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# Glass formation and thermodynamics of 3D simple system

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**ABSTRACT**

*Procedure for molecular dynamics simulation in cooling 3D simple monatomic supercooled liquid from liquid to glassy state is presented. Models contain 2,744 particles interacted via Lennard-Jones-Gauss potential. Evolution of structure and various thermodynamic properties upon cooling from liquid to glassy state is analyzed in detail via radial distribution function, temperature dependence of potential energy, mass density, time - temperature dependence of mean - squared displacement, coordination number distribution, bond-angle distribution, fraction of solid-like atoms, and 3D visualization of atomic configurations. Via intensive molecular dynamics simulation of glass formation in 3D simple supercooled liquids, it was found that fraction of solid-like atoms (i.e. with the slowest mobility) increases monotonously with a sudden increase in the vicinity of glass transition reaching almost 100% at low temperature to form a solid glassy state.*

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## 1 INTRODUCTION

Despite long and intensive efforts for decades, understanding of glass formation is far from complete, even for the simplest system, and it has been under intensive investigations by experiments, theoretical approaches, and computer simulation (Donth, 2001). Glass transition is still an unsolved problem in condensed matter physics. Understanding of the nature of a glass transition is still limited. Most simulations of the glass transition have been performed for the binary liquid, since monatomic simple liquids readily crystallize under cooling from the melts. In fact, many efforts have been made to create materials in the glass state of a simple atomic system. In 1924, Jones gave Lennard-Jones potential (LJ) an interactive representation of the structure and properties of inert gas, particularly with Argon. LJ is used to simulate gas, liquid, solid (glass and crystalline). However, in the glass state, LJ gives lower icosahedra, leading to a labile glass state that is crystallized into face cubic center when the system cooled from liquid with slow rate at low temperatures. Therefore, it is difficult to investigate the thermodynamic properties of single atomic glass states. In order to avoid the crystallization of simple monatomic liquid when cooling the system from high temperature to low temperature, Dzugutov (1992) proposed a new interaction potential compared with that of LJ, Dzugutov potential has a peak at the position equal to the coordinated distance of the second coat in the close-packed crystal Thus, limiting the crystallization of monatomic liquid. In other words, Dzugutov potential increases crystallization of the system. Indeed, the initial state of the system with the Dzugutov potential was quite stable. Thus, the appearance of Dzugutov has promoted deeply study about the structure and the thermodynamic properties of supercooled liquids and the glass state. However, the

glass state will not stable. After recovering at low temperatures for a long time, the glass state turns into quasicrystal) (Kim and Medvedev, 2006), otherwise, the Lennard-Jones-Gaussian interaction (LJG) (Jones, 1924; Belashchenko, 1997; Heyes, 1977; Balbuena and Seminario, 1999; Kim and Medvedev, 2006), shows the stability of the glass state, difficulty to crystallize in 3D and 2D. The liquid and glass state of the Lennard-Jones-Gauss system has a high concentration of icosahedra, similar to that of liquid metals and glass.

## 2 CALCULATION

A system of single-component atoms that interact mutually through the LJG potential was considered (Engel and Trebin, 2007; Mizuguchi and Odagaki, 2009).

$$U(r)=\varepsilon\left\{\left[\left(\frac{\sigma}{r}\right)^{12}-2\left(\frac{\sigma}{r}\right)^{6}\right]-1.5\exp\left[-\frac{(r-1.47\sigma)^2}{0.04\sigma^2}\right]\right\} \quad (1)$$

