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## Melting of monatomic glass with free surfaces

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Melting of monatomic glass with free surfaces has been studied by molecular dynamics simulations in models with Lennard-Jones-Gauss interatomic potential. Models have been heated up from a glassy state toward a normal liquid state. Atomic mechanism of melting has been analyzed via monitoring spatio-temporal arrangements of liquid-like atoms occurred during heating process. Liquid-like atoms are detected via the Lindemann criterion of melting. It is clear that the transition from glass into supercooled liquid of our “ordinary” glass with free surfaces exhibits a non-heterogeneous behavior, i.e., although liquid-like atoms initiate/grow mainly in the surface shell, significant amount of liquid-like atoms also initiates/grows simultaneously in the interior during heating process. We found three characteristic temperatures of melting of glass with a free surface. Temperature dependence of structure and various thermodynamic quantities of the system upon heating is also presented and discussed. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3694532>]

### I. INTRODUCTION

Transformation of glasses into liquids upon heating, i.e., glassy materials lose their rigidity by transforming into liquids, has been under intensive investigations since it is related to their workability for various applications in practice.<sup>1–11</sup> A common view is that this transformation is spatially homogeneous, i.e., it occurs in the same manner throughout the sample and it is independent of the sample size.<sup>1–3</sup> In this view, upon annealing above glass transition temperature ( $T_g$ ), atoms throughout the glass are simultaneously released from the glassy environments to become liquid-like and melting of glass is started. Such a model of glass-to-liquid transition gives reasonable description for the situation in organic and inorganic glass formers.<sup>12,13</sup> Indeed, recent molecular dynamics (MD) simulations of glass-to-liquid transition upon heating support this view.<sup>14,15</sup> Note that MD simulations in Refs. 14 and 15 have been carried out in models under periodic boundary conditions (PBCs), i.e., in the bulk models. Free surface effects on the atomic mechanism of glass-to-liquid transition have not been studied yet. In practice, glasses with free surfaces (i.e., glassy thin films) are frequently employed and our understanding of the glass-to-liquid transition in glassy thin films is still poor. The fact, recent experiments on the highly stable glassy thin films (glasses with a high density and a low enthalpy obtained by vapor deposition on substrate, for convenience we call them “stable glasses”, in contrast to the “ordinary” glasses obtained by quenching from the melt) show that their transformation into supercooled liquid exhibits spatially heterogeneous behavior, i.e., growth of liquid state is initiated at the surfaces of the sample and liquid front propagates into the glassy matrix at constant velocity.<sup>16,17</sup> This is reminiscent of a melting mechanism in

crystals with a free surface,<sup>18,19</sup> i.e., a pre-existing liquid layer at the free surface provides plane sites that initiate growth of the liquid into the stable glass (and/or into crystal).<sup>16,17</sup>

Details of the atomic mechanism of “melting” of glasses with free surfaces can be studied via monitoring spatio-temporal arrangements of liquid-like atoms occurred during heating process and no work in this direction has been found yet. It motivates us to carry out MD simulations of melting of free-standing glassy thin film, i.e., the glassy system with two free surfaces, in order to highlight the situation.

### II. CALCULATIONS

Initial glassy thin film with two free surfaces containing 5832 identical atoms interacting via the Lennard-Jones-Gauss (LJG) potential,<sup>20</sup> previously obtained by quenching from the melt (i.e., an “ordinary” glass),<sup>21</sup> is used in the present work. LJG potential has the form as given below<sup>20</sup>

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

The LJG potential is a sum of the Lennard-Jones potential and a Gaussian contribution yielded a very long-lived simple monatomic glassy model.<sup>22</sup> Following LJ-reduced units are used in the present work: the length in units of  $\sigma$ , temperature  $T$  in units of  $\varepsilon/k_B$ , and time in units of  $\tau_0 = \sigma\sqrt{m/\varepsilon}$ . Here,  $k_B$  is the Boltzmann constant,  $\sigma$  is an atomic diameter, and  $m$  is an atomic mass (for Ar, we have  $m = 0.66 \times 10^{-25}$  kg,  $\varepsilon/k_B = 118$  K,  $\sigma = 3.84$  Å and therefore,  $\tau_0 = \sigma\sqrt{m/\varepsilon} = 2.44$  ps). The Verlet algorithm is employed and MD time step is  $dt = 0.001\tau_0$  or 2.44 fs if taking Ar for testing. The cutoff is applied to the LJG potential at  $r = 2.5\sigma$  like that used in Refs. 21–26. LJG glassy models with two free surfaces have been obtained by cooling from the melt at

