Computer investigation of the energy landscape of amorphous silica

Philippe Jund and Rémi Jullien

Laboratoire des Verres - Université Montpellier 2
Place E. Bataillon Case 069, 34095 Montpellier France

The multidimensional topography of the collective potential energy function of a so-called strong glass former (silica) is analyzed by means of classical molecular dynamics calculations. Features qualitatively similar to those of fragile glasses are recovered at high temperatures: in particular an intrinsic characteristic temperature $T_c \simeq 3500\text{K}$ is evidenced above which the system starts to investigate non-harmonic potential energy basins. It is shown that the anharmonicities are essentially characterized by a roughness appearing in the potential energy valleys explored by the system for temperatures above $T_c$.

Even though the manufacturing of glasses by a quench from the high temperature liquid phase is a standard practice, the precise understanding of what happens at a molecular level in these materials, when lowering the temperature through the “glass transition”, remains an important theoretical challenge. Several approaches have emerged in the literature depending whether the structural or the dynamical aspects are emphasized. In particular the use of the concept of topological frustration or the use of the mode-coupling theory proceeds from completely different points of view. A promising way to conclide these approaches is the analysis of the shape of the potential energy function $\Phi(\vec{r}_1, \vec{r}_2, \ldots)$ in the multidimensional space of the coordinates of the interacting particles. It has been recently shown that the topological analysis of the energy landscape of a fragile glass-forming liquid described by a two-body Lennard-Jones (LJ) potential allows to explain the distinct dynamical regimes experimentally observed.

In this letter, we present for the first time such an energy landscape analysis in the case of a so-called strong glass former, namely vitreous silica, by means of classical molecular-dynamics (MD) calculations. As in the case of fragile glasses, from a quantitative analysis of the inherent potential energy basins explored at various temperatures, one can define an intrinsic characteristic temperature, here equal to $T_c \simeq 3500\text{K}$, above which the system experiences anharmonicities. These findings are in agreement with a recent simulation study in which a change in the dynamical properties of a similar liquid silica system has been observed around this temperature, suggesting that supercooled liquid silica behaves like a fragile glass former at temperatures above $T_c$. Here we show that the anharmonicities exhibited by the energy basins explored at temperatures above $T_c$ are essentially due to a roughness in the shape of the basins, as previously observed in simpler liquid systems. Using an original procedure, we perform a quantitative analysis of this roughness and show that it is characterized by a typical length (in the multidimensional configuration space) of about 0.2Å which is the signature of the annihilation of structural defects along the path down the potential energy valleys.

Our silica system consists of 216 silicon and 432 oxygen atoms confined in a cubic box of edge length $L = 21.48\text{Å}$ which corresponds to a mass density very close to the experimental value of vitreous silica. The constant energy, constant volume classical MD calculations have been performed using the sophisticated potential first introduced by van Beest et al. and justified by ab initio calculations. It has been recently shown to describe quite well structural, and vibrational, as well as relaxation and thermal properties of both, supercooled viscous liquid and glassy silica. We have used the same input parameters and the same modus operandi as in our previous structural study. After a full equilibration of the liquid (about 28 ps) the system has been cooled down to zero temperature at a quench rate of $2.3 \times 10^{14}\text{Ks}^{-1}$ which has been obtained by removing the corresponding amount of energy from the total energy of the system at each iteration. At several temperatures during the quenching process the configurations (positions and velocities) have been saved. With the use of these configurations as inputs of the MD calculations, the system has then been allowed to relax for a maximum duration of 84 ps after the quench (during this constant volume relaxation period the temperature of the system is only slightly increasing). The same procedure has been repeated for ten different initial liquid configurations and consequently all the physical quantities reported below always result from an average over these ten independent samples.

For each collected temperature, immediately after the quench or after a given relaxation time (42 or 84 ps), the typical potential energy basin sampled by the system has been investigated using a procedure described by Della Valle and Andersen which allows to perform a steepest descent from the initial multicomponent space configuration down to the closest underlying potential energy minimum, often called the “inherent structure” in the literature. For that purpose a modified version...
of the MD algorithm is adopted. At each MD step, the scalar product of the velocity by the force is calculated for each particle. If the product is positive the velocity of the particle is replaced by its projection on the force and otherwise the velocity is set to zero. During the descent, both the distance and the potential energy $\Phi$ are calculated, allowing to determine precisely the shape of the energy basin. There are different ways to define the distance per particle in the multiparticle space. We have chosen to calculate either the direct distance $x$ from the initial configuration, defined by \[ x = \sqrt{\sum_i m_i (\vec{r}_i - \vec{r}_i^{(0)})^2} \]

where the sum runs over all the particles located at $\vec{r}_i$ with a mass $m_i$, or the cumulated distance, $X$, calculated along the steepest descent path by:

\[ X = \sum_n \sqrt{\sum_i m_i (\vec{r}_i^{(n)} - \vec{r}_i^{(n-1)})^2} \]

where $n$ labels the MD steps. The process is stopped when $\Phi$, which is a monotonically decreasing function of $x$ (resp. $X$), reaches a minimum $\Phi_m$ at $x = x_m$ (resp. $X = X_m$). Practically we have chosen to stop the descent when $\Phi^{(n)} - \Phi^{(n+1)} < 10^{-6} \text{ eV}$.

