Density effects in a bulk binary Lennard-Jones system

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Properties of local minima as a function of density are studied in a binary Lennard-Jones system for kinetic equipartition temperatures $T = 1.0$ (normal liquid), 0.5 (supercooled liquid), and 0.4 (glass), in reduced units. The number of different local minima sampled, energy, pressure, normal mode angular frequencies, mean distance between all pairs of local minima and partial radial distribution functions are presented. In agreement with previous studies by Sastry [Phys. Rev. Lett. 85, 590 (2000)] a limiting density is found at $\rho_l = 1.06$ with negative pressure, below which the local structure of the glass and the supercooled phases are essentially the same, as evidenced by the partial radial distribution functions. The mean energy, pressure, and normal mode frequencies have values that are practically independent of the temperature below $\rho_l$.

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I. INTRODUCTION

In recent years a considerable research effort has been expended to understand the complex phenomenology of supercooled liquids and glasses. Mode-coupling theory has proved quite successful for supercooled liquids at higher temperatures, before activated dynamics must be accounted for explicitly.\textsuperscript{1, 2, 3, 4} It was Goldstein who first related the behaviour of glass formers to the underlying potential energy surface (PES).\textsuperscript{5} In this approach, the dynamics are separated into vibrational motion about a minimum on the PES and transitions between local minima or ‘inherent structures’.\textsuperscript{6, 7} The PES is partitioned into basins of attraction surrounding the local minima, where a basin of attraction is defined as a set
of points that lead to the same minimum along steepest-descent pathways. Recently, it has been possible to establish connections between the structure, dynamics and thermodynamics of finite systems and the PES in some detail.\cite{8}

Following Angell,\cite{9, 10, 11} glass-forming liquids can be classified as strong or fragile. Fragile systems exhibit non-Arrhenius temperature dependence of transport properties such as the diffusion constant, usually accompanied by a significant heat capacity peak at the glass transition. In contrast, strong systems exhibit Arrhenius dynamics and small or negligible changes in the thermodynamic properties at the glass transition.

Computer simulation based on standard molecular dynamics (MD) or Monte Carlo (MC) techniques, has played a significant role in the testing and development of models for supercooled liquids and glasses.\cite{12} Interest in more direct connections to the PES has recently increased, with Sastry, Debenedetti and Stillinger\cite{13} characterising ‘landscape-influenced’ and ‘landscape-dominated’ regimes for a binary Lennard-Jones system, in agreement with the instantaneous normal modes picture of Donati, Sciortino and Tartaglia.\cite{14} Recently, a kinetic Monte Carlo (KMC) approach\cite{15, 16, 17} was used to provide an alternative view of the dynamics.\cite{18}

In the present contribution we focus on some properties of the energy landscape in a binary Lennard-Jones (BLJ) mixture, namely, the effect of the density on the local minima sampled as a function of temperature. This topic has been previously considered by Malandro et al.\cite{19, 20} and Sastry.\cite{21, 22} In the former studies the volume dependence of the local minima appearances and disappearances were examined. Similar results were found by Heuer.\cite{23} Sastry also analysed the relationship between fragility and the PES and how the former depends on the bulk density. One feature of the BLJ system is that the vibrational contribution to the entropy, within the harmonic approximation, decreases with the potential energy. Furthermore, Sastry found a limiting density, \( \rho_t = 1.08 \) in reduced units, which defines a limit of stability separating spatially heterogeneous structures (below \( \rho_t \)) from more homogeneous structures (above \( \rho_t \)). \( \rho_t \) was also interpreted as a density limit to glass formation. Here, we concentrate on this limit and consider the glass and supercooled liquid structures in more detail as a function of density.
II. METHODS

The model we used is a binary mixture of $N = 256$ atoms in a cubic box with periodic boundary conditions, containing 205 ($\sim 80\%$) A atoms and 51 ($\sim 20\%$) B atoms interacting according to a Lennard-Jones pair potential of the form

$$V_{\alpha\beta} = 4\epsilon_{\alpha\beta} \left[ \left( \frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}} \right)^{6} \right],$$ (1)