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the cooling rate of  $4.836 \times 10^{10}$  K/s and at constant volume of simulation cell of the size of  $19.39\sigma \times 19.39\sigma \times 22.39\sigma$  (see Ref. 21). Note that PBCs are applied only along the  $x$  and  $y$  Cartesian directions, while along the  $z$  Cartesian direction the non-periodic boundaries with an elastic reflection behavior are employed after adding the empty space in order to form free surfaces. Final glassy models obtained at  $T < T_g$  exhibit a thin film shape, i.e., in the  $z$  direction atoms are distributed only in the range  $5.0\sigma \leq z \leq 15.0\sigma$  and the models have two free surfaces in the  $z$  direction. Unrelaxed glassy models obtained at  $T = 0.01$  have been heated up toward a normal liquid state in order to study glass-to-liquid transition. We employ the same  $NVT$  ensemble simulation for simulation cell of the size  $19.39\sigma \times 19.39\sigma \times 22.39\sigma$ . Temperature is increased linearly with time as  $T = T_0 + \gamma \times n$  via the simple atomic velocity rescaling after every MD step. The heating rate  $\gamma = 10^{-6}$  per one MD step (or  $4.836 \times 10^{10}$  K/s if taking Ar for testing) is used,  $n$  is the number of MD steps. In order to improve the statistics, we average the results over two independent runs. Due to a relatively low cooling/heating rate used in the simulations, the present MD simulations can yield equilibrium atomic configurations for the whole temperature range studied. Note that the same curves for the potential energy of unrelaxed and well-relaxed bulk models obtained at the same cooling rate were found indicating a good equilibrium of the obtained atomic configurations.<sup>25</sup> All configurations obtained at each temperature have been relaxed for 5000 MD steps before carrying out any statistical treatments related to the melting process. LJG glass with free surfaces exhibits a characteristic structure, i.e., their interior has a higher density and a stronger local icosahedral order compared to those of the bulk.<sup>21</sup> It may lead to a higher kinetic and thermodynamic stability of the former compared to that of the latter.<sup>21,22</sup>

### III. RESULTS AND DISCUSSIONS

#### A. Thermodynamics

We show temperature dependence or time-temperature dependence of important thermodynamic quantities of the system obtained upon heating in Fig. 1. One can see in Fig. 1(a) that potential energy per atom of the system exhibits the same behavior like that found by cooling the system from the melt,<sup>21</sup> linear part of a low temperature region is related to the glassy state and starting point of deviation from the linearity can be considered as a glass transition temperature. We found that  $T_g = 0.61$  and the same value was obtained previously by cooling system from the melt.<sup>21</sup> Note that  $T_g = 0.61$  is obtained here for the thin film-like system and it is much lower than that found for the bulk due to the free surface effects (for the bulk,  $T_g = 1.00$ , see Ref. 22). Smooth curve of temperature dependence of potential energy indicates a glass-to-liquid transition in the system, i.e., the glassy model transforms into normal liquid via supercooled liquid region without crystallization, although heating rate employed is rather small. Note that there are various scenarios of the heating-induced phase transitions of glasses, i.e., glass-to-liquid or glass-to-crystal-to-liquid can occur depending on the heating rate.<sup>5,14,15</sup> Glass-to-liquid

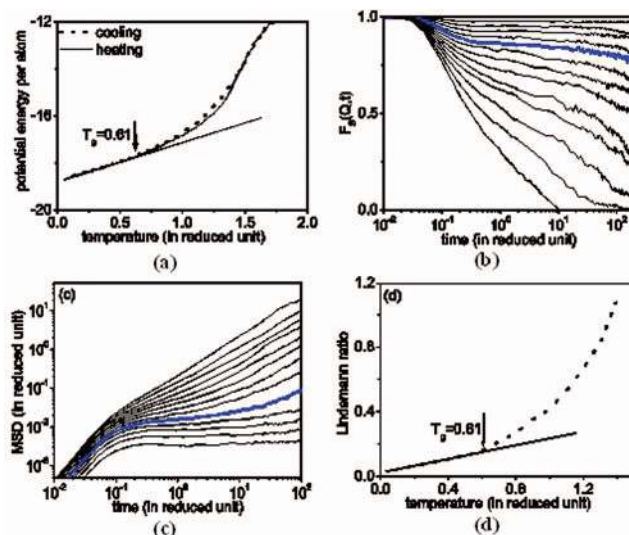


FIG. 1. (a) Temperature dependence of potential energy per atom obtained by cooling from the melt or by heating from the glass, the straight line is a visual guide; (b) Time-temperature dependence of the self-intermediate scattering function. From left to right, for temperature ranging from  $T = 1.4$  to  $T = 0.2$ , the blue line is for  $T = 0.6$  (i.e., close to  $T_g = 0.61$ ); (c) Time-temperature dependence of the MSD of atoms. From top to bottom, for temperature ranging from  $T = 1.4$  to  $T = 0.2$ , the blue line is for  $T = 0.6$ ; (d) Temperature dependence of the Lindemann ratio, the straight line is a visual guide.

