approx 0.3$ at low $T$; and iii) breakdown of the Stokes-Einstein relation. All these results are in agreement with the experimental findings in real “fragile” glasses.

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 the relevant information is obtained by diagonalizing the dynamical matrix. At long time, collective jumps among different stable positions involving many atoms become possible and are controlled by a master equation. These long time relaxations are only apparently in contradiction with the harmonic vibrational dynamics within the local minima; indeed, it has been recently shown that the relevant classical path for relaxation between adjacent minima is practically decoupled from the other degrees of freedom, which are almost harmonic. The transition rates, in turn, are determined by minima energies, barrier heights and other topological properties.

In order to set up the connected network of minima and to determine the transition rates we need the topology of the multidimensional potential energy hypersurface of the system. To this end, we numerically analyse the Potential Energy Landscape (PEL) of small ($N = 11 \div 29$ atoms) Lennard-Jones systems with periodic boundary conditions. The small size of the system allows us an exhaustive investigation of the landscape but, at the same time, exhibits complex enough features and behaviour to capture the physics of the system. The atoms interact via the 6–12 Lennard-Jones potential $V_{LJ}(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}]$, with $\epsilon/K_B = 125.2$ K ($K_B$ Boltzmann’s constant) and $\sigma = 0.3405$ nm, appropriate for Argon. The simulated density is $\rho = 42$ mol/dm$^3$. Due to the
small dimensions of the system, we choose the multi-image method, namely each particle interacts with many images of each other (in practice, due to the cutoff distance that we impose on the pair potential, \( r_{\text{cut}} = 2.6 \sigma \), there are at most 3 interacting images).

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

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 \( d_{a,b} = \text{min}(|\mathbf{r}_a - \mathbf{r}_b|) \), where \( \mathbf{r}_a \) is the position vector of the minima in the \( 3N \) dimension configurational space, and \( \text{min} \) indicates the minimization with respect to all the symmetry operations: continuous translations, permutations of particles and the 48 symmetry operations of the cubic group. Then we analyse the potential energy profile experienced by the system in travelling from one minimum to another and determine the potential energy barrier. Among the different paths joining \( a \) and \( b \), we assume (ii) that the system follows that with the least action. The action integral is defined as \( S(t) = \int ds \sqrt{V(\mathbf{r}(s)) - V_0} \), where \( t \) indicates a generic path, \( s \) the curvilinear coordinate, and \( V_0 = \text{min}\{E_a, E_b\} \). The minimization of \( S(t) \) is performed by dividing the path in \( n = 16 \) intervals and minimizing the action function with respect to the extrema of the \( n \) segments constrained to move in interplanes perpendicular to the straigh path. The highest energy value, \( V_{ab} \), along the least action path (LAP) determines the saddle point of the path. Not all the pairs of minima are directly connected, since, sometimes, the LAP joining them crosses a third minimum. Therefore, there is a non-trivially connected network of minima. Next we measure the curvature, defined as the determinant of the Hessian of potential energy function, in each minimum \( a \) (\( \text{det}\{V_\alpha''\} \)), and \( a-b \) saddle point (\( \text{det}\{V_{ab}''\} \)). 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 \( E_a, \Delta E_{ab} = E_a - E_b, d_{ab}, V_{ab}, \text{det}\{V_a''\}, \text{det}\{V_{ab}''\} \), 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 barriers’ 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:

\[
\dot{p}_a(t) = \Sigma_b W_{ab} p_b(t),
\]

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 non-diagonal 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, \( p_a^0 = p_a(t \rightarrow \infty) \propto (\text{det} V_a'')^{-1/2} e^{-\beta E_a} \), with \( \beta = (k_B T)^{-1} \). \( W_{ab} \) must obey the detailed balance \( W_{ab} p_b^0 = W_{ba} p_a^0 \). Following (iii) we make the ansatz:

\[
W_{ab} = \frac{\omega_{ab}^2}{\gamma \left( \sqrt{\text{det} V_a''} / \sqrt{\text{det} V_{ab}''} \right)^{1/2}} e^{-\beta (E_a - E_b)},
\]

where \( \gamma \) is a friction constant which actually 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 multidimensional motion in the overdamped friction regime (iv).

