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The effect of atom mismatch on the fragility of supercooled Lennard-Jones binary mixtures

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Abstract

The shear viscosity of the well-known binary Lennard-Jones mixture is simulated under constant temperature and constant volume conditions (NVT) by a molecular-dynamics (MD) method. The effect of atomic size mismatch on the fragility parameter and glass-forming ability is studied. The fragility parameters calculated from shear viscosity data decrease with the increment of the atomic size mismatch. The value of the fragility changes from 168.963 to 22.976 when the mismatch changes from 0.023 to 0.25. It is shown that the fragility parameter is sensitive to the atomic size mismatch. The calculated pair distribution functions and mean square displacements indicate that the glass-forming ability increases with the atomic size mismatch.

1. Introduction

A glass forms when an undercooled liquid solidifies without crystallization. Near the glass transition temperature the viscosity increases continuously but rapidly with cooling. Fragility measures the rapidity with which a liquid's properties (such as viscosity) change as the glassy state is approached. Although the relationships between the fragility, configurational entropy, features of the energy landscape and Poisson's ratio [1–4] of a glass-former have been analysed previously, a detailed understanding of the origins of fragility is lacking.

It is well documented that the atomic size mismatch plays a major role in the glass transition. Fang *et al* [5] have demonstrated that the supercooled liquid region has a strong correlation with the atomic size mismatch. According to Qi [6], the radius ratio has a dramatic effect on the propensity for glass formation of Cu_4Ag_6 and CuNi alloys. Mathematical models are used by Lu [7] to measure the effect of the atomic size mismatch on thermal stability and glass-forming ability. However, few reports can be found for the effect of the atomic size mismatch on the fragility parameter.

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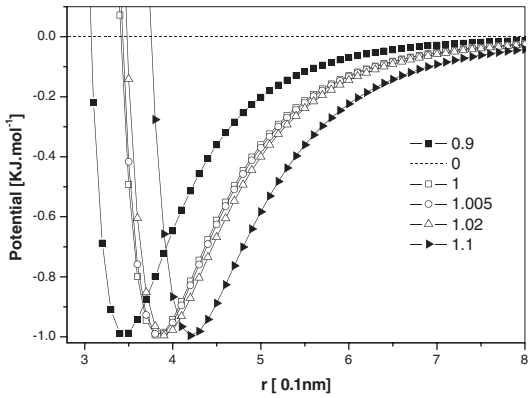

Figure 1. Potential curves of the five systems investigated.

Recently, a binary Lennard-Jones mixture system, originally proposed as a model for $Ni_{80}P_{20}$ [8], has been widely studied as a model glass-former in computer simulations [9–11, 2]. The interaction potential $V_{\alpha\beta}(r)$ takes the form of equation (1)

$$V_{\alpha\beta}(r) = 4\varepsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^{6}] \tag{1}$$

$(\alpha, \beta \in \{A, B\})$. In equation (1), σ is the distance where the energy is zero, and is a measure of the particle's diameter, and ε characterizes the well depth of the pair interaction. Kob used the system to test the mode-coupling theory [9]. Sciortino presented a quantitative description of the thermodynamics in a supercooled binary Lennard-Jones liquid [11]. In these studies, the potential parameters are unchanged. In this work, we present the molecular-dynamics (MD) simulations by changing one of the potential parameters, σ_{AA}, which denotes the diameter of particle A. By a series of simulations, we study different systems with different size mismatches. Some parameters are calculated, such as viscosity, fragility and packing fraction. Our motivation is to investigate the effect of the size mismatch on the fragility of the systems and their glass-forming ability.

2. Models and methods

2.1. Models

We studied the well-known binary Lennard-Jones mixture. The number of A and B particles is 400 and 100, respectively. Units of length and energy are defined by the σ and ε parameters of the A–A Lennard-Jones interaction potential. For argon these units correspond to a length of 3.41 Å and an energy of 120 K k_B. The two types of particles A and B have the same mass, which is chosen to be 1 in reduced units. The potential parameters are set as follows: $\varepsilon_{AA} = 1.0$, $\varepsilon_{AB} = 1.5$, $\varepsilon_{BB} = 0.5$, $\sigma_{AB} = 0.8$, $\sigma_{BB} = 0.88$. These parameters are the same as those studied in other papers [9]. To investigate the effect of size mismatch on fragility we performed a series of simulations with σ_{AA} chosen to be 0.9, 1.0, 1.005, 1.02 and 1.1, respectively. In this way, the diameter of particle A changes in the simulations. In figure 1 the potential curves of the five cases for A–A correlation are displayed. They have the same well depth but an increasing atomic distance.

