VITRIFICATION PROCESS OF MONATOMIC LENNARD-JONES SYSTEM WITH FREE SURFACES

LE NGUYEN TUE MINH[*], VO VAN HOANG[**]

ABSTRACT

Glass formation in simple monatomic LJ system with free surfaces has been studied by molecular dynamics (MD) simulations. Atomic mechanism of glass formation is monitored via spatiotemporal arrangement of solid-like atoms occurred in the system upon cooling from the melt. Free surfaces significantly enhance atomic mobility in the system compared to that of the bulk and induce the formation of so-called layer structure of the interior of glassy state.

Keywords: glass of monatomic Lennard-Jones systems, MD simulation, Free surfaces.

TÓM TẮT

Quá trình thủy tinh hóa của hệ Lennard-Jones đơn nguyên tử với bề mặt tự do

Sự hình thành pha thủy tinh trong quá trình làm lạnh trong hệ đơn nguyên tử đơn giản LJ với bề mặt tự do được nghiên cứu bằng phương pháp mô phỏng động lực học phân tử (MD). Cơ chế nguyên tử của sự hình thành pha thủy tinh được khảo sát thông qua sự sắp xếp không gian-thời gian của nguyên tử đã hóa rắn trong hệ suốt quá trình làm lạnh. Bề mặt tự do làm tăng đáng kể độ linh động của nguyên tử trong hệ so với hệ khối và gây ra sự hình thành cấu trúc lớp của lõi ở trạng thái thủy tinh.

Từ khóa: sự thủy tinh hóa của hệ đơn nguyên tử Lennard-Jones, mô phỏng MD, bề mặt tự do.

1. Introduction

Glasses with free surfaces, i.e. thin film-like ones, have been under intensive investigations due to their scientific and technological importance (see [3], [10], [11], [16] and references therein). It was found that glass transition temperature (T_g) can be suppressed by tens of degrees for the films with thicknesses of tens of nanometers [11]. It is still unclear that depression of T_g is due purely to the small size of the system, or whether it is associated with the presence of free surfaces or interfaces [10]. Importance of free surfaces and interfaces in determination of T_g of thin films was demonstrated. Using an ingenious multilayer geometry in which dye-labeled molecules were inserted in known positions in thin film, they were able to map out the effective T_g as a function of distance from the surface of the film [3]. On the other hand, free surface or interface with substrate can greatly enhance the dynamics of atoms at the surface, i.e., it was assumed that the length scale of the region of enhanced mobility in the surface shell should be an

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order of magnitude larger than that of the region of reduced density [10]. Enhanced surface mobility is important problem, i.e. it is relevant for adhesion, friction, coatings, and nanoscale fabrication such as etching and lithography. Recently, it was found that glassy thin films prepared by physical vapor deposition can be highly stable compared to the ordinary glasses obtained by quenching from the melt [16]. These glasses exhibit lower enthalpy and higher density compared to those of the ordinary glasses. It was suggested that high mobility molecules within a few nanometers of the surface have a time to find low energy packing configurations before they are buried by further deposition and it leads to the formation of ultrastable glassy state [16]. However, more detail information at atomistic level can be provided by computer simulations. Although some simulation works related to the glasses with free surfaces can be found (see [11] and references therein), our understanding of the problem is still poor and it motivates us to carry out MD simulations of monatomic LJ glass with free surfaces.

2. Calculations

Lennard–Jones 12-6 pair potential is described as follows:

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad (1)$$

Here, *r* denotes the distance between atoms. We use the following LJ-reduced unities in the present work: the length in units of σ, temperature T in units of ε / k_B, and time in units of $\tau_0 = \sigma\sqrt{m/\varepsilon}$ (see Eq. 1). Here, k_B is the Boltzmann constant, σ is an atomic diameter, and m is an atomic mass. The cutoff is applied to LJ potential at $r_0 = 3\sigma$ like that used in [12].

Initial fcc configuration of 6912 atoms in a cube of length L = 20.52σ under periodic boundary conditions (PBCs) is melted at the density $\rho_0 = 0.8$ by relaxation for 2×10^5 MD steps at $T_0 = 2.0$. After that, PBCs are applied only along the x and y Cartesian directions, while along the z Cartesian direction, nonperiodic boundaries with an elastic reflection behavior are employed after adding the empty space of a length of $\Delta z = 5\sigma$ at $z = 20.52\sigma$. However, due to using the elastic reflection boundaries, an additional free surface will firstly occur at $z = 0.0$ during further MD simulation. The system is left to equilibrate further for 10^4 MD steps at $T_0 = 2.0$ at a constant volume corresponding to the new boundaries (i.e., NVT ensemble simulation). Then, the system is cooled down from the melt at the constant volume and temperature is decreased linearly with time as $T = T_0 - \gamma\times n$ by simple atomic velocity rescaling. Here, $\gamma = 10^{-5}$ per MD step is the cooling rate, n is the number of MD steps and $T_0 = 2.0$ is an initial temperature. We use the Verlet algorithm and MD time step is $dt = 0.001\tau_0$. If taking Argon for testing (i.e. $m = 0.66\times10^{-25} kg$, $\varepsilon / k_B = 118K$,