The LJG potential is a sum of the Lennard-Jones potential and a Gaussian contribution. The model is performed the molecular dynamics simulation in a cube containing 2,744 atoms because the model is relative and statistically insignificant under periodic boundary conditions. The following LJ-reduced units were used in the present work: the length in unit of $\sigma$, temperature $T$ in unit of $\varepsilon / k_B$, and time in unit of $\tau_0=\sigma\sqrt{m/\varepsilon}$. Here, $k_B$ is the Boltzmann constant, $m$ is an atomic mass, $\sigma$ is atomic diameter, and $\varepsilon$ is a depth of LJ part of LJG potential. For Ar, It has $m=0.66\text{x}10^{-25}$ kg, $\varepsilon / k_B=118$K, $\sigma=3.84$Å, and therefore, $\tau_0=\sigma\sqrt{m/\varepsilon}=2.44$ ps. The Verlet algorithm was used and MD time step is $dt=0.001\tau_0$ or 2.44fs if taking Ar for testing. NPT ensemble simulation was employed where the temperature and pressure are controlled by the standard algorithm. The initial simple cubic structure configurations have been relaxed at temperature as high as $T=2.0$ for $2\times10^5$ MD steps in order to get an equilibrium liquid state. Then the system is cooled, and the temperature is decreased linearly with time as $T=T_0-\gamma\times n$ via the simple atomic velocity rescaling until reaching $T=0.1$. Here, $\gamma=10^{-6}$ per MD step is a cooling rate (or $4.83\text{x}10^{10}$K/s if taking Ar for testing), and $n$ is the number of MD steps. VMD software was used for 3D visualization of atomic configurations.

## 3 RESULTS AND DISCUSSION

Temperature dependence of some thermodynamic quantities of the system upon cooling from liquid to glassy state can be seen in Figure 1. Temperature dependence of potential energy per atom is rather continuous indicated a glass formation in the system (Figure 1a). The linear part of the high temperature region of the curves is related to the equilibrium liquid state. Therefore, the starting point of deviation from the linearity, $T_A=1.66$, is a crossover temperature where the change in mechanism of diffusion occurs. The relatively linear part of the low temperature region of the curves is related to the glassy state. The starting point of deviation from the linearity is a glass transition temperature, $T_g=0.91$.

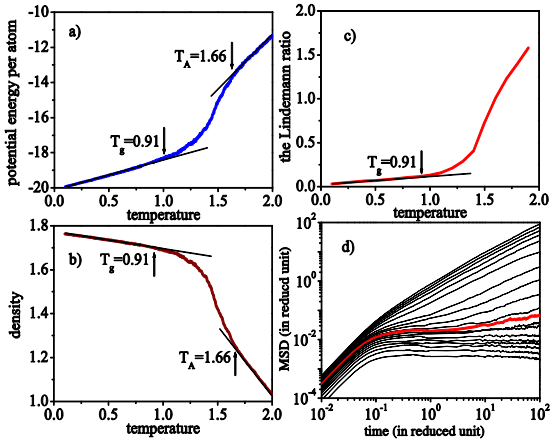



**Fig. 1: Temperature dependence of potential energy per atom (a), mass density (b), the Lindemann ratio (c), and Time-temperature dependence of MSD (d) (the bold line is $T_g=0.91$, from top to bottom for temperature ranged from $T=1.9$ to $T=0.1$)**

As shown in Figure 1b, temperature dependence of mass density increases with decreasing temperature. Therefore, atomic arrangement becomes more close-packed with decreasing temperature; especially mass density strongly increases for the region $T_g<T<T_A$, reaching the saturated value for glassy state of around $\rho=1.703$ at $T_g$. The Lindemann ratio in the system is also calculated (Figure 1c) (Lindemann, 1910), e.g. the Lindemann ratio for the ith atom: $\delta_i=<\Delta r_i^2>^{1/2}/\bar{R}$. Here, $<\Delta r_i^2>^{1/2}$ is the mean-squared-displacement (MSD), and $\bar{R}=0.9\sigma$ is a mean interatomic distance. For the supercooled and glassy states, $\bar{R}$

does not change much with temperature and that this value was fixed for calculations. The Lindemann ratio $\delta_L$ of the system is defined by averaging of $\delta_i$ overall atoms in the system, $\delta_L = \sum_i \delta_i / N$. On the other hand, MSD of atoms in the system exhibits a common behavior of glass-forming system. In Figure 1d, it can be seen that the MSD has three regimes: the ballistic regime at the beginning of motion, followed by the plateau regime, which relates to the caging effects, and finally the diffusive regime over longer time. These three regimes are seen clearly at low temperature.