2.2. Simulation details

The simulations were performed under constant temperature and constant volume (NVT) MD conditions in a cubic box with three-dimensional (3D) periodic boundary conditions. The truncation distance for the potentials is chosen to be 2.5σ. The systems were first equilibrated at a high temperature $T = 5.0$, corresponding to $T = 600$ K, for 2×10^5 steps with a step of 3×10^{-5} ps and subsequently cooled down at the reduced density $\rho^* = 1.2$. The reduced temperatures investigated were $T = 5.0$, 4.0, 3.0, 2.0 and 1.0, corresponding to 600, 480, 360, 240 and 120 K. Then, the systems were cooled down with a step of 6×10^{-5} ps at temperatures $T = 0.8$, 0.7, 0.6 and 0.5 (96, 84, 72 and 60 K). The pressure was chosen as 0 bar.

2.3. Green–Kubo relation and fragility

According to the Green–Kubo relation, i.e. the relations between transport coefficients and correlation functions involving fluxes of conserved quantities [12], the shear viscosity η can be derived from

$$\eta = \frac{V}{k_B T} \int_0^\infty \mathrm{d}t \, \langle P_{xy}(t + t_0) P_{xy}(t_0) \rangle \tag{2}$$

where V is the volume of the system, k_B is the Boltzmann factor and P_{xy} denotes an off-diagonal component of the stress tensor; $\langle \cdots \rangle$ is the ensemble average. The components of the stress tensor are defined by

$$P_{xy}(t) = -\frac{1}{V} \sum_{i=1}^{N} \left(M v_i^x(t) v_i^y(t) + \sum_{j>i}^{N} r_{ij}^x(t) f_{ij}^y(t) \right), \tag{3}$$

where N is the number of atoms in the unit cell, v_i^x represents the x component of the velocity 1 of atom i, r_{ij}^x the x component of the vector separation between atoms i and j, and f_{ij}^y the y component of the force on atom i due to atom j. There are five independent components of the traceless stress tensor, P_{xy}, P_{yz}, P_{zx}, $\frac{1}{2}(P_{xx} - P_{yy})$ and $\frac{1}{2}(P_{yy} - P_{zz})$. From each of those components the stress autocorrelation function (SACF) can be constructed by averaging $P_{xy}(t+t_0)P_{xy}(t_0)$ over time origins t_0. The Green–Kubo relation has been successfully applied to first principles calculations of the viscosity of liquid Se and Al in [13, 14].

The fragility of liquids is defined as the apparent activation energy of shear viscosity η or structural relaxation time τ_α at the glass transition temperature T_g, normalized to T_g [15]:

$$m = \left. \frac{\mathrm{d} \log \eta}{\mathrm{d}(T_g/T)} \right|_{T=T_g}. \tag{4}$$

Generally, the glass transition temperature T_g is where the viscosity reaches a value of 10^{12} Pa s.

3. Results and discussion

The pair distribution function (PDF) is given as:

$$g(r) = \frac{1}{N} \sum_{ij} \delta(r - r_{ij}), \tag{5}$$

where N is the number of particles. This function gives the probability of finding atoms at a distance r apart, relative to the probability expected for a completely random distribution (with $g(r) = 1$) at the same density.

In figures 2–4, the PDFs of the systems $\sigma_{AA} = 0.9$, $\sigma_{AA} = 1$ and $\sigma_{AA} = 1.0$ are shown, respectively. For clarity the individual curves for different temperatures have been displaced

