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Low-temperature behaviour of the Kob–Andersen binary mixture

Ashwin S S and Srikanth Sastry

Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur Campus, Bangalore 560064, India

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Abstract

The dynamical behaviours of glass-forming liquids have been analysed extensively via computer simulations of model liquids, among which the Kob–Andersen binary Lennard-Jones mixture has been a widely studied system. Typically, studies of this model have been restricted to temperatures above the mode coupling temperature. Preliminary results concerning the dynamics of the Kob–Andersen binary mixture are presented at temperatures that extend below the mode coupling temperature, along with properties of the local energy minima sampled. These results show that a crossover in the dynamics occurs alongside changes in the properties of the inherent structures sampled. Furthermore, a crossover is observed from non-Arrhenius behaviour of the diffusivity above the mode coupling temperature to Arrhenius behaviour at lower temperatures.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The emergence of slow dynamics as a liquid is cooled, as a precursor to glass formation at low enough temperatures in the absence of crystallization, has been studied extensively. In particular, computer simulations have played an important role in elucidating many details not accessible to experiments, and not amenable to simple theoretical modelling and calculation. Such simulation studies have been performed either for simplified model potentials [1–3], or empirical potentials for specific substances such as water, silica, and orthoterphenyl (OTP) [4–6]. A widely studied [7–9] model system in the former category is the Kob–Andersen binary Lennard-Jones mixture (KA BLJM) [2]. Until recently, molecular dynamics simulations of the KA BLJM as well as other systems have largely been performed at temperatures above the mode coupling temperature [10]. A notable exception has been the case for silica, where it has been observed that a crossover takes place in the temperature dependence of the diffusivities, from super-Arrhenius dependence at intermediate temperatures to Arrhenius temperature dependence at low temperatures [5].

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Among the approaches that have been extensively employed in analysing aspects of slow dynamics and the glass transition is the inherent structure approach [11], wherein the configuration space explored by the liquid at a given state point is characterized via the statistics and properties of local potential energy minima (inherent structures) sampled. Computer simulations have played a significant role in pursuing this approach, as they permit a detailed analysis of the dynamics of the system, as well as the generation and analysis of local energy minima. In addition to the energy minima, attention has also been paid recently to the analysis of saddle points [12], their connection to the study of instantaneous normal modes [13], as well as more global aspects of connectivity in the energy landscape, which may be employed in developing dynamical models for describing relaxation in liquids at low temperature [14–16].

Some of the studies mentioned above have been directed at understanding the nature of the dynamical crossover that is associated with the critical temperature of mode coupling theory. In [7], evidence was presented for a change in the local topography of the energy minima sampled above and below this crossover temperature, as well as for a change in the heights of barriers separating energy minima. A detailed analysis of the dynamics of transitions between energy minima [3] provided evidence that below a crossover temperature, one begins to observe a clear separation between vibrations within basins of individual energy minima and transitions between them, as discussed long ago by Goldstein [17]. The analysis of the order of saddle points sampled by the liquid as a function of temperature [12] shows that the saddle order extrapolates to zero at the estimated mode coupling temperature; thus, the nearest extremum point on the potential energy surface below the mode coupling temperature is a minimum. A similar analysis, in terms of negative eigenvalue instantaneous normal modes [18], led to the same conclusion. However, the studies mentioned above were based on simulations which were performed above the crossover temperature in question. It is of interest to revisit some of these analyses with simulations performed both above and below the crossover temperature. We present preliminary results here from a set of simulations of the KA BLJM liquid, which extend to temperatures below the mode coupling temperature.