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:

\[
Z(\beta) = \beta^{-3N/2} \Sigma_a (\text{det} V_a'')^{-1/2} e^{-\beta E_a}.
\]

In fig. 1 we show the potential energy of a LJ system with \( N = 29 \) particles as obtained through MD and as calculated from (iv) by taking into account either all minima (dotted line), or only the glassy ones (full line). The MD data are obtained progressively heating the glass (\( \phi \)) up to the liquid phase, and then cooling the system.
slowly (•), to obtain crystallization. We observe a quantitative agreement between the MD data and the model up to \( T \approx 150 \, \text{K} \), a temperature well above the melting point (\( T_m \approx 80 \, \text{K} \)). 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 \( v_a(n) \), with \( n = 1 \ldots M \). In particular:

\[
p_a(t|b) = \sum_n v_a(n) v_b(n) \frac{p_0^n}{p_0^b} e^{-\lambda(n)t}. \tag{4}
\]

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 \( b \):

\[
< O(t) > = \sum_b p_0^b \sum_a O_{ab} p_a(t|b). \tag{5}
\]

We consider three observables: the mass diffusion coefficient \( D \), the shear viscosity \( \eta \), and the structural relaxation time \( \tau \). In the first case \( O_{ab} = |L_a - L_b|^2 \), and \( D = \lim_{t \to \infty} < O(t) > /6t \). For the two other cases, we first determine the correlation function, of the off-diagonal elements of the stress tensor, \( C(t) =< \sigma^{zz}(0)\sigma^{zz}(t) > \), with \( \xi^z \):

\[
\sigma^{zz} = -\sum_{i>j} \frac{z_i x_{ij} x_{ij}}{r_{ij}} V^{\prime}(r_{ij}). \tag{6}
\]

In the notation of eq. (3), \( O_{ab} = \sigma^{zz}_a \sigma^{zz}_b \), (where \( \sigma_a \) is the value of the stress tensor calculated at minimum \( a \)). Then the shear viscosity is calculated as

\[
\eta = (K_B T V)^{-1} \int_0^\infty dt C(t), \tag{7}
\]

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

We report the values obtained for \( M = 400 \) and averaged over 50 different extraction 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 \( \beta_K \) is also reported. We remind that our model reproduces only the structural (a) relaxation processes usually explained in term of intra-basins transitions, at variance with other fast relaxation processes taking place inside the basins.

This explain the presence of only one step relaxation in \( C(t) \). We also observe that: i) the relaxation dynamics is well represented by a stretched exponential decay; and ii) the stretching parameter \( \beta_K \) is strongly temperature dependent, implying a violation of the time-temperature superposition principle [9]. Moreover \( \beta_K \) decreases from 1 at high \( T \) (Debye relaxation) down to \( \approx 0.35 \) at low \( T \), a value consistent with experimental findings [10] and theoretical prediction [11] in fragile glass-formers.

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

In fig. 3b we report the inverse diffusion coefficient, \( D^{-1} \), versus the ratio \( \eta/T \). The Stokes-Einstein (SE) relation would predict direct proportionality, i.e. \( D \propto T/\eta \). The full line (slope 1) indicates that, at high \( T \), the SE relation asimptotically holds. Upon decreasing \( T \), the slope \( \xi \) decrease towards \( \xi \approx 0.28 \), indicating a breakdown of the SE relation, as observed in different experiments [12]. In particular, the crossover between the two regimes occurs in the same temperature region where \( \beta_K \) deviates from 1. It is tempting to note that the crossover position, at \( \eta/T \approx 0.1 \, \text{Poise/K} \), 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 [13].

In conclusion, we 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 are able to investigate the long time (low temperatures) dynamics. We recover, in the simple LJ system, some important features of real glass-former, in particular: a) stretching of the relaxational dynamics; b) failure of the time-temperature superposition principle (T-dependence of \( \beta_K \)); and c) breakdown of the Stokes-Einstein relation.

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**CAPTIONS**

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 the minima (dotted line) or only the glassy minima (full line).

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

Fig. 3 - a) Shear viscosity and relaxation time versus inverse temperature. b) Inverse diffusion coefficient, $D^{-1}$, versus the ratio $\eta/T$. According to the Stokes-Einstein relation, a linear proportionality is expected (dashed line). The full line, with slope 0.28, is the best fit to the low temperature data.
Fig. 1 - Connected network of minima.... - Angelani et al.
Fig. 3a - Connected network of minima. - Angelani et al.
Fig. 3b - Connected network of minima... - Angelani et al.