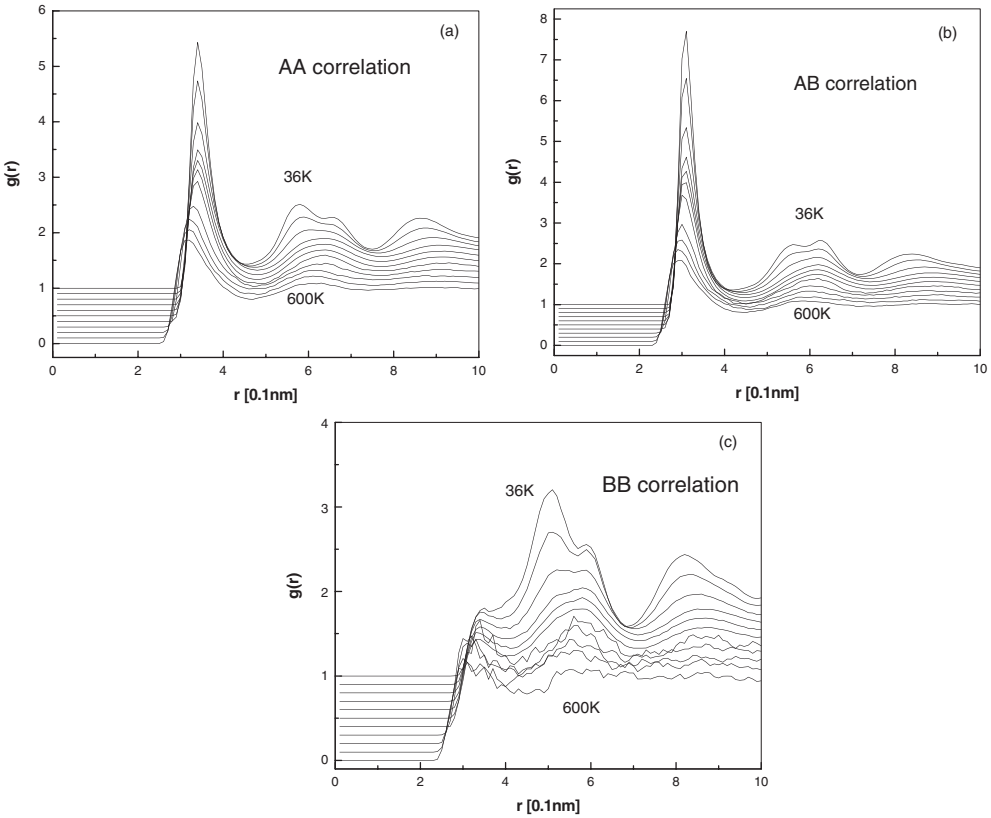

Figure 2. Pair distribution function (PDF) of the system $\sigma_{AA} = 0.9$ for AA (a), AB (b) and AA (c) correlation for all temperatures investigated. For clarity the individual curves have been shifted vertically by $0.1\,n, n = 0, 1, 2, 3\ldots$.

vertically. The three systems are uniform except for the diameter of particle A. The mismatch δ is defined as equation (6)

$$\delta = (r_A - r_B)/r_B \tag{6}$$

in which r_A and r_B are the diameters of particles A and B, respectively. The calculated mismatches are listed in table 1. For the AA and AB correlations of the three cases, a significant second-peak split appears at temperatures of 60, 120 and 240 K respectively. The split in the second peak indicates the structural randomness, which is a unique characteristic of an amorphous material. Thus the conclusion can be drawn that when the size mismatch increases the system has a stronger glass-forming ability. In figures 2–4, the BB correlations show that when the temperature is lowered the first peaks are reduced to small shoulders. This is due to the fact that the attraction between two B particles is smaller than the one between the AA pair or an AB pair. Thus two B particles will try to stay apart at low temperature and the first peak will become smaller. Similar results have been reported by Kob *et al* [9].

Figure 5 shows the height of the first peaks at temperatures investigated in PDFs for AA correlation for the cases $\sigma_{AA} = 0.9, \sigma_{AA} = 1$ and $\sigma_{AA} = 1.02$. When the temperature is lowered, the height of the first peak increases. This indicates that clusters with A–A short-range order enhanced in the supercooled liquid phase. With the variation of the size mismatch from 0.023 to 0.159, the height of the first peak increases at all temperatures. This suggests that the