As a first result we present in Fig.1, the potential energy minima $\Phi_m$ obtained at different temperatures. The curve obtained immediately after the quench is similar to the one obtained previously with a different potential \[ \Phi_m \] as shown by Vollmayr et al. \[ \Phi_m \] for Lennard-Jones glasses and can be interpreted in the same manner. The squared distance $x_m^2$ is linear with temperature up to a characteristic temperature $T_c \simeq 3500 \text{K}$ (here very close to $T_g$) above which anharmonicities appear. The same analysis as the one done in \[ \Phi_m \] shows that $T_c$ corresponds to a change in the nature of the relaxation process, i.e. from diffusion above $T_c$ to hopping below $T_c$. This is consistent with the recent work of Horbach and Kob on the same system \[ \Phi_m \] who found a breakdown of the Arrhenius behavior of the transport coefficients above a temperature close to 3300K and suggested that this characteristic temperature corresponds to the $T_c$ predicted by the mode coupling theory. A more striking result is that the curves in Fig.2, in contrast with those in Fig.1, are not very sensitive to the duration of the relaxation process after the quench. This is also true for another characteristic quantity of the energy basins leading to the inherent structures, namely $\Delta \Phi = \Phi^{(0)} - \Phi_m$, the energy difference between the initial structure and the inherent structure, which has been plotted versus $T$ in the inset of Fig.2. It exhibits the same departure from the expected harmonic linear regime ($\Delta \Phi = \frac{1}{2} k_B T$ represented by the dashed line in the inset) at $T_c$ and also the same remarkable stability against relaxation. This shows that as the aging time increases the system explores deeper and deeper basins (especially around $T_g$) as shown by the variation of $\Phi_m$ in Fig.1 but the intrinsic characteristics of these basins, the mean width and the mean height (associated with $x_m^2$ and $\Phi^{(0)} - \Phi_m$ resp.), do not depend on their absolute position $\Phi_m$ in the energy scale. Therefore the characteristic temperature that we can define here, $T_c \simeq 3500 \text{K}$, is intrinsic and does not depend on the quenching rate. The fact that we obtain $T_c$ close to $T_g$ is simply due to our very large quenching rate. It is worth noticing that the same qualitative behavior than the one observed in Fig.2 is also obtained by plotting $X_m^2$ the square of the cumulated distance instead of $x_m^2$. In that case the departure from a linear regime above $T_c$ is
even more pronounced as we find that the ratio $X_m/x_m$ remains constant (of order 1.2) for $T < T_c$ and increases markedly with temperature for $T > T_c$.

