Potential energy topology and relaxation processes in a model glass

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We use computer simulation to investigate the topology of the potential energy $V(\{R\})$ and to search for doublewell potential’s (DWP) in a model glass. By a sequence of Newtonian and dissipative dynamics we find different minima of $V(\{R\})$ and the energy profile along the least action paths joining them. At variance with previous suggestions, we find that the parameters describing the DWP’s are correlated among each others. Moreover, the trajectory of the system in the 3N-d configurational phase space follows a quasi-1-d manifold. The motion parallel to the path is characterized by jumps between minima, and is nearly uncorrelated from the orthogonal, harmonic, dynamics.

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Among many unanswered questions concerning the dynamics of topologically disordered materials, two are related to the low energy excitations. The first one regards the excitations responsible for the low temperature thermal properties of glasses. Since the pioneering works of Phillips [1] and Anderson et al. [2], who introduced the Two Level Systems (TLS) as the origin of the anomalous specific heat behaviour below 1 K, many works were devoted to identifying the degrees of freedom associated to the TLS in real glasses, but a definite answer has not yet been reached. The second question regards the excitations responsible for: (i) the thermal behavior in the $1\div10$ K region, where a plateau in the thermal conductivity and a peak in $c_p/T^3$ are observed [3]; and (ii) the boson peak appearing in the inelastic neutron scattering (INS) [4–6,11] and Raman spectra [7–11]. This second question is also largely unanswered, and different hypotheses on the nature of these excitations have been proposed, ranging from an excess of acoustic-like modes to highly anharmonic and localized excitations. A link between the above questions is suggested by the so-called Soft Potential Model (SPM) [12], which assumes the existence of few highly anharmonic degrees of freedom with a potential energy function described by a fourth order polynomial. The coefficients of the polynomial are supposed to be uncorrelated, and to give rise to a large variety of curves, including doublewell potentials (DWP’s). Among the DWP’s, those that are isolated, have low asymmetry and have barrier height resulting in a tunneling splitting around 1 K, are candidate to be TLS.

Computer Simulations (CS) of model glasses might help to answer the previous questions, and, in particular, to verify the existence of TLS and to clarify the nature of DWP in glasses. To our knowledge the direct CS inspection of the passage from minimum to minimum in glasses is limited to a few cases. Among them we mention the search for TLS performed by Stillinger and Weber [13] and by Heuer and Silbey [14,15]. The conclusions of these works can be summarized as follows: i) low barrier bistable degrees of freedom exist in binary glasses with considerable variation in their physical parameters (barrier height, asymmetry, minima distance, etc.); ii) these parameters are strongly correlated, DWP with large asymmetry typically have large barrier heights; iii) in agreement with SPM, the coefficients of the fourth order polynomial describing the potential energy of the reaction coordinate, are found to be uncorrelated; iv) using a factorized probability distribution function for these coefficients, it is possible to try an estimate of the number of TLS per atom; v) typically from 5 to 10 atoms participate in the motion in the DPW.

In this letter we investigate by CS the topology of the potential energy hypersurface of a Lennard-Jones glass with the aim to check whether the TLS can be observed in this system, the characteristics of the DWP’s, and the extent to which the harmonicity of the system is affected by the presence of DWP’s. We will discuss the procedures used to search the minima of $V(\{R\})$ and to identify the Reaction Coordinate (RC) and the Least Action Path (LAP) joining pairs of minima. The main conclusions of the present work are the following: a) no isolated doublewells are found in the system, i.e. in the investigated temperature range ($T > 5$ K) all the minima pertain to a network, and the thermally activated jumps among them are not controlled only by the energetic barriers, because, depending on temperature, a significant role is also played by the entropic term [16]. b) At variance with previous findings [14,15] (see item iii) above) and with the hypothesis at the base of the SPM [12] the coefficients of the polynomial representation of the energy profile felt by the RC, are found to be highly correlated. c) The degrees of freedom orthogonal to the LAP feel an almost harmonic potential, whose curvature is independent on the RC, i.e. on the position along the LAP itself.

We investigated a sample of $N = 864$ atoms interacting via the 6-12 Lennard-Jones potential, here we use $\epsilon/k_B = 125.2$ K and $\sigma = 0.3405$ nm, appropriate for Argon. A microcanonical molecular dynamics simulation [17] is carried out at the fixed density of 42 mol/dm$^3$, and at different temperatures $T$ ($T = 15, 12, 10, 7.5$ and $6$...
K). Each run consists of a sequence of newtonian and dissipative dynamics. The newtonian trajectory is followed for 1 ps (50 integration time steps), subsequently a modified steepest descent method procedure (relaxation-like dynamics) is applied to quench the system and to find the inherent configuration \( \{X_i\} \) \((i = 1...N)\), corresponding to a local minimum. The newtonian dynamics is then started from the same point in phase space where it was interrupted before the quenching, and the procedure is repeated up to 25,000 times for each temperature. The two minimum configurations obtained with successive quenching, \( \{X_i^a\} \) and \( \{X_i^b\} \), are often the same.