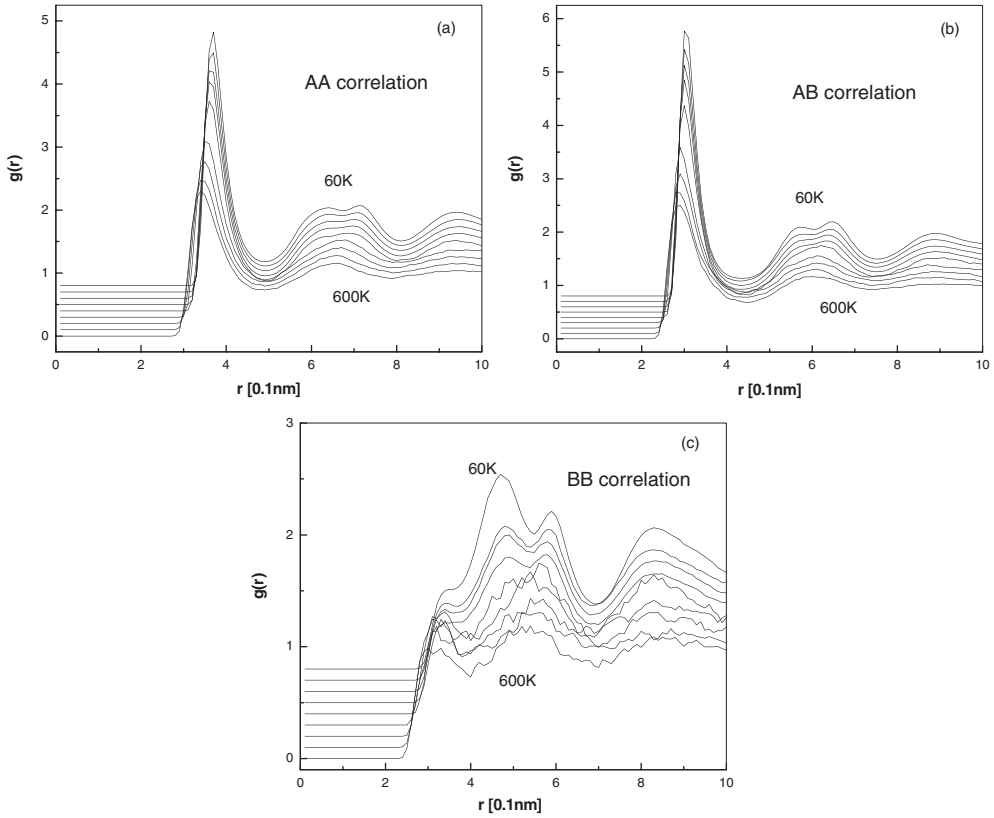

Figure 3. Pair distribution function (PDF) of the system $\sigma_{AA} = 1$ for AA (a), AB (b) and AA (c) correlation for all temperatures investigated. For clarity the individual curves have been shifted vertically by 0.1 n, $n = 0, 1, 2, 3 \ldots$.

Table 1. Mismatches, fragilities and packing fractions for the different cases investigated.

σ	Mismatch	Fragility	Packing fraction
0.9	0.023	168.963	0.454
1	0.136	156.918	0.591
1.005	0.142	137.354	0.598
1.02	0.159	24.963	0.622
1.1	0.25	22.976	0.758

A–A short-range order grows with the mismatch. It reveals that the mismatch contributes to the formation of clusters. The result is consistent with the cluster model of the glass transition [16].

The mean square displacement (MSD) $\langle r^2(t)\rangle$ takes the form $\langle r^2(t)\rangle = \langle |r(t) - r(0)|^2\rangle$. The time dependences of the MSD for the binary Lennard-Jones mixtures for the cases $\sigma_{AA} = 0.9$, $\sigma_{AA} = 1$ and $\sigma_{AA} = 1.1$ at different temperatures are plotted in figures 6(a), (b) and (c), respectively. The figures are double logarithmic plots [9]. At higher temperatures the MSD curves are typical for simple liquids [17]. In figures 6(b) and (c), a plateau gradually appears with the decreased temperatures at intermediate times (from 0.4 to 4 ps). The two figures are similar to the results reported by Kob *et al* [9], while in figure 6(a), a plateau is not very obvious. It can be concluded that the larger the atomic size mismatch, the higher the temperature at which