2. Computational details

The results presented here are from molecular dynamics simulations of the KA BLJM, with 204 type A and 52 type B particles. The particles interact via the Lennard-Jones (LJ) potential, with parameters $\epsilon_{AB}/\epsilon_{AA} = 1.5$, $\epsilon_{BB}/\epsilon_{AA} = 0.5$, $\sigma_{AB}/\sigma_{AA} = 0.8$, and $\sigma_{BB}/\sigma_{AA} = 0.88$, and $m_B/m_A = 1$. The LJ potential is modified with a quadratic cut-off and shift at $r_c^{\alpha\beta} = 2.5\sigma_{\alpha\beta}$. All quantities are reported in reduced units: length in units of σ_{AA}, volume V in units of σ_{AA}^3 (density $\rho \equiv N/V$, where N is the number of particles, in units of $\sigma_{AA}^{-3} \equiv \rho_0$), temperature in units of ϵ_{AA}/k_B, energy in units of ϵ_{AA}, and time in units of $\tau_m \equiv (\sigma_{AA}^2 m/\epsilon_{AA})^{1/2}$, where $m = m_A = m_B$ is the mass of the particles. A time step of 0.003 τ_m is used in most of the runs, but a bigger time step of 0.01 τ_m is used for the lowest temperature studied. All the simulations are performed at the reduced density of 1.2. Molecular dynamics simulations are performed at constant energy (N, V, E), over a wide range of temperatures, using the velocity Verlet integration. The temperatures for the runs are calculated, as usual, from the average kinetic energy of the particles. Run lengths range from 4.5 million time steps (29.1 ns, using argon units for the A-particles, i.e. $\epsilon_{AA} = 119.8\,\mathrm{K} \times k_B$, $\sigma_{AA} = 0.3405$ nm, $m_A = 6.6337 \times 10^{-26}$ kg) at the highest temperature to 510 million time steps (11 μs) at the lowest temperature. Equilibration at low temperatures is ascertained by monitoring the mean squared displacements and ensuring that they do not show any systematic initial time dependence (ageing), and that they are large enough (40 or above). Further, run lengths are typically tens of times longer than the largest relaxation times obtained from the intermediate-scattering function. Local energy

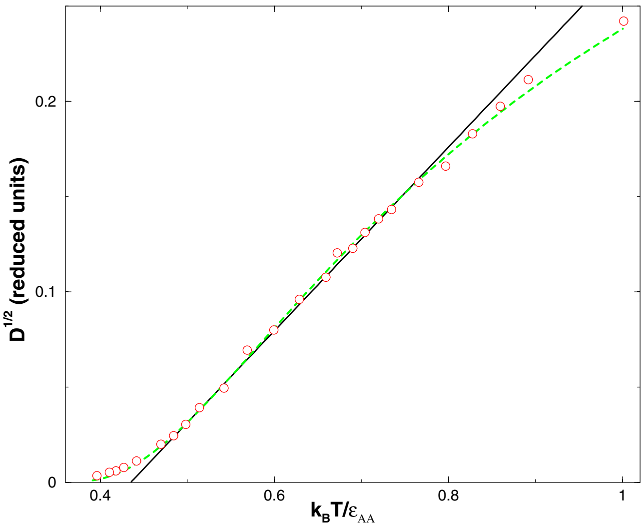

Figure 1. Diffusivity of A-particles, raised to the power $1/2$, plotted against temperature. The data points are linear in the intermediate-temperature range. Also shown are the straight-line fit (solid curve; corresponding to power-law behaviour), and the VFT fit to the data (dashed curve).

minimizations are performed for a few thousand configurations for each temperature, to obtain a sample of typical local energy minima or 'inherent structures' [11]. The Hessians (the matrices of second derivatives of the potential energy) evaluated at the minima are diagonalized to obtain the vibrational frequencies.

3. Results

The mean squared displacements of A- and B-particles are calculated from the MD trajectories as a function of time. The slopes of the mean squared displacements versus time, reported as the diffusivities D, are shown in figure 1 for the A-particles. In [2], the mode coupling temperature T_c was estimated to be 0.435, and the power-law exponent γ was estimated to be 2. A plot of $D^{1/\gamma}$ versus temperature should linearize the data in the range where the mode coupling behaviour holds. This is seen to be the case for the intermediate-temperature range shown in figure 1. Also included in the plot are the power-law fit (straight, solid, line) and a VFT fit (dashed curve) to the data. It is clear that for temperatures below 0.469, the diffusivities deviate from the power-law behaviour.