To investigate further the nature of the anharmonicities of the energy basins explored by the system for temperatures above $T_c$, we propose a quantitative analysis of the curves $F(X) = -d\Phi/dX$ where $X$ is the above defined cumulated distance (we have used $-d\Phi/dX$ instead of $-d\Phi/dx$ because it corresponds better to a local characteristic of the shape of the basins). Typical examples of such curves are given in Fig.3 for samples relaxed during 84 ps after the quench (as already shown in Fig.2 the aging time does not influence significantly the numerical results). It turns out that for $T > T_c$, the $\Phi(X)$ curves, while always decreasing, exhibit step-like singularities evidenced by clearly visible peaks in the derivative. Note that another manifestation of what can be called a roughness is the increase with temperature of the ratio $X_m/x_m$ above $T_c$, mentioned earlier (the same observation has already been done for LJ glasses [6]). To analyze quantitatively the roughness of the $F(X)$ curves, we have first eliminated the overall mean general evolution by calculating the difference $f(X) = F(X) - <F(X)>$ where $<F(X)>$ is a local average of the data between $X - \delta X$ and $X + \delta X$ (for convenience we have chosen $\delta X = X_m/20$ and limited the range of $X$ values between $4\delta X$ and $X_m - \delta X$). The $f(X)$ curves corresponding to the $F(X)$ curves depicted in Fig.3 are shown in the inset of the figure (they have been artificially shifted in the vertical direction for clarity). Subsequently the roughness of the curves $f(X)$ has been analyzed by following a standard method [13] which consists in calculating the power spectrum $S(k)$ defined as the Fourier transform of the autocorrelation product $g(\xi) = <f(X + \xi)f(X)>$ where the average is performed not only over the $X$ values but also over ten independent samples. The results of this analysis are reported in Fig.4. In this figure we have reported as a function of temperature the mean intensity of the peaks measured by the standard deviation $\sigma_f$ of the $f(X)$ curves, which is equal to the square root of $g(0)$. Despite the error bars the curve exhibits a characteristic sigmoidal shape, indicating that the roughness only exists in the higher energy basins explored for $T > T_c$ and that the mean intensity of the peaks seems to saturate at very high temperatures. Furthermore, for $T > T_c$, we observe that the power spectrum goes through a maximum and decays like $k^{-1}$ after this maximum. This means that there exists a typical length (the inverse of the location of the maximum) $X_r$ characteristic of the mean distance between successive peaks while the curve between two peaks can practically be considered as “smooth”. For $T < T_c$ there is no visible maximum in the power spectrum which behaves roughly as $k^{-1}$ over the whole $k$ range. This is a further indication that the very weak roughness in the basins explored below $T_c$ has no significance and that the low temperature basins can be considered as smooth. The estimated values for $X_r$ above $T_c$ have been reported in Fig.4. This typical length increases slightly with $T$ from about 0.15 Å at 4000K to about 0.23 Å at 7000K. It is interesting to relate the typical distance $X_r$ in the multidimensional configuration space to peculiar structural rearrangements occurring during the down-hill potential energy minimization process. On some specific high temperature samples we have compared the configurations between two successive peaks in $F(X)$ and we have in each case observed the elimination of a single specific defect like a triconnected silicon atom or edge-sharing tetrahedra etc... In such rearrangements a “perturbed” cluster of about 30 to 50 connected atoms, is observed. Generally the largest displacement of about 0.5 to 0.7 Å is observed for an oxygen atom at (or very close to) the defect. Therefore the typical value of $X_r$ results from an average between the largest displacement near the defect and the “screening cloud” of displaced atoms connected to it. One can understand that $X_r$ becomes insignificant below $T_c$ because the defects become rare in the low temperature basins as already shown in [13].

In conclusion we have numerically investigated the potential energy landscape of super cooled liquid silica described by the BKS potential using a steepest-descent molecular-dynamics scheme. We have shown that the inherent structures sampled depend strongly on the effective cooling-rate especially around $T_g$ similarly to what was found in a Lennard-Jones glass [14]. Nevertheless at a given temperature the characteristics of the energy basins (mean height and mean width) seem to be insensitive to the history of the system. From a quantitative analysis of the potential energy valleys explored at various temperatures we have evidenced a characteristic temperature $T_c$ above which non-harmonic effects become dominant. This is consistent with an other recent study [15] and indicates that strong and fragile glass formers are quite similar when studied near $T_c$ where a change in the nature of the relaxation process takes place in the liquid phase. We think that the distinct characteristics of a strong glass former appear mainly in the supercooled liquid and glassy phases below $T_c$. Unfortunately the high value of $T_g$ that we obtain in our MD simulations does not allow us to study the temperature range between $T_g$ and $T_c$. Furthermore using an original quantitative analysis, we have shown that the anharmonic character of the higher energy valleys explored by the system above $T_c$, is due to some roughness occurring in the shape of the potential energy basins. The existence of such roughness has already been invoked in the case of simpler systems [15] but not quantitatively analyzed. In the case of silica we have shown that this roughness is characterized by a typical length of about 0.2 Å in the multi-dimensional configuration space, and can be associated with a sequential elimination of defects when following the path leading down to the inherent structures.
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FIG. 1. Plot of $\Phi_m$, the minimum value of the potential energy basin explored by the system, as a function of the temperature $T$ down to which the system has been cooled from the liquid state. The three curves correspond to the different durations of the relaxation period after the quench: $\square$: no relaxation; $\circ$: 42ps; $\bullet$: 84 ps. The data result from an average over ten independent samples.

FIG. 2. Plot of $x^2_m$, the mean square distance between the initial configuration and the corresponding minimum potential location as a function of temperature. The three curves correspond to the different durations of the relaxation period after the quench: $\square$: no relaxation; $\circ$: 42ps; $\bullet$: 84 ps. The data result from an average over ten independent samples.
FIG. 3. Plot of the derivative $F(X) = -\frac{d\phi}{dX}$ of some typical energy basins explored at different temperatures in the case of a sample relaxed 84 ps after the quench. From left to right the curves correspond to $T = 1000, 3000, 5000$ and 7000 K, respectively. In inset are shown the corresponding curves $f(X)$ obtained by making the difference between $F(X)$ and a local average as explained in text. In the inset the curves have been arbitrarily shifted vertically for clarity.

FIG. 4. Plot of the mean-square intensity $\sigma_f (\bullet)$ of the roughness in the space-derivative of the potential curve as a function of temperature after averaging over ten samples with a relaxation period of 84 ps after the quench. On the same figure the typical distance $X_r (\square)$ between the peaks in $f(X)$ is plotted as a function of temperature (right vertical axis).