$\sigma = 3.84\,\text{Å}$ and therefore, $\tau_0 = \sigma\sqrt{m/\varepsilon} = 2.44ps$), we have $dt = 0.001\tau_0 = 2.44fs$ and corresponding cooling rate is $\gamma = 4.836\times10^{11}K/s$. To improve the statistics, we average the results over two independent runs.

3. Results and Discussions

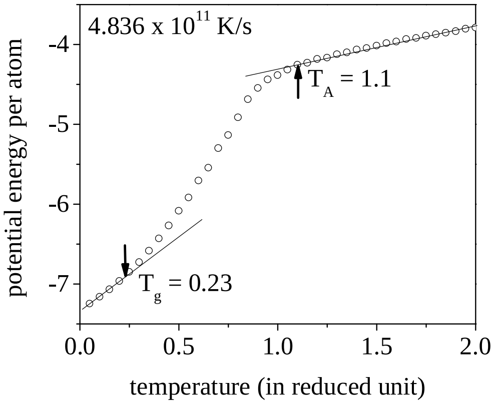

Fig 1. *Temperature dependence of the potential energy per atom in the system. The straight line is a visual guide*

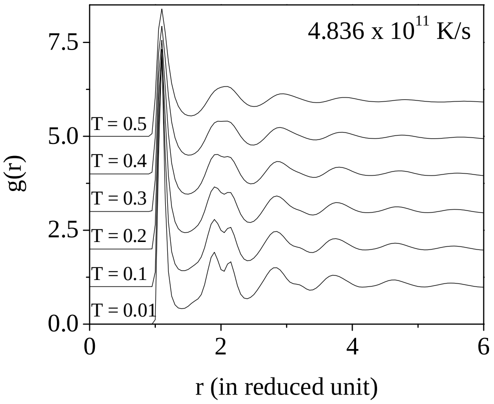

Fig 2. *RDF in the models obtained upon cooling from the melt*

We can see in Fig. 1 that the temperature dependence of potential energy per atom is typical for supercooled glass-forming system like that found for the Lennard-Jones-Gauss (LJG) system [9], i.e. the linear part of high temperature region is related to the equilibrium liquid state and the linear part of the lowest temperature region is related to the glassy state. The starting point of deviation from the linearity of the highest temperature region, $T_A = 1.1$, is a crossover temperature where the change in mechanism of diffusion occurs. The starting point of deviation from the linearity of the lowest temperature region, $T_g = 0.23$, is a glass transition temperature. In Fig. 2, the evolution of the RDF upon cooling is typical for glass-forming system, i.e. it exhibits normal liquid behavior at high temperature and at low one it has splitting of the second peak, which is suggested to be related to the local icosahedral order in the system. It indicates a glassy state of the system like that found and discussed in [7]. The glass transition temperature $T_g = 0.23$ is correct since splitting of the second peak can be seen clearly only at $T \leq T_g$. The T_g found in the present work is smaller than that found for the bulk matter models [7], i.e. it ensures that free surfaces have a tendency to reduce T_g like that found and discussed [4].

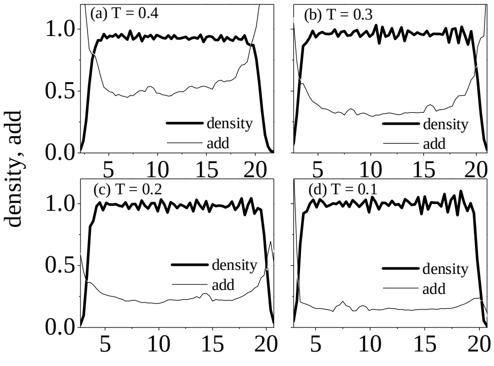

Fig 3. ***Density profile and add in the models obtained at different temperatures. For add, we employ the same scale as that for the density profile***