$r_{\alpha\beta}$ being the distance between particles $\alpha$ and $\beta$. The values of the Lennard-Jones parameters are $\epsilon_{AA} = 1.0$, $\epsilon_{BB} = 0.5$, $\epsilon_{AB} = 1.5$, $\sigma_{AA} = 1.0$, $\sigma_{BB} = 0.88$ and $\sigma_{AB} = 0.8$.\[24\] The units of distance, energy, temperature, pressure, and time were taken as $\sigma_{AA}$, $\epsilon_{AA}$, $\epsilon_{AA}/k_B$ ($k_B$ is the Boltzmann constant), $\epsilon_{AA}\sigma_{AA}^3$ and $\sigma_{AA}(m/\epsilon_{AA})^{1/2}$, with $m$ the mass of both A and B atoms. The initial density was $1.2\sigma_{AA}^3$ with a fixed cutoff of $2.5\sigma_{AA}$ along with the minimum image convention. We truncated and shifted the potential with a quadratic function, so that the energy and its first derivative are continuous at the cutoff value.\[13, 25\]

This BLJ model has been extensively studied in the glasses community, as it does not crystallise on the molecular dynamics time scale.\[12, 13, 14, 18, 21, 22, 24, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40\] However, we have recently found that there are crystalline minima for this system, based on face-centred-cubic A atoms with trigonal or square prismatic B-A coordination.\[41\] Previous work has shown that this system exhibits a significant degree of non-Arrhenius behaviour at low temperatures, i.e. it is fragile in Angell’s terminology.\[24, 33, 34, 35\]

Microcanonical molecular dynamics simulations were carried out, where the classical equations of motion were integrated using a Verlet algorithm. We employed $10^5$ equilibration steps, followed by $10^6$ data collection steps with a time step of 0.003 in reduced units.\[40\]

In order to study the local minima the instantaneous system configuration was quenched, every 1000th configuration, to locate a minimum. Quenching was performed using a modified version of Nocedal’s limited memory Broyden-Fletcher-Goldfarb-Shanno (L-BFGS) algorithm.\[8, 42, 43\] Each quench was finished using a few eigenvector-following steps\[44, 45\] to converge the root-mean-square gradient below $10^{-7}$ reduced units, employing full diagonalisation of the analytical Hessian matrix to ensure that the stationary points have the correct Hessian index (the number of negative eigenvalues). In this manner we generated a
sample of minima at density $\rho = 1.2$.

For each local minimum, the density of the system was changed by 0.02 in reduced units. To do this we changed the box length to give the density required, without rescaling the coordinates of the atoms in the box. Then, the potential energy was reminimized using the methods described above. This process was repeated in order to follow the properties of the minima over a wide range of density.

We have analysed the behaviour of the local minima at densities in the range $0.6 \leq \rho \leq 1.3$, and for three different initial kinetic equipartition temperatures 1.0, 0.5 and 0.4. It is known for this system that the glass transition temperature, $T_g$, occurs between 0.5 and 0.4.[13, 18, 32, 40]

III. RESULTS

In this section we present the results obtained for the behaviour of the local minima at different temperatures and densities. At the initial density $\rho = 1.2$, the number of different local minima that we found from the 1000 instantaneous configurations, $N_{\min}$, was 1000, 991, and 268 at $T = 1.0$, 0.5, and 0.4, respectively. These values reflect the increasing residence times in the local minima as the temperature is decreased, with a dramatic fall in $N_{\min}$ below $T_g$. We found that $N_{\min}$ is basically independent of the density in the range of densities studied.

We have also evaluated the mean potential energy for the local minima as a function of density for three different initial samples at $T = 1.0$, 0.5 and 0.4. In Fig. 1 we can see how the lowest value of the energy occurs around $\rho = 1.2$ for each temperature. However, at $T = 0.4$ the minimum of the curve is slightly displaced to higher density, namely, to $\rho = 1.22$.

A clear change of slope appears in Fig. 1 (the system is mechanically unstable) at $\rho_l = 1.06$ for each temperature, and for $\rho < \rho_l$ the mean potential energy is practically independent of $T$ and increases as the density decreases.