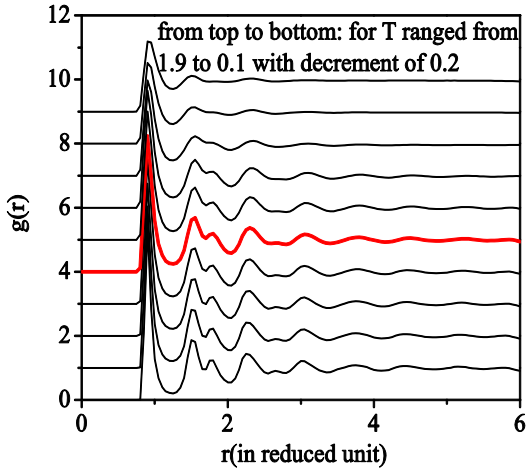



**Fig. 2: Evolution of radial distribution function of the system upon cooling from $T = 2.0$ to $T$=0.1**

Glass formation in the system is also confirmed via evolution of RDF for temperature ranged from $T$=2.0 to $T$=0.1 (Figure 2). It can be seen that at high temperature, the RDF is rather smooth, and the height of its peaks is small, exhibiting a clearly normal liquid state. However, the height of first and second peaks is enhanced when temperature decreases. At $T_g$=0.91, additional peaks appear, and multi-peak RDF exhibits clearly a glassy state of 3D LJG system. It indicated that vitrification of the system at low temperature. More detailed information about the local structure in the system can be found via coordination number and bond-angle distributions shown in Figure 3. That, coordination number distribution is broad, indicated the inhomogeneous structure of a model, and it is typically seen for isotropic potential (Doye, 2003). Figure 3 shows that atoms in the amorphous model are mainly surrounded by 12, 13 or 14 neighbors, which may be related to the icosahedra with 12 vertices or polytetrahedra of 13 or 14 vertices (Honeycutt and Andersen, 1987; Doye, 2003). On the other hand, bond-angle distribution in the model has a single peak at around, indicating the domination of equilateral or slightly distorted equilateral triangles in the system, which may be related to the faces of icosahedra and polytetrahedra (Doye, 2003). Almost the same coordination number and bond-angle distributions have been found (Van Hoang and Odagaki, 2008).

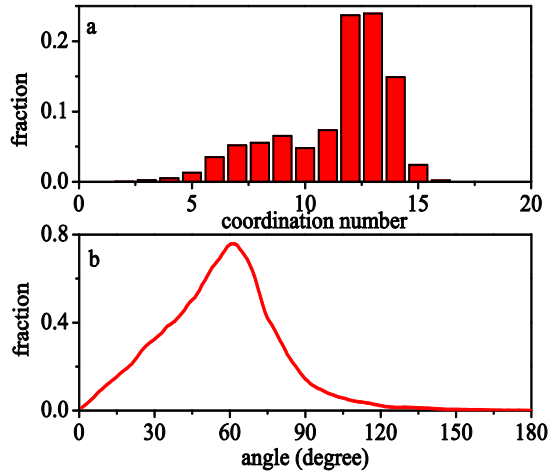



**Fig. 3: Coordination number (a) and bond-angle (b) distribution in model obtained at $T$=0.1**

Solid-like atoms are dectected by the Lindemann criterion $\delta_i \le \delta_C$. Hence, it can be found the critical value for $\delta_L$ in Figure 1c and $T$=$T_g$ it is equal to 0.162. It is noted that a purely Lindemann criterion established that melting occurs when a root of MSD is at least 10% (usually around 15%) of the atomic spacing (Lindemann, 1910; Flores-Ruiz and Naumis, 2009). In the present work, atoms with $\delta_i \le \delta_C$ are classified as solid-like, and atoms with $\delta_i > \delta_C$ are classified as liquid-like. This means that the critical value for the Lindemann ratio is $\delta_C = 0.162$. Therefore, atoms with $\delta_i \le 0.162$ can be considered as solid-like. It is noted that for bbc crystal $\delta_C = 0.18$ (Stillinger, 1995), for Lennard-Jones fcc crystal $\delta_C = 0.22$ (Tomida and Egami, 1995), for 3D systems $\delta_C = 0.21$ (Hoang and Odagaki, 2011).

