Potential Energy Landscape in Lennard-Jones binary mixture model

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Abstract

The potential energy landscape in the Kob-Andersen Lennard-Jones binary mixture model has been studied carefully from liquid down to the supercooled regime, from $T = 2$ down to $T = 0.46$. One thousand of independent configurations along the time evolution have been examined at each investigated temperature. From the starting configuration we searched the nearest saddle (or quasi-saddle) and minimum of the potential energy. The vibrational densities of states for the starting and the two derived configurations have been evaluated. Besides the number of negative eigenvalues of saddle, other quantities show some signature of the approaching of the dynamical arrest temperature.
I. INTRODUCTION

In recent years a considerable research effort has been devoted to understand the complex phenomenology of supercooled glass forming liquids and in particular the enormous increase of relaxation times and viscosity by many order of magnitude upon decreasing the temperature. It was Goldstein\textsuperscript{[1]} who first related the behaviour of glass formers to the underlying Potential Energy Landscape (PEL) and proposed to characterize the dynamics of the system through the motion of a point in the complex high-dimensional PEL (3N-dimensional if N is the total number of particles). Further, he suggested to focus onto the PEL local minima where the system is supposed to be trapped at low enough temperatures. At low temperatures, but above the glass transition, the phase space spanned by the system at equilibrium can ideally be characterized by two different types of processes: a ”fast” relaxation into local minima (or basins) and the ”slow” relaxation due to the crossing between loosely connected basins (the so called ”hopping” from basin to basin even if, in the classical mechanics PEL language, there exist only tortuous and crooked ways connecting two admissible basins). Goldstein focused the attention on the minima of PEL, but before the system is spending much of the time in a given basin, there are situations where ”fast” and ”slow” relaxations are not recognizable, diffusion is still high and a lot of minima are visited in a continuous way. In this case, it was searched to relate the diffusion dynamics to unstable directions in equilibrium (or instantaneous) PEL configurations, i.e. in the context of Instantaneous Normal Mode approach\textsuperscript{[2, 3]}, however other special points than PEL minima, are found to characterize better the dynamics of the system: they are the minima of the modulus square of the gradient of the potential energy, i.e. saddles (absolute minima) and what we call ”quasi-saddles” (local minima). Indeed the unstable directions of a saddle give some piece of information about the number of different minima are existing in that PEL region and therefore about the diffusion processes. In the past, the relevance of saddles for the dynamics of glassy systems has been already recognized in the context of mean-field spin-glasses\textsuperscript{[4, 5]}. A large number of recent works has renew interest in PEL and its characterization through saddle and minima points to better understand the continuous transition from liquid to glass\textsuperscript{[6, 7, 8, 9, 10]}.

The purpose of the present work is to investigate in detail the statistical properties of the PEL of a binary Lennard-Jones system from the liquid down to the supercooled regime near
the structural arrest. To do that, a set of temperature above the glass transition have been considered and for each of them a set of independent configurations has been examined. Nearest saddles and minima have been searched and the normal mode analysis has been performed on all configurations.

II. NUMERICAL COMPUTATIONS

The system under consideration is a binary mixture of classical particles. The system is equal to that considered by Kob and Andersen[11], apart from a detail in the truncation of the potential. The mixture is made of 256 particles, 205 of A and 51 of B (about 80% of A and 20% of B). Both particles have the same mass and interact each other via a Lennard-Jones potential, i.e. \( V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r}\right)^{6}\right] \) with \( \alpha, \beta \in \{A, B\} \).

The parameters of the potentials are: \( \epsilon_{AA} = 1.0, \sigma_{AA} = 1.0, \epsilon_{BB} = 0.5, \sigma_{BB} = 0.88, \epsilon_{AB} = 1.5, \sigma_{AB} = 0.8 \). In the following all the results will be given in reduced units, i.e. length in units of \( \sigma_{AA} \), energy in units of \( \epsilon_{AA} \), temperature in \( k_B/\epsilon_{AA} \), and time in units of \( (m_A\sigma_{AA}^2/\epsilon_{AA})^{1/2} \).

The interaction potential at long distance is tapered between 0.95 \( r_2 = r_1 \leq r \leq r_2 = 2.56 \sigma_{AA} \) with the following fifth-order smoothing function \( T(r) = 1 + (r_1 - r)^3(6r^2 + (3r + r_1)(r_1 - 5r_2) + 10r_2^2)/(r_2 - r_1)^5 \). In this way the potential, the forces and their derivatives are continuos and it is possible to keep the energy constant better than \( 1/10^5 \) over 100 millions of molecular dynamics (MD) time steps near the critical temperature. The MD was performed in NVE ensemble using the leapfrog algorithm with a time step of \( 1.5 \times 10^{-3} \) at temperature above \( T = 1.0 \) and \( 2 \times 10^{-3} \) at lower temperatures. A neighbor-list was used to speed up the calculation.