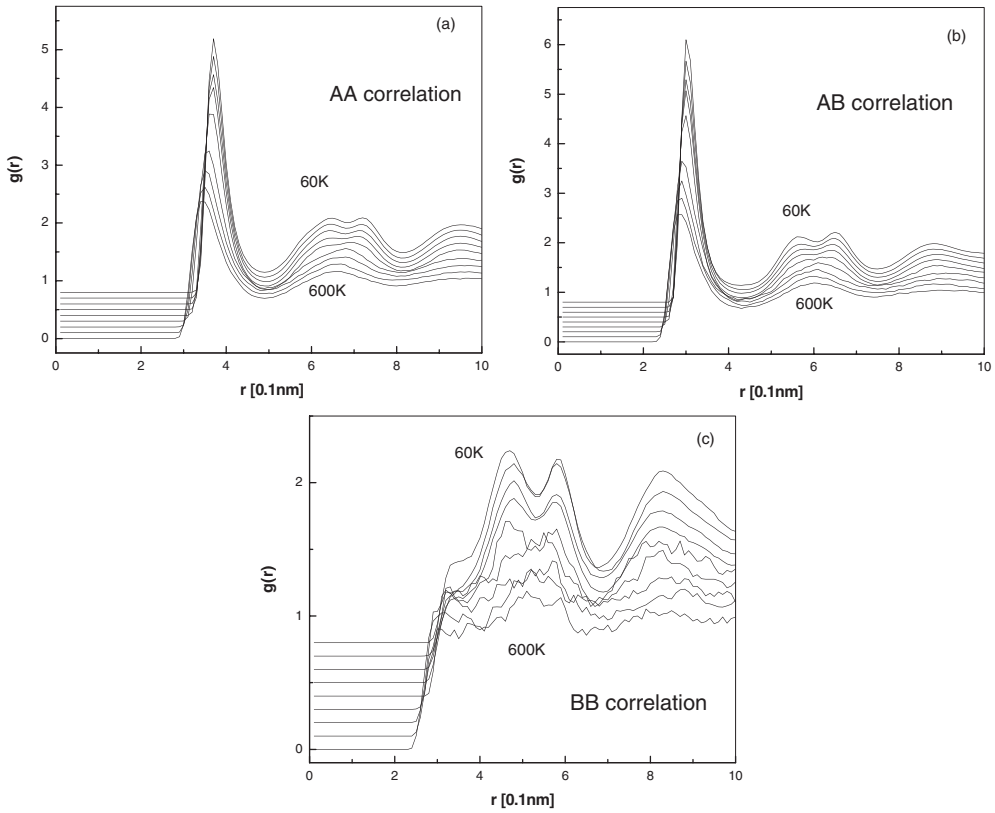

Figure 4. Pair distribution function (PDF) of the system $\sigma_{AA} = 1.02$ for AA (a), AB (b) and AA (c) correlation for all temperatures investigated. For clarity the individual curves have been shifted vertically by 0.1 n, $n = 0, 1, 2, 3 \ldots$.

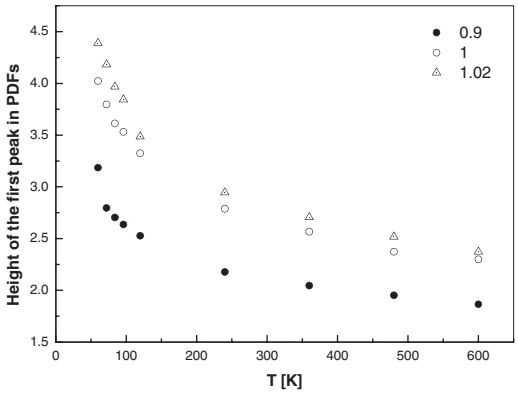

Figure 5. The temperature dependences of the height of the first peaks in PDFs for AA correlation for the cases $\sigma_{AA} = 0.9$, $\sigma_{AA} = 1$ and $\sigma_{AA} = 1.02$.

the plateau appears. According to the mode-coupling theory (MCT) [18, 19], the initial stage (before 0.4 ps) of the MSD is due to the vibrational (ballistic) motion of the particles and the stage following the plateau is caused by long-range diffusion. The occurrence of the plateaus