Solid-like atoms have a tendency to form clusters even in the initial stage of their formation. If two atoms are connected in one cluster when their distance is less than the radius of the first coordination sphere, i.e., $R_0 = 1.213\sigma$. This cutoff radius is equal to the position of the first minimum after the first peak in RDF of a glassy state obtained at $T$=0.1. Figure 4 presents the temperature dependence of a fraction of solid-like atoms $(n_S / N)$ and the ratio of the size of the largest cluster of solid-

like atoms to the total number of atoms in the system ($S_{max}$ / $N$). It is found that solid-like atoms form in the early stage of the supercooled region, i.e. the first 7 or 8 solid-like atoms form throughout the model at $T$=1.66 and $n_S / N$ increases with decreasing temperature. The increment is small in the first stage, and then it progressively increases, leading to the percolation threshold of solid-like clusters at $T$=1.3 when the fraction of solid-like atoms reaches 24.85%. This fraction grows up to 78.87% at the glass transition and reaches 100% at $T$=0.1.

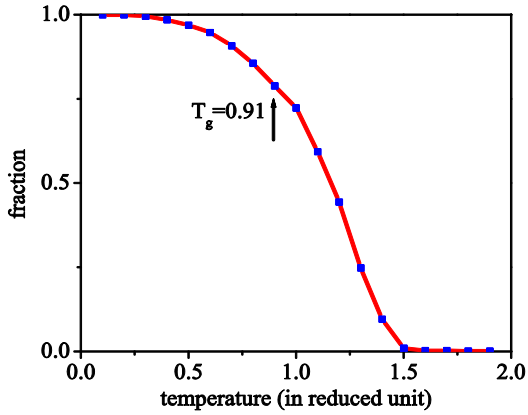
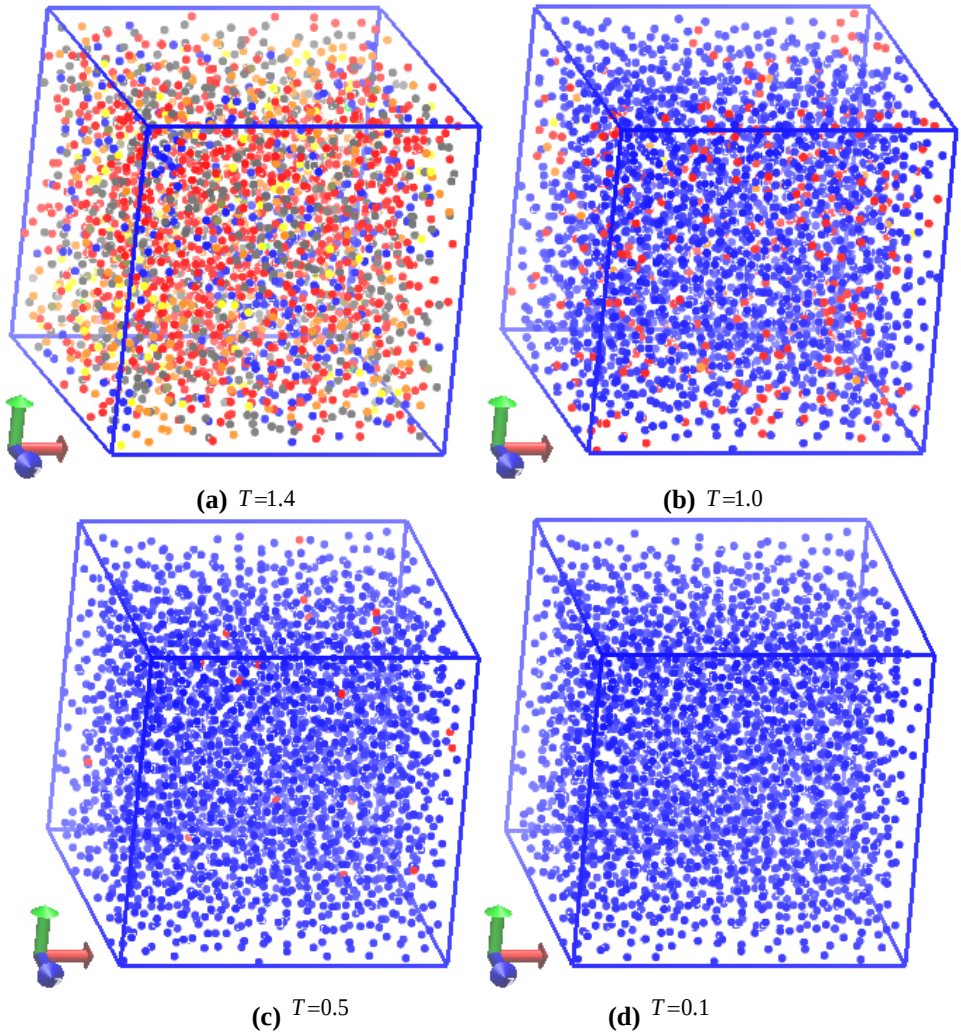