transition occurs at a relatively low heating rate indicating a high stability crystallization of the LJG glass. On the other hand, the curves obtained by cooling/heating almost coincide with each other indicating a reversibility of the glass-to-liquid transition (see Fig. 1(a)). Moreover, time-temperature dependence of the self-intermediate scattering function,  $F_S(Q, t)$ , and mean-squared-displacement (MSD) of atoms in the system upon heating confirms the point that glass-to-liquid transition occurs without crystallization of glass. In the present work,  $F_S(Q, t)$  is calculated for  $Q = 8.665\sigma^{-1}$  which is the location of the first peak in structure factor,  $S(Q)$ , of the bulk.<sup>22</sup> The function form is given below

$$F_S(Q, t) = \frac{1}{N} \sum_{j=1}^N \langle \exp(iQ \cdot [r_j(t) - r_j(0)]) \rangle, \quad (2)$$

where  $r_j(t)$  is the location of the  $j$ -th atom at time  $t$  and  $Q$  is a wave vector. It is clear that  $F_S(Q, t)$  is typical for the supercooled glass-forming systems (Fig. 1(b)). At low temperature (at  $T < T_g$ ),  $F_S(Q, t)$  has almost only two regimes: the ballistic regime in the beginning time and a plateau one at a longer time. A plateau regime is lasting for a long time due to strong caging effects of a glassy state. In contrast, at higher temperature (at  $T > T_g$ ) a plateau regime is followed by a non-exponential long time part of the relaxation behavior regime like that found for various glass-forming supercooled liquids.<sup>22,27,28</sup> This means that system transforms into a supercooled liquid region. However, a plateau regime becomes weaker with temperature and finally it disappears while a relaxation behavior regime becomes more exponential and  $F_S(Q, t)$  decays at short time, i.e., it exhibits a normal liquid-like behavior. Similarly, MSD has three different regimes: the ballistic one in the beginning of a motion

followed by the plateau one which is related to the caging effects and diffusive regime at a longer time (Fig. 1(c)). These three regimes are seen clearly at low temperatures. In other words, temperature dependence of both  $F_S(Q, t)$  and MSD shows clearly that glass transforms into a normal liquid via an intermediate supercooled liquid region. Moreover, one can see in Figs. 1(b) and 1(c) that  $T_g = 0.61$  is a bound between the glassy and supercooled liquid states. This indicates that  $T_g = 0.61$  obtained via temperature dependence of potential energy is correct. We show in Fig. 1(d) temperature dependence of other important quantity, i.e., the Lindemann ratio. The Lindemann ratio for the  $i$ -th atom is given below<sup>29</sup>

$$\delta_i = \langle \Delta r_i^2 \rangle^{1/2} / \bar{R}. \quad (3)$$

Here,  $\langle \Delta r_i^2 \rangle$  is the MSD of the  $i$ -th atom and  $\bar{R} = 0.91$  is an interatomic distance which is considered equal to the position of the first peak in radial distribution function (RDF). For the supercooled and glassy state,  $\bar{R}$  does not change much with temperature and that we fix this value for the calculations. MSD in Eq. (3) is defined after a characteristic time  $\tau_C = 5\tau_0$  (i.e., 5000 MD steps or 12.2 ps). One can see in Fig. 1(c) that  $\tau_C = 5\tau_0$  is located at the end of a plateau regime of MSD at  $T = T_g$ . This time is large enough for atoms to overcome a plateau regime to diffuse if atoms are liquid-like and it is close to that found for the bulk, thin film-like and nanoparticles.<sup>21,22,26</sup> The same  $\tau_C = 5\tau_0$  was used for monitoring atomic mechanism of glass formation in LJG supercooled liquid with free surfaces.<sup>21</sup> The mean Lindemann ratio  $\delta_L$  of the system is defined by the average of  $\delta_i$  over all atoms,  $\delta_L = \sum_i \delta_i / N$ . Figure 1(d) shows that  $\delta_L$  has the same temperature dependence like potential energy indicating a close correlation between two quantities in the glass-to-liquid transition process. Again, the point of deviation from the linearity of a low temperature region is a glass transition temperature, i.e.,  $T_g = 0.61$ . Critical value for the Lindemann ratio at  $T = T_g$  is  $\delta_C = 0.157$  (see Fig. 1(d)), atoms with  $\delta_i < \delta_C$  are classified as solid-like and atoms with  $\delta_i \geq \delta_C$  are classified as liquid-like. By this way, via analysis of spatio-temporal arrangements of liquid-like atoms, we can monitor melting process of the glass. A purely Lindemann criterion established that melting occurs when a root of MSD is at least 10% (usually around 15% and it is close to our  $\delta_C = 0.157$ ) of the atomic spacing.<sup>29,30</sup> Moreover, there are experimental evidences that this criterion is also applicable for glasses.<sup>31-33</sup>

Furthermore, density profile and atomic displacement distribution (*add*) along the  $z$  direction in the models obtained at different temperatures are presented in Fig. 2. Density profile at a given temperature is calculated by partitioning the system along the  $z$  direction into slices of the thickness  $0.2\sigma$ , then we divide the number of atoms in each slice by the volume of a given slice. In contrast, *add* is found via dividing a total displacement of all atoms in the slice by the number of atoms in a given slice, i.e., *add* corresponds to the displacement of atoms in the slice after a characteristic time  $\tau_C = 5\tau_0$ . One can see that both density profile and *add* exhibit surface and interior behaviors. In the interior, although density shows a layering, i.e., it contains orderly high and low density layers, and density fluctuates around a high constant value. However,