Another interesting property is the variation of the pressure with density (Fig. 1). In this case, the pressure, $P$, was calculated using the virial equation[46]
\[ PV = (N - 1)T + \frac{1}{3} \left< \sum_{i} \sum_{j>i} r_{ij} \cdot F_{ij} \right>, \quad (2) \]

where \( V = N/\rho \) is the volume of the supercell, \( N \) is the number of atoms, \( r_{ij} = r_i - r_j \) and \( F_{ij} \) is the force on the \( i \)th particle due to \( j \)th particle. A factor \( N - 1 \) appears because of momentum conservation. We used \( T = 0 \) to calculate the pressure for the local minima.

The lowest value of \( P \) is reached for each temperature around \( \rho_l = 1.06 \). This value is very close to Sastry’s result of \( \rho_l = 1.08 \) [21] (his supercell contained 204 A atoms and 52 B atoms). For \( \rho < 1 \), the mean pressure is practically independent of the temperature. Fig. 1 also shows that the pressure is nearly zero at densities corresponding to the lowest values of the mean energy.

The geometric mean normal mode frequency at each local minimum is

\[ \nu = \prod_{i=1}^{3N-3} (\nu_i)^{1/(3N-3)}, \quad (3) \]

where the \( \nu_i \) are obtained by diagonalising the Hessian matrix. A mean angular frequency, averaged over all the local minima, can be defined as

\[ < \omega > = 2\pi < \nu >, \quad (4) \]

and this quantity is plotted in Fig. 2. The frequencies are important for dynamics because they appear in the usual transition state theory rate constant for barrier crossing. If we also use the information obtained in Fig. 1 we can see that for \( \rho > 1.2 \), which corresponds to positive pressures (compressed regime), \( < \omega > \) increases with energy, in agreement with Sastry [22]. However, between \( \rho \sim 1.2 \) and \( \rho_l = 1.06 \), which corresponds to negative pressures (stretched regime), we see the opposite behaviour, i.e. \( < \omega > \) decreases as the density decreases. Then, it increases again to reach a constant value of 13 below \( \rho \sim 1.0 \) independent of \( T \).

We have also calculated the mean value of the distance between all pairs of local minima sampled:

\[ d_{ij} = \sqrt{\frac{1}{N} \sum_{k=1}^{N} |r_{ik} - r_{jk}|^2}, \quad (5) \]

where \( i \) and \( j \) indicates the \( i \)th and \( j \)th local minima. It is clear from Fig. 2 that this quantity increases with the initial temperature used to generate the samples and with decreasing
density. On the other hand, the initial MD trajectories sample the PES less extensively at low temperature for the same simulation time. In the regime \(\rho_l = 1.06 \leq \rho \leq 1.3 < \langle d_{ij} \rangle\) does not change much, while below \(\rho_l = 1.06\) it increases steadily.

The above results were checked by studying the partial radial distribution functions (PRDF) for all the local minima sampled:

\[
g_{\alpha\alpha}(r) = \frac{V}{N_\alpha(N_\alpha - 1)} \left\langle \sum_{i} \sum_{j \neq i} \delta(r - |r_{ij}|) \right\rangle
\]

(6) and

\[
g_{\alpha\beta}(r) = \frac{V}{N_\alpha N_\beta} \left\langle \sum_{i} \sum_{j} \delta(r - |r_{ij}|) \right\rangle,
\]

(7) where \(\delta(r)\) is the delta function. In Fig. 3 we show the PRDF for A particles as a function of the density for reoptimized local minima generated from the run at \(T = 1\).

The first peak is the highest in the PRDF for all densities, indicating that the AA correlation takes place at the first coordination shell. However, as the density is reduced from \(\rho = 1.3\), this peak is slightly displaced to longer distance, i.e. it reflects the lower density, and then reaches a maximum value at density \(\rho_l = 1.06\). Below this density, the system shows the opposite trend due to the formation of voids and fractures, allowing the AA distances to relax back closer to their ideal value.

Similar behaviour is exhibited in \(g_{\alpha\beta}\) in Fig. 3. The strong attractive interaction between A and B particles is reflected in the first peak. However, \(g_{\beta\beta}\) in Fig. 4 exhibits some new features. The weaker attractive interaction between B particles is reflected in the intensities of the peaks. The BB correlation takes place mainly in the first, second and third coordination shells, but for \(\rho = 0.6\) the first coordination shell is more important. Furthermore, a clear splitting appears in the second peak, indicating that the local structure for B particles is more ordered at low density. This is because at low density, with the formation of voids in the structure, a dense packing appears. A similar signature is known at high pressure.