To get more detailed information about the local structure and dynamics in the system, we present the density profile and atomic displacement distribution (add) in the z direction in the models (Fig. 3). The density profile and add at a given temperature are calculated similarly like that used in [9], but with the thickness of the slices is 0.3σ and the specific time is $\tau_c = 10\tau_0$ (i.e., 24.4*ps* or 10×10^3 MD steps). One can see that both density profile and add exhibit surface and interior behaviors. In the interior, the density profile shows a layer structure of orderly high and low values, and the layer structure is enhanced with decreasing temperature. However, the layering is not strong. Note that, density in the surface shell decreases with distance from the interior indicating a more porous structure in this part of the system compared to that of the interior. We find that thickness of our models with free surfaces (in the z direction) decreases with decreasing temperature, leading to the formation of a glassy state with enhanced density in the interior. This may lead to enhancement of stability of the obtained glassy state like that found and discussed in [14]. It is also in accordance with stability observed for the freestanding thin film of the binary LJ mixture [15]. Layering at liquid surface was also found for various systems [1]. Origin of layering is still unclear. It was argued that layering depends on the ratio T_m / T_c (i.e., T_c is a critical temperature for the system) and monatomic LJ liquid does not exhibit a layering. However, cooling of the LJ liquid well below T_m generates layering structure similar to those observed for the other systems, although the interpretation is subtle [1]. The same results have been found in the present work, i.e., the layer structure of the system starts to occur at a temperature just above T_g, and the discrepancies between the high and low values of density at a given temperature are smaller than that found for the LJG system in [9] (not shown). Our results give additional understanding of the phenomenon in general.

In contrast, add remains at a constant value in the interior and in the surface shell it increases with the distance from the interior leading to the formation of a mobile surface layer. Some points can be drawn as follows: (i) Our calculations show clearly the existence of a mobile surface layer in liquid and glass with free surfaces and it confirms the suggestion or evidence (indirectly or partially) induced by both experiments and computer simulations [10], [15]; (ii) The length scale of the region of enhanced mobility is the same as that found for the region of reduction of density and it is contrary to that suggested in the past, i.e., the former should be an order of magnitude larger than that of the latter [10]; (iii) The discrepancy between atomic mobility in the interior and that in the surface shell also has a tendency to grow with temperature (not shown here but it can be seen primarily in Fig. 3). Therefore, it does not support a suggestion that the dynamics near surface has a weaker temperature dependence compared to that in the interior and difference in the dynamics between the surface and interior gets smaller as temperature approaches T_g from below. [13]

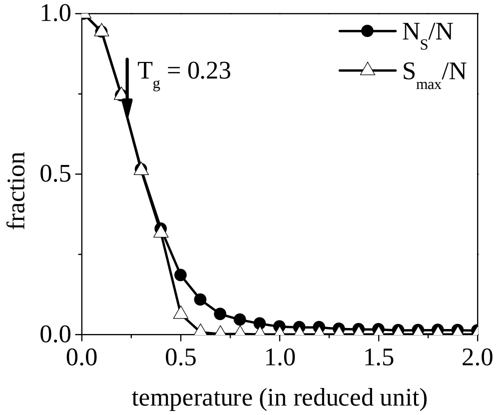

Fig 4. *Temperature dependence of the fraction of solid-like atoms (N_s / N) and size of the largest solid-like clusters ($S_{\max} / N$) to the total number*

of atoms in the system (N)

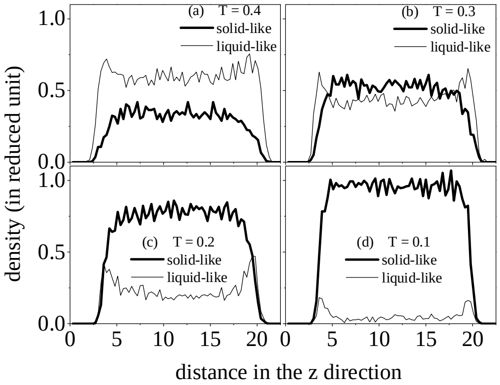

***Fig 5.** Distributions of solid-like and liquid-like atoms in the z direction in models obtained at different temperatures*