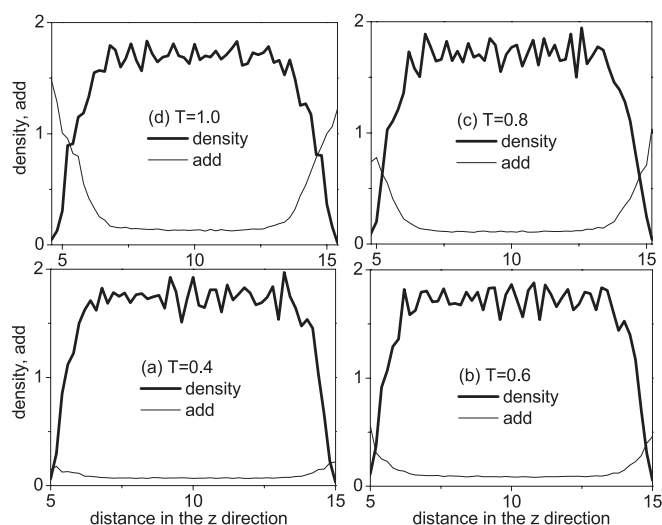


FIG. 2. Density profile and *add* along the  $z$  direction in models obtained at different temperatures upon heating. For *add* we employ the same scale as that for the density (*add* is an atomic displacement distribution).

in the surface shell it decreases down to zero (Fig. 2). The point at which density starts to decrease can be considered as the bound between surface shell and interior. In contrast, *add* remains constant at a small 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 (Fig. 2).

Layering at liquid surface was also found for various systems.<sup>34,35</sup> 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.<sup>34</sup> Layering of LJG system with free surfaces has been found for the whole temperature range studied (from  $T = 2.0$  to  $T = 0.01$ ) and it is enhanced with decreasing temperature.<sup>21</sup> A strong layering in the density profile was also found for the molecular model of trehalose and it was suggested to be the origin of an ultra-high stability of the vapor-deposited glasses.<sup>36</sup>

Concerning on the *add*, 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;<sup>36-39</sup> (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 more than an order of magnitude larger than that of the latter.<sup>38</sup> On the other hand, thickness of a mobile surface layer (denoted as  $d$ ) and discrepancy between atomic mobility in the surface and that in the interior (denoted as  $h$ ) have a tendency to increase with temperature for the whole temperature range studied (Figs. 3(a) and 3(b)). It shares some trends found for the liquid surface width of an isotropic dielectric liquid, i.e., tetrakis(2-ethoxyhexoxy)silane.<sup>35</sup> It was found that for the glassy region of polystyrene  $d$  also increases with temperature.<sup>40</sup> The existence of a mobile surface layer for the whole temperature range studied is new since it was suggested that convergence of the surface and bulk dynamics

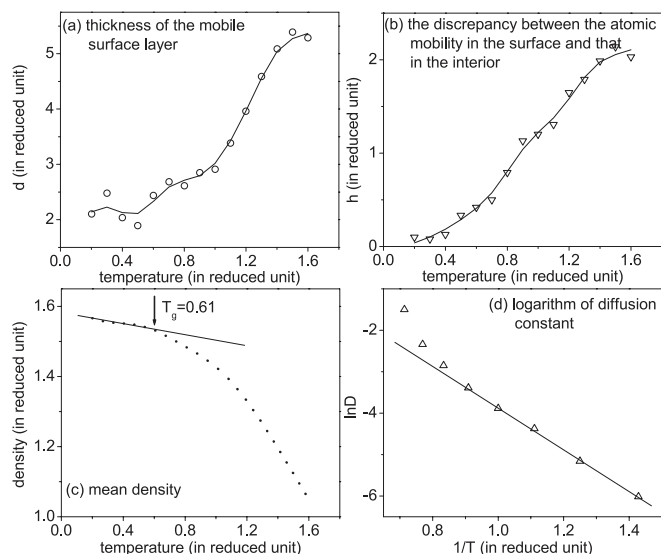


FIG. 3. (a) Temperature dependence of the thickness of a mobile surface layer, the solid line is the averaged curve; (b) Temperature dependence of the discrepancy between mobility in the surface and that in the interior, again, the solid line is the averaged curve; (c) Temperature dependence of the mean density of the system; (d) Inverse temperature dependence of logarithm of diffusion constant, straight line is a visual guide.

should be complete at high temperatures (i.e., at  $T > T_g + 5$  K for the freestanding polystyrene thin film<sup>40</sup>); (iii) The discrepancy between atomic mobility in the interior and that in the surface shell also has a tendency to grow with temperature up to the normal liquid region (Fig. 3(b)). 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.<sup>40</sup>