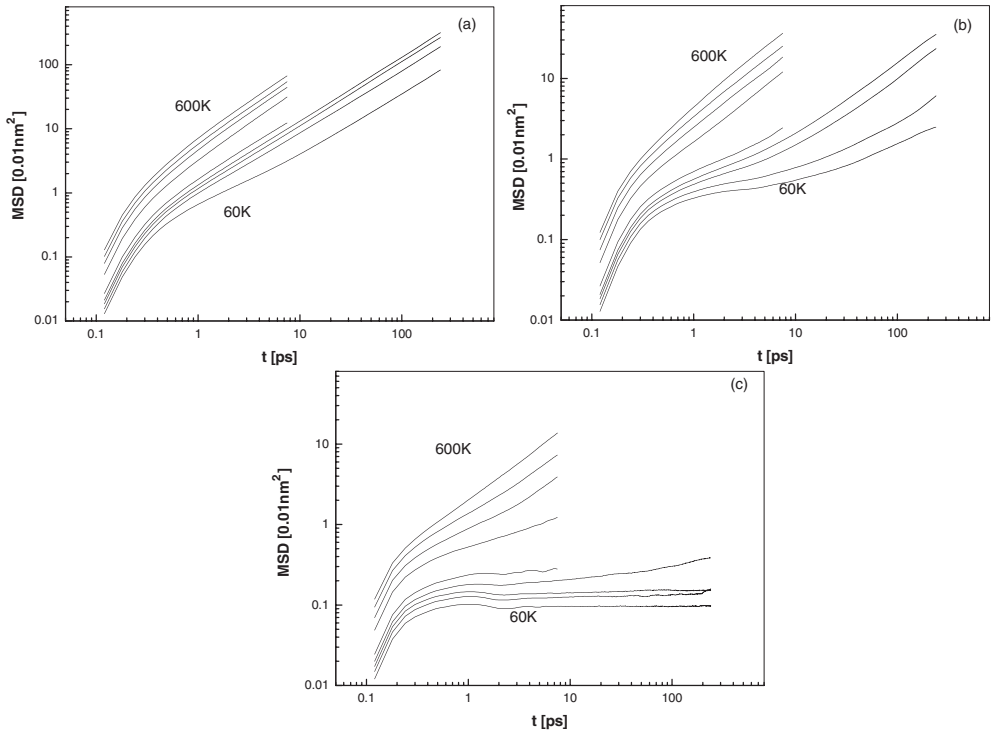

Figure 6. Time dependences of the MSDs for reduced temperatures $T = 5$, 4, 3, 2, 1, 0.8, 0.7, 0.6 and 0.5. They are double logarithmic plots. (a) $\sigma_{AA} = 0.9$, (b) $\sigma_{AA} = 1$ and (c) $\sigma_{AA} = 1.1$.

results from the so-called 'cage effect' for a tagged particle. It takes some time for a particle to escape from the 'cage' formed by its surrounding neighbours [20]. The lower the temperature, the longer the time required, thus the more distinct the plateau. In MCT, the approach to and the subsequent departure from the plateau defines the β-relaxation regime. The initial plateau in the MSD reflects the cage trapping. The end of this plateau where the MSD rises corresponds to cage rearrangement [21]. With the increment of the atomic size mismatch, the appearance of the plateau at a higher temperature indicates that the particles find it more difficult to escape from the 'cage'. Thus the stability of the structure increases, indicating a higher glass-forming ability.

Figure 7 shows the SACF of the case $\sigma_{AA} = 1$ at 96 K, the curve steadily decays towards zero. The oscillations of SACF about zero are due to statistical noise. The shear viscosity can be calculated by the time integrals of the SACFs. Figure 8 shows the viscosity data at various temperatures for the case $\sigma_{AA} = 1$. The viscosity increases rapidly as the temperature approaches the glass transition temperature. The data were fitted by the Vogel–Fulcher–Tammann (VFT) relation, given as equation (7):

$$\eta = \eta_0 \exp[DT_0/(T - T_0)], \tag{7}$$

where η_0 is pre-exposed factor, T_0 the VFT temperature, T the temperature and D the fragility parameter. The parameter T_0 may be considered as the Kautzman temperature at which the excess configurational entropy is zero or the so-called 'ideal' glass transition temperature [22–24]. The fitted result of η_0, D and T_0 are 0.239 Pa s, 2.542 and 42.216 K, respectively. From figure 8, it can be seen clearly that the VFT relation can be used to fit the calculated results.