**Fig. 4: Temperature dependence of fraction of solidlike atoms** ($n_S / N$)



**(a)** $T$=1.4 **(b)** $T$=1.0 **(c)** $T$=0.5 **(d)** $T$=0.1

**Fig 5: 3D visualization of atoms with the same (or close) atomic displacement ($ad$, in reduced unit) after relaxation for 5000 MD steps at a given temperature, atoms are colored as follows: blue for $ad = [0.0 - 0.2)$, red for $ad = [0.2 - 0.4)$, gray for $ad = [0.4 - 0.6)$, orange for $ad = [0.6 - 0.8)$, yellow for $ad = [0.8 - 1.0)$, tan for $ad = [1.0 - 1.2)$, silver for $ad = [1.2 - 1.4)$, green for $ad = [1.4 - 1.6)$, pink for $ad = [1.6 - 1.8)$, cyan for $ad = [1.8 - 2.0)$**

Atoms with different atomic displacements ($ad$) are colored and it is found that atoms with the same or very close mobility are strongly correlated (Figure 5). At very high temperature, dynamics of atoms is rather homogeneous and heterogeneous dynamics is enhanced with lowering temperature.Atomic configurations are showed at temperature above and below $T_g$=0.91 in Figure 5. Some important points can be drawn: (i) Atoms with the same or very close mobility have a tedency to aggregate into clusters; (ii) Population of atoms with high mobility have a tendency to decrease while population of atoms with low mobility have a tedency to increase with decreasing temperature; (iii) Atoms with a high mobility have a tendency to aggregate into string-like form clusters (Figures 5a and 5b) while atoms with very slow mobility (the 'blue' ones) have a tendency to aggregate into more compact clusters (Figures 5b and 5c); the latter grows into the largest one which spans almost throughout model at temperature much below $T_g$ (Figure 5d). The results are consistent with previous results of 2D system (Hoang et al., 2015).

## 4 CONCLUSIONS

Many characters of MD simulation of glass formation in 3D simple supercooled liquids with LJG interatomic potential, and some important conclusions of this paper can be drawn as follows:

– Phase transition temperature ($T_g$=0.91) is lower than Hoang and Odagaki's (2011) ($T_g$=1.0), because the cooling rate $\gamma$=$10^{-6}$ is smaller than $\gamma = 2 \times 10^{-6}$. Results are more accurate than Hoang et al., 2011. Because, the faster of the cooling rate, the higher temperature of the phase transition will be.

– The process of glass formation of the supercooled simple monatomic liquid happened along with the separation of the second peak of the g(r), which indicates the formation of close-packed structure of the model at the glass temperature. At the same time, three regimes of MSD were observed at low temperatures: the ballistic regime at the beginning of motion, the plateau regime and finally the diffusive regime over a longer time.

– At $T_g = 0.91$, coordination number distribution is broad, indicating an inhomogeneous structure of the system. It can be found that bond-angle distribution at $T = 0.1$ in the model has a single peak at around $60^o$. Bond-angle distribution indicated the domination of equilateral triangles in the system, which may be related to the faces of icosahedra and polytetrahedra.

– Solid-like atoms have a tendency to form clusters even in the initial stage of their formation. Fraction of solid-like atoms increase with decreasing temperature. The increment is small in the first stage, and then it progressively increases, leading to the percolation threshold of solid-like clusters at $T = 1.3$ when the fraction of solid-like atoms reaches 24.85%. This fraction grows up to 78.87% at the glass transition and reaches 100% at $T$=0.1 .

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