The adopted procedure ensures that different minima, when found, are close to each other in the 3N-d configurational space. About 130 different minima have been found in the present work: their energies are spread in an interval of about 1 J/mole centered at about 300 J/mole above the absolute minimum representing the crystal. All the minima belong to an inter-connected network and the system is observed to perform temporarily closed loop in the configurational phase space. In order to study the topopogy of the potential energy, and to find the easiest way to jump among neighbouring minima, a fast and efficient algorithm is developed to evaluate the Least Action Path (LAP). The LAP is determined as the path between \( X_i^a \) and \( X_i^b \) that minimize the classical action integral, \( \int_{X^b}^{X^a} ds \sqrt{V(R(s)) − V_0} \), with \( V_0 = \min \{ V(\{X_i^a\}), V(\{X_i^b\}) \} \). We studied \( \approx 100 \) pairs of minima, evaluating the LAP joining them; in Fig. 1a we compare the potential energy profile evaluated along the LAP with that along the straight path. Although the LAP is not very far from being straight in the configurational space, as shown in Fig. 1b, the potential energy along the LAP is significantly lower, making the LAP itself highly preferred for the jump among minima. Moreover, the present analysis shows that the derivation of the DWP properties from the profile of the potential energy along the straight path between minima gives unreliable results. The potential energy profile along the LAP between the minima \( a \) and \( b \) has been characterized by the energy difference between the two minima \( \Delta V_{ab} \), their euclidian distance \( D_{ab} \), the displacement of the atom that moves most \( d_{ab} = \max_i \{|X_i^a − X_i^b|\} \), the barrier height \( \Delta V_{ab} \) (measured with respect to the higher minimum) and finally by the number of participation, defined as \( P_{ab} = \sum_i |X_i^a − X_i^b|^2 / \sum_i |X_i^a − X_i^b|^4 \). It turns out that: \( i) \) the participation is always around 20; \( ii) \) among the 20 atoms involved in the jump, 1 or 2 account for 90% of the entire distance; \( iii) \) for each pair of minima \( \Delta V^m \) is always higher than \( \Delta V^b \).

Next we analyse the statistical correlation among the DWP’s parameters. In Fig. 2a we see that the different pairs of parameters that characterize the DWP are strongly correlated. To give a statistical significance to the correlation, for each pair of parameters we calculated the correlation coefficient \( r \). The values of \( r \), reported in the first part of Table I, indicate statistical correlation between the parameters (with \( n_{H/F} = 141 \), at the 5% of significance level, the threshold for correlation is \( r = 0.165 \)). Two other representations of the DWP are reported in the literature, these are the ”m” representation, used in the soft potential model [2], \( E = \epsilon (w_2(x/\sigma)^2 − w_3(x/\sigma)^3 + (x/\sigma)^4) \), and the ”w” representation introduced in ref. [3], \( E = \epsilon \left( w_3(x/\sigma)^2 − w_3(x/\sigma)^3 + w_4(x/\sigma)^4 \right) \). The SPM assumes that there is no correlation among the parameters of the set \( \{w_0, w_2, w_3\} \), while the authors of ref. [1], noticing the correlation of the \( u \) set, made use of the uncorrelation among \( \{w_2, w_3, w_4\} \) to determine the number of TLS in model glasses. As can be seen in Figs. 2b and 2c, and in Table I, we found statistical correlation also in the case of the \( u \) set. It is beyond the scope of the present work to explain this inconsistency, that can lie on the different glass examined or, more likely, on the different procedure used to determine the potential energy profile (LAP here, straight path in [2]).