In their paper, Kob and Andersen[11] truncated and shifted the potential at a cutoff distance of 2.5 \( \sigma_{\alpha\beta} \). In the uniform density approximation, our tapering correspond to an average cutoff distance of about 2.5 \( \sigma_{AA} \), and the resulting potential energy is shifted (downward) only by about 0.56 energy units with respect to the values of the quoted reference[12].

First the configurations were produced at high temperature and then thermalized at the highest investigated temperature (\( T = 2.0 \)). The initial configurations at lower temperatures were obtained in sequence by cooling and thermalizing a set of different temperature (1.8, 1.6, 1.4, 1.2, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.48, 0.46). Not all the configurations were analyzed.
in full details.

For each temperature, 1000 independent configurations were stored and then analyzed. The minimum number of steps between two subsequent configurations to be independent was determined in test runs. Two subsequent configurations are classified as independent if different potential minima are always obtained practically. We used a separation of 1000 steps at high temperatures down to $T = 1.0$, then we increased this number following the viscosity trend, so we used $10^4$ steps at $T = 0.7$ and $10^5$ steps at $T = 0.46$. The procedure is similar to that used to study the inherent dynamics by Schroeder et al. \[13\]

To characterize the states of the supercooled binary mixture, we searched the nearest saddle point ("W") and the nearest minimum ("V") of the PEL from the initial equilibrium ("I") configurations. The saddle (or quasi-saddle as explained after) configurations correspond to minimizing the sum of the squared forces, i.e. $W = |\nabla V|^2$ where $V$ is the sum of all interaction potential of our system and $\nabla$ is the gradient on all the particle coordinates. If $|\nabla V|^2$ is really vanishing, i.e. is an absolute minimum, the configuration correspond to a real saddle, otherwise we call it quasi-saddle since usually there is only one direction with zero or nearly zero eigenvalue and non zero force\[14\]. The minima of $V$ are always absolute minima of $|\nabla V|^2$.

To obtain good nearest configurations of $W$ and $V$ minimum from an initial equilibrium configuration of our system of 256 particles is a very stiff problem. The details of the two search procedure we used, is too long and will be described elsewhere\[15\]. Here we want to stress that various standard algorithms have been employed during the search and various criteria have been adopted for switching among the different algorithms. From the numerical point of view, the obtained minima are quite satisfactory. Indeed at the start, the value of $|\nabla V|^2$ is of the order of $10^7$ (in internal MD units) while at the minimum of $W$ is in the range $10^{-1} \div 10^2$ for quasi-saddles and in the range $10^{-8} \div 10^{-2}$ for true-saddles. At the minimum of $V$ is always less than $10^{-3}$ (in the range $10^{-8} \div 10^{-2}$). In the worst case, the value of $|\nabla V|^2$ is reduced by a factor of $10^5$. This happens when the flex point is on a high sliding surface.

In figure\[4\] we plot the distribution of $|\nabla V|^2$ at the $W$ minima for two extreme values of temperature. It should be noted that: i) the temperature strongly affects the distribution; ii) the number of true-saddles (for which $|\nabla V|^2$ is vanishing) is strongly decreasing with temperature; iii) the force residuals, i.e. $|\nabla V|^2$ values, are larger at low temperatures in
FIG. 1: The distribution at high ($T = 2.0$, black lines) and low ($T = 0.48$, grey lines) temperature of the $|\nabla V|^2$ values for $W$ minimization. True-saddles are grouped around $-10$ value of $\ln(|\nabla V|^2)$.

contrast with what one can expect intuitively. Moreover the temperature variation of the distribution is nearly confined to the low temperature side (below $T = 1.0$). The second point is the reason why it becomes more and more difficult to analyze the low temperature data by using only these configurations which have the $W$ minima as true-saddles. Therefore we choose to analyze all the configurations and to inspect if true-saddles and quasi-saddles share the same pieces of information.

III. ANALYSIS OF THE RESULTS

A. Behaviour of potential energy at minima and saddles

In figure 2 we have reported the behaviour of the potential energy versus temperature of the quasi-saddles ("$W$") and minima ("$V$"). As you can see, the potential energy of "$W$" is decreasing rapidly with temperature while that of "$V$" is practically constant, as already reported in ref. 6. Close and closer to the temperature of structural arrest, even the "$V$"
FIG. 2: Panel A on the left. Potential energy (internal units) of quasi-saddles ("W", upper part) and potential minima ("V", lower part) versus temperature. Panel B on the right. Cartesian distance in box units of potential minima ("V", upper part) and quasi-saddles ("W", lower part) from the starting equilibrium configuration versus temperature. The thin vertical line on both the panels is drawn at $T_c=0.435$.

potential energy becomes a decreasing function of the temperature, as it has been already shown by Sastry et al. In the right panel of the same figure we have shown the Cartesian distances (in box units) of "V" and "W" from the starting equilibrium configurations. In that case the temperature behaviour of the two kind of minima is reversed between "V" and "W", i.e. the average distances of quasi-saddles from equilibrium configurations are practically temperature independent while those of minima strongly decrease with decreasing temperature. This kind of behaviour can be expected because the potential energy of the starting equilibrium configurations is known to be nearly proportional to temperature and configurations that are not very "distant" from equilibrium are reasonably dependent on temperature.