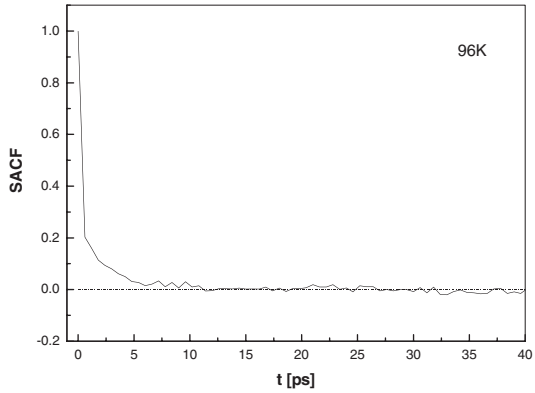

Figure 7. Normalized stress autocorrelation function for the case $\sigma_{AA} = 1$ at 96 K.

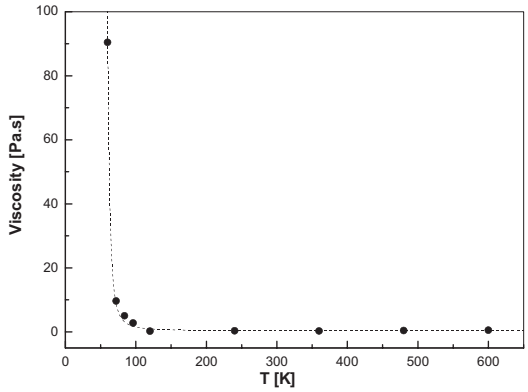

Figure 8. The viscosity data for the binary mixture system ($\sigma_{AA} = 1$). The dotted line is the Vogel–Fulcher–Tammann fit.

Figure 9 shows an Angell plot of viscosity for different cases. The curves for $\sigma_{AA} = 1.02$ and $\sigma_{AA} = 1.1$ show a steady, linear increase, while others display a much steeper dependence on $1/T$, indicating that the former are 'strong' liquids, and the latter, 'fragile' [25, 26]. The fragility parameters calculated from equation (4) are summarized in table 1. The value of fragility changes from 168.963 to 22.976 when the mismatch changes from 0.023 to 0.25. This demonstrates that the greater the atomic size mismatches, the smaller the fragility. It is obvious that the fragility parameter is sensitive to the mismatch. The glass-forming ability increases with the enhanced atomic size mismatch. This result is well consistent with the previous result from computer simulations [27].

The packing fraction is defined as the ratio of the total volume occupied by the particles to the total volume. The packing fractions were calculated for different cases, and the values are listed in table 1. It can be seen that the packing fraction increases with the atomic size mismatch. In our simulations, the volume and density are constant. Therefore, the free volume decreases when the diameter of particles A increases. Since the configurational redistribution of elements of a material with a high packing fraction is relatively difficult compared to a state with a low packing fraction, the densely packed material needs more time to rearrange [28] and the system will in turn more easily experience the glass transition and the value of fragility will decrease. Provided the packing fraction remains constant as the size of the particles A

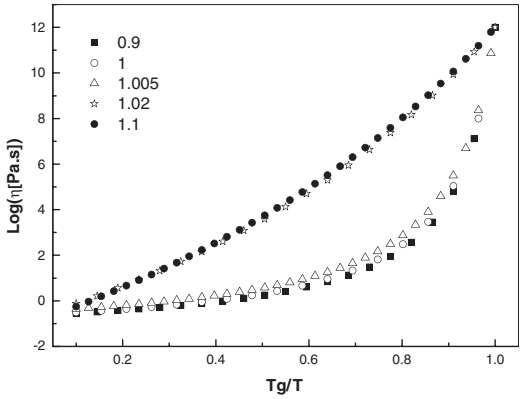

Figure 9. Angell plot of the viscosities of the five cases $\sigma_{AA} = 0.9$, 1, 1.005, 1.02 and 1.1.

is varied, that is, the volume of the simulation box increases with increasing σ_{AA}, the large atomic size mismatches will still decrease the ability of the particles to move. This will retard the nucleation process and, in turn, promote glass formation.

4. Conclusions

In this paper, a binary Lennard-Jones mixture system was studied by a MD method. Both the viscosities and the fragilities were calculated for five cases with different atomic size mismatch. The results indicate that the greater the atomic size mismatch, the smaller the value of the fragility. The fragility parameter is very sensitive to the configurable parameter.

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