In order to describe the low temperature anomalies of glasses, the most important quantity is the total splitting of the ground state associated to the TLS. To our knowledge, only one attempt has been made to estimate the energy splitting due to the tunneling through TLS energy barriers. It \( a) \) assumes the existence of isolated pairs of minima and \( b) \) treats the problem as it were 1-dimensional (1-D) [4]. From the present simulation, hypothesis \( a) \) can be neither cibfirmed nor rejected because we did not directly identify any candidate TLS (i.e. pairs of minima with asymmetry < 1 K); recent results on Argon clusters [5] indicate that pairs of minima with low asymmetry are ”isolated” in the sense that a third quasi-degenerate, adjacent minimum has not been observed. As for item \( b) \), the \((3N−3)\)-dimensional tunneling problem can be treated as an 1-dimensional one if the Schrödinger equation can be factorized into \( 3N−3 \) independent equations [3]. We shall assume that the reduction to 1-D can be made under the less restrictive condition that the relevant classical path (i.e. the LAP) is independent of all the others. To this end we have studied the curvatures of the potential energy surface along the LAP by calculating the dynamical matrix eigenvalues \( \lambda_j(n) \) \((j = 1..., 3N−3)\) and the corresponding eigenvectors in \( 42 (n = 1..42) \) equally spaced configurations along the LAP itself. In Fig. 3, we report, for each configuration along the LAP joining a typical pair of minima, the \( 20 (j = 1..20) \) lowest frequencies \( \omega_j = \sqrt{|\lambda_j|} \) (we have assigned the minus sign to the frequencies associated to negative eigenvalues). As can be seen, in the present case only one eigenvalue becomes negative, indicating a first order saddle point in the 3N-dimensional space, and only the lowest frequencies change appreciably along the LAP. In Fig. 4 we report, for the seven lowest eigenvalues, the projections of the eigenvectors on
the local tangent at the LAP. Along the path, the main contribution comes from the lowest eigenvalue, while approaching the minima, an increasing contribution comes from other eigenvalues. The same results are found for all pairs of minima. They indicate that the dynamics parallel and orthogonal to the reaction coordinate are nearly independent: quasi-harmonic vibrations control the orthogonal dynamics, by a set of eigenfrequencies that are independent of the position along the path. The reaction coordinate is associated with a single eigenvalue (often the lowest one), as shown by the large value of the projection of only one eigenvector in the path direction.

In conclusion, the picture emerging from the depicted scenario is that of a network of connected minima, where each pair is joined together by a 1-dimensional path. The reaction coordinate along the path follows a LAP in the 3N-configurational space, described by DWP with statistically correlated parameters (asymmetry, height, etc.). The potential energy experienced by the system along the LAP is significantly lower than that one along other paths, like, for example, the straight path. Orthogonally to the LC, the dynamics is harmonic, and the set of frequencies are nearly independent on the specific value of the RC. In the present simulation a single interconnected quasi-1-dim path has been found, indicating that no more than one DWP is active at the time. Extrapolating this result, we can state that the number of DWP’s coexisting with harmonic excitations is $N_{DWP} < 10^{-3}$ atoms$^{-1}$.

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| $\Delta V^m$ | $\Delta V^B$ | $D$ | $d$ | $P$ |
|-----------|-----------|-----|-----|-----|
| $\Delta V^m$ | - | 0.45 | 0.86 | 0.78 | 0.13 |
| $\Delta V^B$ | - | - | - | - | - |
| $D$ | - | - | - | - | - |
| $d$ | - | - | - | - | - |
| $P$ | - | - | - | - | - |

TABLE I. The upper right part of the three matrices reports the correlation coefficients $r$ among all the couple of parameters used to describe the DWP in the physical representation $\{\Delta V^m, \Delta V^B, D, d, P\}$, and in the two different polynomial representations $\{w_2, w_3, w_4\}$ and $\{u_0, u_2, u_3\}$. The lower left part of the correlation matrices indicates whether the two parameters are (●) or are not (○) correlated at the 5% level of confidence.
**CAPTIONS**

Fig. 1 - a) Comparison between the potential energy profile along the LAP (●) and along the straight path (○) joining two typical minima. $E_x$ is the energy of the crystalline minima. b) Orthogonal distance between the LAP and the straight path as a function of the reaction coordinate.

Fig. 2 - Example of correlation between the parameters describing the DWP. Each point represent the values found for the couple of parameters a) $(\Delta V^m, D)$, b) $(w_4, w_3)$, and c) $(u_3, u_2)$ in the description of each DWP.

Fig. 3 - The 20 lowest eigen-frequencies $\omega = \sqrt{|\lambda|}$ of the system evaluated in 42 equispaced atomic configurations along the LAP are reported as a function of the reaction coordinate for a typical pair of minima. Negative eigenvalues $\lambda$ are reported as negative eigen-frequencies $\omega$.

Fig. 4 - The projection on the LAP of the six lowest frequency eigen-vectors of the modes of Fig. 3 are reported as a function of the reaction coordinate.
Fig. 1 - "Potential energy topology ....." by F. Demichelis et al.
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