In figure 3, we plot the number of negative eigenvalues of the Hessian matrix at quasi-saddle points versus temperature. This number goes fast to zero at the critical temperature, i.e. the temperature of structural arrest, as already found by a similar analysis performed in ref. A solid vertical line in the figure represent the value of the mode coupling critical temperature ($T_c\approx 0.435$) derived from the power law behaviour of the diffusion constant. The same value is obtained by a power law fitting of saddle order versus temperature.
FIG. 3: Saddle order (number of negative eigenvalues) for each quasi-saddle configuration at different temperatures. Full diamonds represent average values. Solid line is a power law fit to average values: const \((T-T_c)^\gamma\) with const \(\approx 38.5\), \(T_c \approx 0.435\), \(\gamma \approx 0.77\). A solid vertical line is drawn at \(T_c\). In the inset a blow-up of the lowest temperature data is shown.

This confirms the number of negative eigenvalues of quasi-saddles (or saddles) to be strictly connected with the diffusion constant. In contrast, a negative eigenvalue of an equilibrium configuration, i.e. a negative curvature of the instantaneous potential energy, is not always connected with a path joining two different minima, i.e. a diffusion path.

B. Quasi-saddles characteristics

As already noted in ref. \[7\], the quasi-saddles at different temperatures explore different regions of the PEL. Therefore at low temperatures we have low values of the potential energy
FIG. 4: Potential energy of quasi-saddles versus saddle order (number of negative eigenvalues) at some chosen temperatures: $T = 0.46$ (dots), $T = 0.8$ (open squares), $T = 1.4$ (open circles) and $T = 2.0$ (plus signs).

We underline that the potential energy itself is not sufficient to determine the number of negative eigenvalues of the Hessian matrix. Indeed even at the same value of the potential energy the number of negative eigenvalues is substantially different for quasi-saddles (“$W$”) and initial equilibrium configurations (“$I$”), as shown in figure 5 where we plotted the potential energy of “$I$” and “$W$” versus the number of negative eigenvalues at different temperatures. From the values and distribution in energy of “$I$” and “$W$” at the same temperature, we can easily derive that the enormous decrease of diffusion (and increase
in viscosity) lowering the temperature in supercooled regime, is due essentially to entropic barriers, i.e. to difficulties in reaching the saddle points, and not to activated processes [18].

C. Spectral densities of potential minima, saddles and initial configurations

To better understand the modifications of the PEL around ”I”, ”W”, ”V” configurations that occur lowering the temperature we have study the frequency distribution of the vibrational states derived from the Hessian matrix of the potential energy. To visualize all the spectral features in a single plot, the eigenfrequencies of unstable directions (i.e. the square roots of negative eigenvalues) are reported as negative frequencies.

In figure 6 we reported the histogram of the average vibrational density of states (DOS) at two extreme temperatures. From the figure we can infer that by lowering the temperature
FIG. 6: On the upper panel: the average density of states at high temperature in the liquid regime from the normal mode analysis performed on the three different configurations, "I" (solid line), "W" (dotted grey line) and "V" (dashed line). On the lower panel, the same average DOS is shown near $T_c$ in the supercooled regime. Imaginary frequencies (square root of negative eigenvalues) are reported as negative frequencies. In the channel around zero of the histogram we found the three zero frequency eigenvalues (connected to translational invariants); for quasi-saddles another zero frequency eigenvalue is found due to the change of curvature in one direction of the potential energy hypersurface ($3N = 768$ dimensions). In the supercooled regime, approaching $T_c$, the "W" DOS becomes more and more similar to the "V" DOS.

all the three DOS will collapse into a single one (when the glass will be confined to a single minimum). In the supercooled regime, approaching $T_c$, the "W" DOS from quasi-saddles becomes more and more similar to the "V" DOS from potential minima. At $T=0.46$, the "W" DOS is nearly coincident with the "V" DOS while the "I" DOS of initial
FIG. 7: The average DOS at intermediate temperature (liquid regime) from the normal mode analysis performed on the subset of different configurations giving rise to true-saddles: "I" open circles, the true-saddle (grey crosses) and the potential minimum (open diamonds) configurations. The average DOS from all the investigated configurations at this temperature are reported as in Figure 2, i.e. "I" (solid line),"W" (dotted grey line) and "V" (dashed line). Within the statistical uncertainties the DOS are equal to those obtained from the true-saddle subset.

equilibrium configuration still remain separated. We want to underline that in the channel of the histogram around zero frequency, we found always the three eigenvalues connected to the three translational invariants; for quasi-saddles (true-saddles apart) another zero frequency eigenvalue is found due to the change of curvature in one direction of the potential energy hypersurface. This is the reason why the zero channel of the "W" DOS has nearly four eigenvalues.