Detailed definition of the quantities  $d$  and  $h$  is clearly presented in Ref. 21. In addition, almost the same temperature dependence of  $d$  and  $h$  has been found based on the data of the models obtained by cooling from the melt,<sup>21</sup> i.e., it confirms a high precision and reliability of the data observed. Moreover, mean density of the system decreases with temperature and glass transition temperature ( $T_g = 0.61$ ) can be found again here as a point of deviation from the linearity of low temperature region (Fig. 3(c)). In addition, temperature dependence of diffusion constant in the system shows an Arrhenius law at low temperature and deviation from the law occurs at higher one (Fig. 3(d)). Deviation of an Arrhenius law at high temperature is related to the change in the atomic mechanism of diffusion in supercooled liquids.<sup>25</sup> Diffusion constant is found via the Einstein relation after relaxation of model at a given temperature for  $2 \times 10^5$  MD steps like that done in Ref. 21. There is evidence that free surfaces can greatly enhance atomic mobility in the system. Indeed, it was found clearly that diffusion constant in LJG supercooled liquids with free surfaces is always larger than that in the bulk for the whole temperature range studied and discrepancy is of some orders of magnitude at low temperature.<sup>21</sup>

Evolution of structure of LJG glass with free surfaces upon heating toward a normal liquid state can be seen via RDF

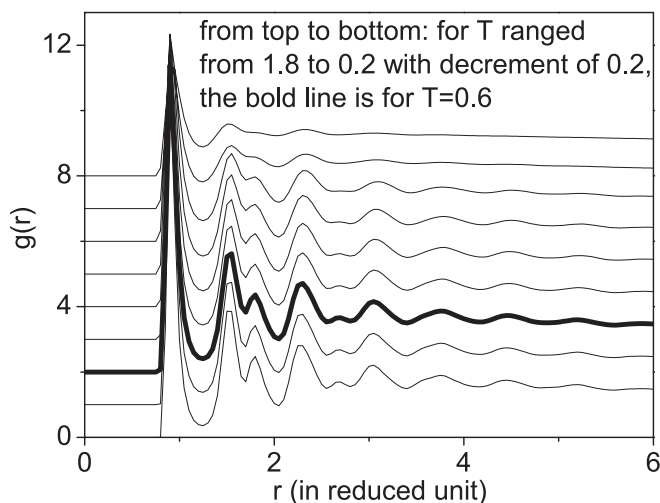


FIG. 4. Evolution of RDF upon heating.

of the models (Fig. 4). One can see that evolution of RDF is typical for the glass-forming systems. That is, at low temperatures system exhibits a glass-like behavior with a splitting of the second peak in RDF. Splitting of the second peak in RDF is suggested to be related to the local icosahedral order in the system. Upon further heating, splitting becomes weaker and disappears if temperature is high enough indicating transformation of the system into a normal liquid state via an intermediate supercooled liquid state without crystallization of glass. Note that crystallization of the monatomic LJ glass occurs if the heating rate is slow enough, i.e., additional peaks of the crystalline structure occur in RDF and further heating leads to the melting of obtained crystal.<sup>15</sup>

## B. Atomic mechanism of melting

Atomic mechanism of melting of glass with free surfaces is monitored via analyzing spatio-temporal arrangements of the liquid-like atoms occurred during heating process. As described above, atoms become liquid-like if their Lindemann ratio satisfies the condition  $\delta_i > \delta_C$ . One can see in Fig. 5 that liquid-like atoms occur first at temperature far below  $T_g = 0.61$ . The temperature at which a significant amount of liquid-like atoms occurs first can be considered as the limit of a thermal stability of glassy matrix, i.e., denoted as  $T_{lt}$ , and it is equal to around 0.3 (see Fig. 5). Number of liquid-like atoms grows fast with temperature and at  $T = T_g$  their fraction is equal to around 0.20. At  $T > T_g$ , the system transforms into a supercooled liquid state, in which there is a competition between the liquid-like and solid-like clusters since the formers grow fast with temperature. Liquid-like atoms also have a tendency to form clusters and size of the largest cluster grows upon heating. At temperature well above  $T_g$ , the largest cluster contains about 99% of liquid-like atoms in the system and it is formed via merging smaller clusters and single liquid-like atoms (at around  $T = 0.9$ , see Fig. 5). However, this largest cluster does not percolate the system and the percolation threshold should occur at much higher temperature. This means that melting of glass with free surfaces does not relate to the percolation of liquid-like clusters in the system unlike