Sastry et al. [47] suggested that the limiting density, in our case \(\rho_l = 1.06\), is a lower limit to glass formation. In order to elucidate this signature we compare the PRDF averaged over reoptimized local minima initially sampled at \(T = 0.5\) and \(T = 0.4\). The results in Fig. 5 reveal a clear difference between the two samples for densities above \(\rho_l = 1.06\). For the lower temperature, corresponding to the glassy phase, the structure is more ordered. However,
below $\rho_l = 1.06$ the PRDF are nearly the same, so it is not possible to differentiate between the glass and supercooled liquid structures in this way. Similar behaviour is exhibited by $g_{BB}$ in Fig. 6. However, $g_{AB}$, illustrated in Fig. 5, does not separate the two phases, indicating that the A-B disorder is similar in the glass and the supercooled liquid.

The formation of a void in one particular local minimum sampled at $T = 1$ is shown in Figure 7. The void starts to form at the limiting density $\rho_l = 1.06$ and then increases when the density is reduced further.

### IV. CONCLUSIONS

In this paper we have considered the effect of the density on local minima of a binary Lennard-Jones system sampled at kinetic equipartition temperatures $T = 1.0$, $0.5$ and $0.4$. A limiting density is found around $\rho_l = 1.06$, below which fractures and voids begin to form. The latter features cause discontinuities in various properties, in agreement with Sastry’s results.\[21\]

In the regime $\rho_l = 1.06 \leq \rho \leq 1.3$ the main peaks in the PRDF for AA, BB, and AB particles are slightly displaced to longer distance relative to $\rho = 1.3$. Below $\rho_l$, fractures and voids begin to form and the main peaks then move in the opposite direction. In the PRDF for BB particles at low density, a clear splitting of the second peak appears as a consequence of a more ordered local structure. Furthermore, below $\rho_l$, the PRDF for AA, BB and AB particles for the samples generated at $T = 0.5$ and $T = 0.4$ are indistinguishable, so it is not possible to differentiate between the glass and supercooled liquid structures at low density in this way.

The lowest value of the mean pressure also occurs around $\rho_l$ for each temperature. Below this density, the mean potential energy changes almost linearly with $\rho$ due to a transition from homogeneous local minima to inhomogeneous structures with voids.\[47\] The minimum of the mean energy potential as a function of the density corresponds to a pressure close to zero.

On the other hand, at positive pressure (compressed region), we found that the mean normal mode frequencies increase with energy but, at negative pressure (stretched region), the opposite behaviour appears. At lower density, the mean frequency is practically the same for samples obtained at each temperature, and reaches a limiting value as the density
decreases.

The initial MD trajectories sample fewer local minima at low temperature, as expected.

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FIG. 1: Mean potential energy (top) and pressure (bottom) as a function of the density for the three reoptimized samples of local minima.
FIG. 2: Mean angular frequency (top) and distance between all pairs of local minima (bottom) as a function of the density for the three samples of reoptimized local minima.
FIG. 3: Partial radial distribution function for A particles (top) and A and B particles (bottom) averaged over reoptimised local minima initially sampled at $T = 1$. For clarity, the curves have been displaced vertically.
FIG. 4: Partial radial distribution function for B particles averaged over the reoptimised local minima initially sampled at $T = 1$. As the number of B particles is relatively small, $g_{BB}$ is somewhat noisy. For clarity, the curves have been displaced vertically.
FIG. 5: Partial radial distribution function for A particles (top) and A and B particles (bottom) averaged over reoptimised local minima from the samples generated at $T = 0.5$ and $T = 0.4$. For clarity, the curves have been displaced vertically.
FIG. 6: Partial radial distribution function for B particles averaged over reoptimised local minima from the samples generated at $T = 0.5$ and $T = 0.4$. For clarity, the curves have been displaced vertically.
FIG. 7: Perspective view of the A (gray) and B (black) atoms for one particular local minimum reoptimised at different densities and initially located in an MD run with $T = 1$ as the kinetic equipartition temperature.