We try to clarify atomic mechanism of glass formation in the system via analyzing spatiotemporal arrangements of solid-like atoms in the system upon cooling from the melt. Solid-like atoms are detected via the Lindemann ratio, i.e. we found $\delta_i = \left\langle \Delta r_i^2 \right\rangle^{1/2} / R$ and then we inferred the Lindemann ratio (δ_L) of the system by the averaging of δ_i over all atoms, $\delta_L = \sum_i \delta_i / N$. Here, $\left\langle \Delta r_i^2 \right\rangle$ is mean-squared displacement (MSD) of *i-th* atom and $R = 1.1$ is a mean interatomic distance which is adopted as a position of the first peak in RDF at $T = 0.1$. MSD is found during a characteristic time $\tau_{c} = 10^3$MD steps like that used for LJ bulk [5]. At $T = T_g$, the Lindemann ratio has the critical value $\delta_c = 0.17$ which is close to that commonly found for different systems [5], [6], [8]. Atom with $\delta_i \le \delta_c$ is classified as solid-like. Two atoms located at the distance less than $R_0 = 1.4\sigma$ (position of the first minimum after the first peak in RDF, see Fig. 2) are considered belonging to the same cluster. Atomic mechanism of glass formation in the system is as follows. Upon cooling from the melt, solid-like atoms occur almost throughout the system although they mainly concentrate in the interior (Fig. 5) and they have a tendency to form clusters (Fig. 4). Further cooling stimulates intensively growth of number of solid-like atoms and they are strongly correlated to form more compact atomic configurations, i.e. clusters of large size appear (Fig. 4). Note that solid-like atoms firstly occur in the interior and solid-like domain grows outward to the surface with further decreasing temperature (Fig. 5), i.e. it exhibits “heterogeneous-like” behavior unlike homogeneous one observed in similar bulk models [8]. However, it is similar to that found for glass formation in nanoparticles [6]. In the deep supercooled region, single percolation spanned throughout the system occurs via merging of small-size coarse clusters and single solid-like atoms when fraction of solid-like atoms reaches the critical value $p_c = 0.32$ at $T = 0.4$ (the point where two curves of N_s / N and $S_{\max} / N$ coincide, see Fig. 4) which located within the range $0.15 \le p_c \le 0.45$ suggested in [2]. Number of solid-like atoms aggregated in this percolation cluster grows fast and reaches majority (around 67%, see Fig. 4) in the system at $T = T_g$ to form a relatively rigid glassy phase. Full solidification occurs at $T_f = 0.01$, i.e. it is much lower than T_g like that found in [6], [8] (see Fig. 4).

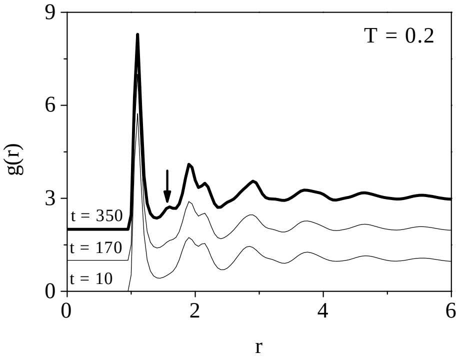

***Fig 6.** RDF of glassy models obtained at* $T = 0.20$ *after different annealing times (in reduced unit)*

It is commonly found that bulk monatomic LJ glass (i.e. under PBCs) easily crystallizes after annealing for 0.24 – 0.37 ns [7]. However, our LJ glass with free surfaces exhibits rather higher stability against crystallization compared to that of the bulk. We found that the system starts to crystallize just after annealing time of around $t = 350\tau_0$ (or 0.854 ns) for model obtained at $T = 0.20$, i.e. small additional peak at $r \approx 1.60\sigma$ (see the arrow in Fig. 6) occurs and starts to grow after around $t = 350\tau_0$. This peak is related to the occurrence of close-packed crystalline orders such as fcc or hcp in the system [12]. However, for glassy model obtained at $T = 0.01$ crystallization does not occur after all simulation time studied (i.e. after $t = 700\tau_0$ or $t = 1.708 ns$). Due to free surfaces, i.e. atomic configuration is under "real vacuum", significant amount of atoms in the system has more freedom and their mobility is greatly enhanced compared to that in the bulk matter system. Therefore, they have a time to find low energy packing configurations of high stability (or high density) during relatively slow cooling process. It leads to the formation of "practical stable" glassy state [12]. This point is important, i.e. one can improve stability of monatomic glassy models against crystallization via employing free surfaces and using appropriate cooling procedure.

4. Conclusions

We have carried out MD simulations of glass formation in simple monatomic supercooled liquids with free surfaces. Some conclusions can be drawn here:

(1) The glass transition temperature in the free surface matter models is smaller than that in the bulk one, i.e. free surfaces have a tendency to reduce T_g like that found and discussed in thin polymer film models [4].

(2) Glass with free surfaces has two distinct parts: the interior and the surface shell. The surface shell has a porous structure with low density. Besides, it exhibits a mobile surface layer in liquid and glass. In contrast, the interior has a higher density which may lead to enhancement of stability of the obtained glassy state. One more interesting thing is that the interior exhibits a layer structure although the interpretation is subtle. Layering exists for the lowest temperature range studied, from the region around T_g into the deep glassy region. This finding clears the existence of layer structure for the temperature range below T_g.

(3) The atomic mechanism of glass formation in supercooled liquids with free surfaces exhibits heterogeneous behavior, unlike the homogeneous behavior observed in the bulk [8]; i.e., the solid-like domain initiates/enhances in the interior and simultaneously grows outward to the surfaces.

(4) Due to the free surfaces, almost all atoms in the system have more freedom, and their mobility is greatly enhanced compared to that in the bulk. Therefore, they have time to find the low-energy packing configurations of high stability during a relatively slow cooling process, leading to the formation of a "practical stable" glassy state.

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