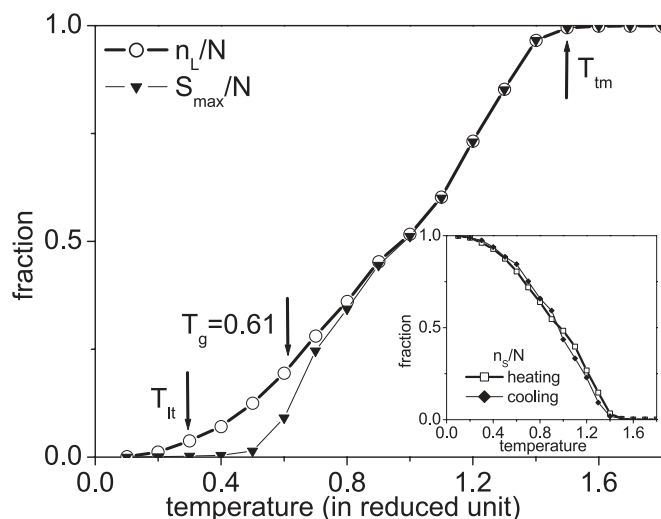


FIG. 5. Temperature dependence of fraction of the liquid-like atoms ( $n_L/N$ ) and size of the largest liquid-like cluster ( $S_{\max}/N$ ) to the total number of atoms in the system ( $N$ ). The inset shows temperature dependence of fraction of solid-like atoms in the models obtained by heating from the glass and by cooling from the melt ( $n_S/N$ ).

that found for melting of the bulk LJ glass.<sup>14</sup> Furthermore, total melting is reached at much higher temperature when fraction of liquid-like atoms equal to 1.0 (denoted as  $T_{tm}$  and it is equal to 1.5, see Fig. 5). We also show fraction of atoms in the system remaining solid-like upon heating compared to that obtained by cooling from the melt (the data for cooling from the melt are taken from Ref. 21), see the curves for  $n_S/N$  in the inset of Fig. 5. Interestingly, that the curves obtained by heating/cooling almost coincide with each other confirming again a reversible behavior of a glass-to-liquid transition in the system. More detailed information of mechanism of melting of glass can be seen via 3D visualization of the appearance of liquid-like atoms in the system upon heating (Fig. 6). Although liquid-like atoms initiate/grow mainly in the surface shell, at the same time, however, significant amount of liquid-like atoms also initiates/grows in the interior indicating a non-heterogeneous behavior of melting. In other words, melting in our glass with free surface occurs not just via surface-initiated growth front unlike that observed in the thin films of stable glasses.<sup>16,17</sup>

A more detailed picture of melting of glass with free surfaces can be seen via distributions of the solid-like and liquid-like atoms along the  $z$  direction (Fig. 7). Indeed, liquid-like atoms initiate/grow mainly in the surface shell together with a smaller initiation/growth in the interior (Figs. 7(a) and 7(b)). However, at  $T \leq T_g$  liquid-like atoms do not form a purely liquid-like surface layer but just a mobile surface layer. At around  $T = T_g$ , concentration of liquid-like and solid-like atoms in the surface shell is equal to each other, i.e., we have a mixed phase of the solid-like and liquid-like atoms with equal concentrations. This point clears out the debate about the existence of the so-called “glasses with liquid-like surfaces”.<sup>37,38,41</sup> This means that “pre-melting” of glass with free surfaces does not accompany by the formation of a liquid-like surface layer unlike that thought in the past.<sup>37,38,41</sup> In addition, it is clear that a high concentration of liquid-like

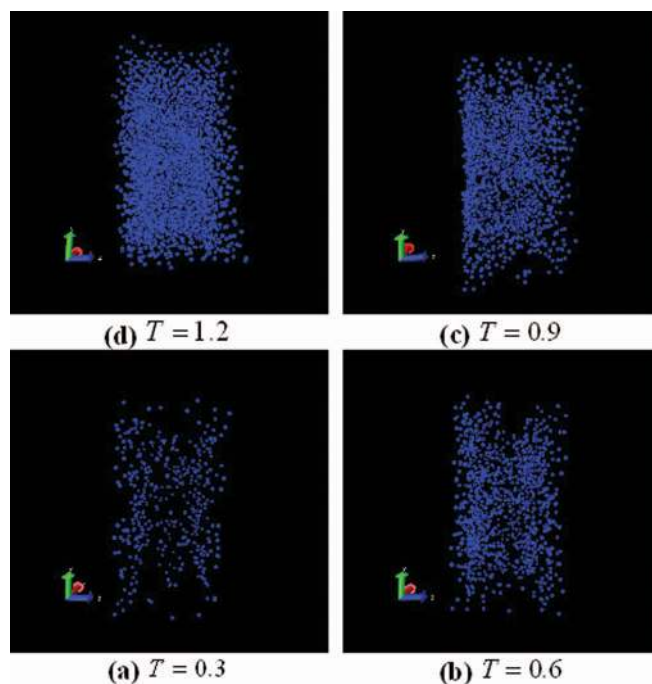


FIG. 6. 3D visualization of the appearance of liquid-like atoms in the system upon heating from a glassy state.