The diffusivity data for both A- and B-particles are shown in figure 2, in an Arrhenius plot. It is seen that above $T = 0.469$, the diffusivities show non-Arrhenius behaviour, which has previously been reported [19]. Below $T = 0.469$, however, the temperature dependence is seen to be Arrhenius. Also shown in the figure are the power-law (solid curve) and VFT (dashed curve) fits for the A-particles. In both cases, the fits are obtained for data above $T = 0.469$. It is seen that neither fit describes well the data at lower temperatures. The diffusivities for the B-particles show a similar trend. However, the ratio of the A-particle and B-particle diffusivities is temperature dependent; at high temperatures (above $T = 1.0$), the ratio is roughly constant with a value of about 1.25, but increases progressively at lower temperatures, reaching a value of about 4.25 at the lowest temperature shown (data not shown). The behaviour of the relative diffusivities of the two particle types is interesting to analyse,

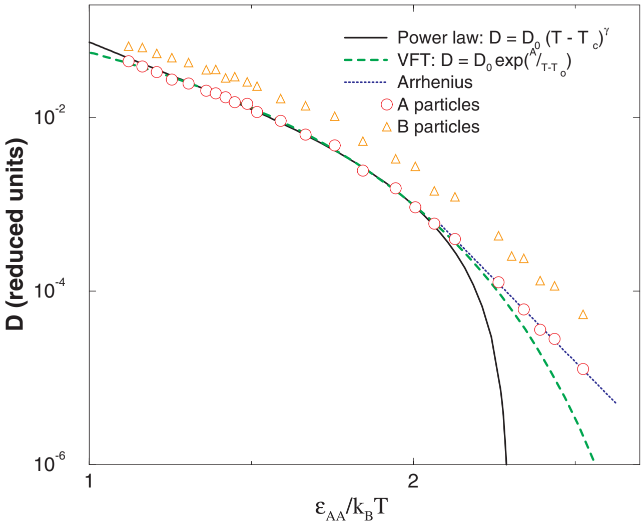

Figure 2. Diffusivity of A-particles (circles) and B-particles (triangles), shown in an Arrhenius plot. Also shown are the straight-line fit (solid curve; corresponding to power-law behaviour), the VFT fit to the data (dashed curve), and the low-temperature Arrhenius fit, for the A-particles.

and this will be pursued elsewhere. A crossover to Arrhenius temperature dependence has been observed in the case of silica, in which case the experimentally observed behaviour is Arrhenius. The observation of Arrhenius temperature dependence in the Kob–Andersen liquid, which is generally described in the literature as a typical ‘fragile’ liquid (as opposed to silica, the archetypal ‘strong’ liquid), is somewhat surprising and needs to be properly understood. Similar behaviour was observed for a smaller system ($N = 65$) in [15], but attributed to finite-size effects. Results of the analysis of this behaviour, currently being pursued, will be presented elsewhere.

Next we present results concerning the local energy minima sampled by the liquid as a function of temperature. The mean squared distance (MSD) between typical liquid configurations and the local energy minima to which they map was considered in [7]. It was observed that the temperature dependence of this quantity shows a change in slope around the mode coupling temperature previously estimated [2]. In addition, evidence was also found for a change in the energy barriers separating basins of minima. However, in [7], the simulations were performed at specified cooling rates, and the cooling rates used were not small enough to permit equilibration at temperatures below the mode coupling temperature. The MSD separating instantaneous configurations and the corresponding local energy minima, averaged over the sampled configurations, is shown in figure 3 as a function of temperature. Consistently with the observation in [7], the MSD values show a change in slope across the temperature where the diffusivities show a deviation from power-law temperature dependence. For comparison, we calculate the plateau value of the mean squared displacement obtained from MD trajectories, calculated at $t = 1.2$. The time $t = 1.2$ corresponds to the beginning of the plateau in a log–log plot of the mean squared displacement versus time, for low temperatures where a clear plateau is discernible. These values track the inherent structure MSD values, as seen in figure 3, although the difficulty of determining the plateau value of the mean squared displacements at higher temperatures makes the comparison difficult.