In figure 7 the three DOS calculated from only the true-saddle configurations, i.e. those configurations for which the forces at "W" points are really vanishing, are shown and compared with the DOS averaged over all configurations. We want to stress that within the statistical uncertainties the three DOS are not dependent on the chosen subset. This is
FIG. 8: The average reduced DOS in the supercooled regime from the "I" (crosses), "W" (circles) and "V" (solid line) configurations.

not obvious for "W" DOS and it is an important result of our study: at least with respect to the distribution of vibrational frequency, true-saddles and quasi-saddles share the same information.

Even if the "W" and "V" DOS seem to be very similar near $T_c$ (see lower panel of figure 8) there are yet significant differences at low frequency. In figure 8 we reported the reduced density of states (RDOS) at low frequencies for the three configuration at $T=0.48$, i.e. the DOS divide by the frequency square. In the Debey solid approximation the reduced density is a constant, while the well-known "Boson peak" is found in real glasses. In the supercooled regime of figure 8 a peak is clearly visible in the "V" RDOS, starts to appear in "W" RDOS, while is (yet) completely absent in the "I" RDOS.
IV. CONCLUSIONS

We have investigated the dynamics of a model glass-forming liquids in terms of its potential energy landscape by investigating numerous independent configurations at different temperatures in the liquid and supercooled regime. Potential energy minima, quasi-saddles and true-saddles are derived from equilibrium configurations. The temperature behavior of potential energy, saddle order, Cartesian distance, and vibrational density of states for equilibrium, quasi-saddle and minimum configurations has been studied. In the average the quasi-saddles lie on a more sliding hypersurface at low than high temperatures. The number of true saddles is a decreasing function of temperature, so it is important to establish that it is possible to extract also information about the dynamics of the system from the quasi-saddles configurations. It has been demonstrated that the vibrational density of states is practically the same for true- and quasi-saddles. At different temperatures, different regions of the PEL are statistically visited by the system, due to the fact the accessible configuration volume is exponentially growing with the temperature. The potential energy and the number of unstable directions (i.e. negative eigenvalues) are statistically correlated both for saddles and equilibrium configurations, but at the same potential energy saddles and equilibrium configuration have different number of negative eigenvalues, at least in the investigated liquid-supercooled region. An excess density of states at low frequency is always present in the investigated system, but a ”Boson peak” like structure is clearly visible only in the DOS derived from potential energy minima.

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[15] Sampoli M, to be published; a brief sketch is in the following. All the tested programs for finding minima in a multidimensional space (768 dimension in our case) stick in some points when a tortuous deep valley is encountered. Usually they decrease the step more and more, the search becomes very slowly and possibly stops. The procedure can be tested easily in the case of "V" minima, because a potential minimum requires the sum of the squared forces to be zero and the Hessian matrix to have all positive eigenvalues (except three zeros). Different algorithms usually stick in different points and the same algorithm with a larger step can be effective in overcoming some critical situations. Therefore a complex flow chart with different algorithms (steepest descent, Gauss-Newton, Levenberg-Marquardt, preconditioned conjugate gradient, etc.) was used. In both "W" and "V" minima we started with a steepest descent search.
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[18] Sampoli M, to be published. A brief summary is reported here where, only the case of the lowest temperature (T= 0.46) is examined. The simulation was performed in NVE, so the fluctuations in "I" potential energy were equivalent to the fluctuations in kinetic energy. From the "I" potential energy values, the mean potential energy and its standard deviation was estimated. From the mean temperature or the value of total energy, the mean kinetic energy and its standard deviation (equal to the standard deviation of potential energy) was derived. The classical vibrational potential energy was assumed to be equal to kinetic energy and the contributions of diffusive modes were neglected at this temperature. The combined
fluctuations of potential and kinetic energy was estimated by considering the two sources as statistically independent. If no activated process is necessary to reach a saddle point, the saddle point energies must be in the usual fluctuation range. With a fluctuation of two standard deviations, 71.6% of saddle points can be reached and 95.2% with three standard deviations. It must be noted that the microcanonical ensemble was used to calculate this estimate, whereas also the fluctuations in total energy must be taken into account in real systems. That further favors an essential entropy barrier explanation. Large contributions from activated processes are probably confined to low temperature glassy phases.