atoms in the surface shell of glass leads to the reduction of the surface rigidity. Number of liquid-like atoms in the surface shell increases upon heating toward  $T_g$  from below (see Figs. 7(a) and 7(b)), therefore, surface rigidity correspondingly becomes weaker with temperature. This is the origin of striking experimental observation by Fakhraai and Forrest,<sup>41</sup> i.e., they used atomic force microscopy to image the filling of the nanoindentations on the polystyrene glass surface over time at various annealing temperatures. It was found that at 20 K below  $T_g$  the process takes a few minutes; whereas at 100 K below  $T_g$  the holes fill in a few weeks due to a higher surface rigidity. Therefore, the suggestion that existence of

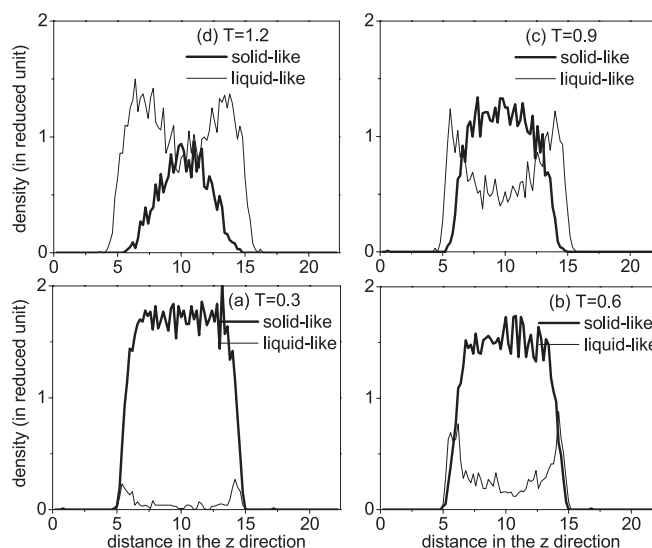


FIG. 7. Distributions of solid-like and liquid-like atoms in the  $z$  direction in models obtained at different temperatures upon heating.

a highly mobile liquid surface layer of glass is the origin of the filling of the nanoindentations on the polystyrene glass surface may be incorrect.<sup>37,41</sup> In addition, the suggestion that mobility at the surface of a glass can be viewed as the motion of a thin liquid-like layer that responds to the surface tension may be incorrect.<sup>37</sup> Indeed, surface of glasses is not so glassy like that stated in Ref. 37. The terminology “a quasi-liquid like surface layer” is the most suitable for the surface of glasses in the “pre-melting” region which exhibits structural, dynamical properties that are intermediate between those of the glassy solid and normal liquid.<sup>42</sup> Upon further heating above  $T_g$ , a purely liquid-like surface layer forms and melting reaches a new stage (like a “superheated” stage proposed in Ref. 43), i.e., liquid-like surface front propagates into the interior together with a smaller growth of liquid-like atoms in the interior (Figs. 7(c) and 7(d)). It naturally raises a question of the atomic mechanism of melting of crystals with free surfaces since pre-melting of crystals is not fully understood.<sup>42,44</sup> Note that diffusion constant profile in the  $z$  direction observed in  $Ni_{0.5}Zr_{0.5}$  metallic glass films<sup>45</sup> also has the same form like that found for *add* in the present work. It was also found that decrease of mobility with depth of thin film is exponential with a smooth transition between surface and interior behavior.<sup>45</sup> A Landau analysis was applied for interpreting the diffusion constant profile in the  $z$  direction.<sup>45</sup>

It is also interesting to discuss in more details about the atomic mechanism of melting of glassy thin films observed in the present work. As found previously,<sup>14,15,21</sup> liquid-like atoms often occur in the non-close-packed atomic arrangement regions of glasses since these regions are less stable and it is easy for atoms located in these regions to escape from their positions to diffuse due to the thermal vibrations, i.e., to become liquid-like. By this way, melting of glasses starts and grows upon heating. On the other hand, it was found that surface shell of glasses exhibits a non-close-packed atomic arrangement structure, i.e., it contains a large amount of under-coordinated sites.<sup>21</sup> Due to inhomogeneous structure of glass, small non-close-packed atomic arrangement regions also distribute in the interior but with a smaller concentration compared to that in the surface shell.<sup>21</sup> Therefore, upon heating initiation/growth of liquid-like atoms in the surface shell also accompanies by their smaller initiation/growth in the interior. In addition, local non-close-packed atomic arrangement regions in glassy matrix can be considered as structural defects.<sup>21</sup> Therefore, our simulations support the speculation that structural defects of the sample can initiate growth fronts that propagate into the surrounding glassy matrix.<sup>16</sup> Moreover, our simulations show that two models of melting of the thin films of stable glasses proposed in Ref. 43, i.e., melting occurs either via the growth of the supercooled liquid into the stable glass from the surface or via the bubble growth in the interior of the films, are also not relevant for melting of our “ordinary” glass. It is clear that although liquid-like atoms also occur in the interior of our glassy thin films, the separated bubbles of liquid-like atoms are not formed during the melting process (see Fig. 6). It is clear that atomic mechanism of melting of our “ordinary glass” is quite different from that of the stable glasses, i.e., melting of the latter initiates in the surface and liquid front propagates into the interior based on the data

obtained by the secondary mass spectroscopy experiments.<sup>16</sup> Note that “vapor-deposited stable glasses” of trehalose have been obtained by MD simulations and indeed, “computer stable glasses” also exhibit a higher density, a lower enthalpy, and a higher onset temperature compared to those of “ordinary glasses”.<sup>36</sup> Although it is evident that free surface is a primary mechanism for relaxation in stable glasses,<sup>36</sup> however, it is of great interest if one can carry out MD simulations of melting of such a “computer stable glass” via analyzing spatio-temporal arrangements of liquid-like atoms occurred during heating process so that one can get a detailed information at the atomistic level.