The vibrational frequencies for the sampled minima are calculated by diagonalizing the Hessian matrix (the matrix of second derivatives of the potential energy). In the harmonic

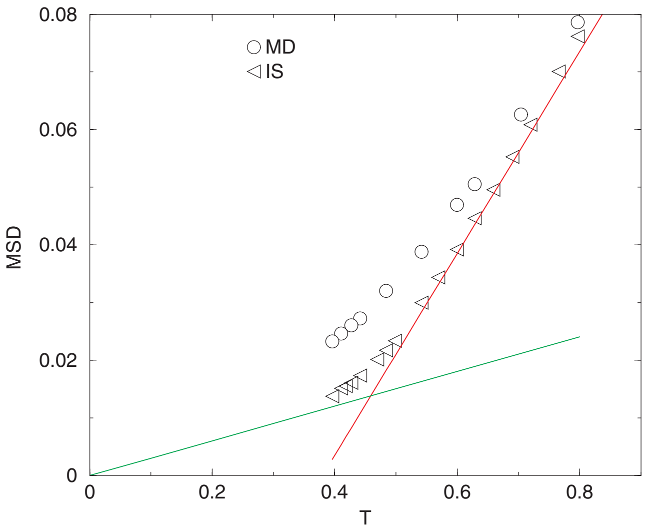

Figure 3. The MSD between instantaneous configurations and the corresponding local energy minima (triangles), showing a crossover in slope around the mode coupling temperature. High-and low-temperature straight lines are drawn as a guide to the eye. The mean squared displacements from MD trajectories are also shown (circles), at time $t = 1.2$. This choice corresponds to the mean squared displacement at the beginning of the plateau of the mean squared displacement versus time curves.

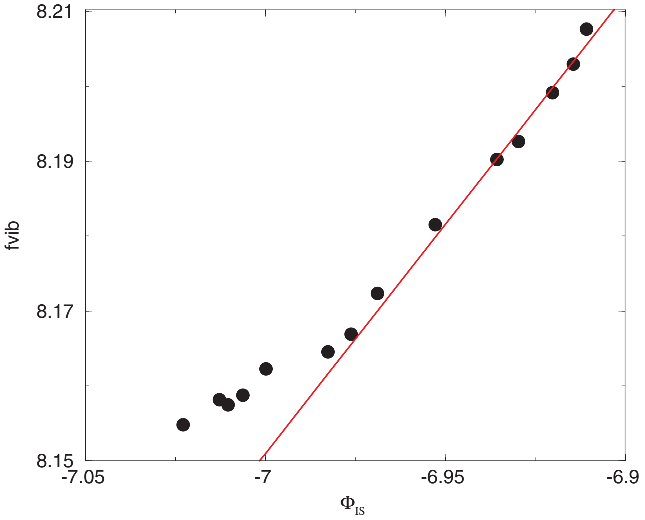

Figure 4. The average of the logarithm of vibrational frequencies, f_{vib}, shown as a function of the average inherent structure energy per particle. The straight-line fit to the higher-energy points is shown as a guide to the eye.

approximation to the basins, the basin free energy is proportional to the average of the logarithm of the frequencies, which we refer to as f_{vib} (see, e.g., [8]). It has been observed that this part of the basin free energy depends linearly on the energy of the minima in the temperature range previously studied [20]. This quantity is shown in figure 4 as a function of the average inherent structure energy. It is observed that f_{vib}, while displaying the nearly linear dependence on the inherent structure energy for the higher temperatures, begins to deviate from such linear behaviour below $T = 0.469$ (corresponding to inherent structure energy per particle ~ -6.98). This must reflect a change in the topography of the basins sampled at lower temperatures, but further analysis is needed to characterize the nature of the change, and its significance.

4. Summary

Results concerning the dynamics and properties of the local energy minima have been presented for the KA BLJM liquid for a range of temperatures that extends below the mode coupling temperature previously estimated. The diffusivity displays a crossover at low temperatures to Arrhenius temperature dependence. The MSD between instantaneous configurations and the corresponding local energy minima, as well as the vibrational frequencies, display a crossover in behaviour across the mode coupling temperature.

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