Finally, in order to highlight the effect of a free surface on atomic mobility in the system we show *add* along the  $y$  and  $z$  directions in the model with free surfaces obtained at  $T = 1.0$  compared to that of the bulk (Fig. 8). Note that *add* is calculated after relaxation for 5000 MD steps as described above. Bulk model containing 2744 atoms under PBCs, previously obtained in Ref. 22, is heating up from  $T = 0.01$  to  $T = 1.0$  using *NPT* ensemble simulation at a constant zero pressure and at the same heating rate used in the present work. For the bulk, *add* is calculated along the  $y$  direction. However, it is axis-independent due to a homogeneous nature of the bulk. Some important points can be drawn from Fig. 8 as follows: (i) There is no heterogeneity in the distribution of atomic mobility along the  $y$  axis even at the edges of a model, i.e. atomic mobility along the  $y$  direction fluctuates around a constant value for the whole  $y$  axis length of model; (ii) *add* along  $y$  axis in the bulk is homogeneous as expected, i.e., it is rather constant for the whole length studied; (iii) Free surfaces significantly enhance atomic mobility in the system leading to the formation of a mobile surface layer while interior exhibits a bulk dynamics-like that thought in the past (see *add* along the  $z$  direction compared to that of the bulk in Fig. 8). However, atomic mobility along the  $y$  axis (despite PBC applied in the  $x$ - $y$  plane) is significantly higher than that in the bulk indicating free surface enhancement of atomic mobility in the model (Fig. 8). Note that we also check *add* in models obtained at  $T < T_g$  (at  $T = 0.4$ ) and the same results have been found.

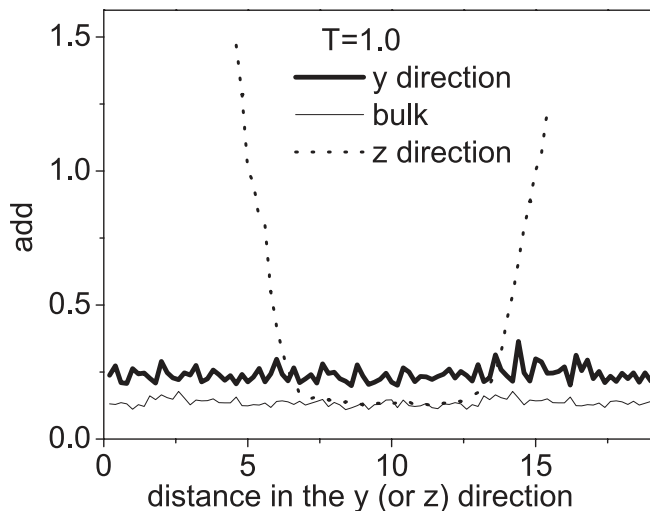


FIG. 8. Atomic displacement distribution (*add*) along the  $y$  and  $z$  directions obtained at  $T = 1.0$  in model with free surfaces compared to that of the bulk.

#### IV. CONCLUSIONS

We have studied melting of monatomic “ordinary” LJG glass with free surfaces by MD simulations and some conclusions can be made as follows:

- (i) Atomic mechanism of melting of “ordinary” glass with free surfaces can be drawn as follows. Upon heating, liquid-like atoms occur first at temperature located far below  $T_g$  and they initiate/grow mainly in the surface shell together with a smaller initiation/growth in the interior leading to a non-heterogeneous melting. Number of liquid-like atoms grows with temperature and it reaches a significant amount at  $T = T_g$ . At  $T \leq T_g$ , liquid-like atoms do not form a purely liquid-like surface layer but just a mobile surface layer, i.e., they mainly concentrate in the surface shell together with solid-like atoms. At  $T = T_g$ , concentration of the solid-like and liquid-like atoms in the surface shell is equal to each other. At  $T > T_g$ , system transforms into the supercooled liquid region—a new stage of melting, a purely liquid-like surface layer is formed and it propagates into the interior together with a smaller growth of liquid-like atoms in the interior. Total melting occurs at temperature much higher than  $T_g$ .
- (ii) We found three characteristic temperatures for melting of glass with free surfaces:  $T_{li}$ —a limit of a thermal stability of glass at which a significant amount of liquid-like atoms occurs in the system and collapse of glassy matrix is started,  $T_{li}$  is located far below  $T_g$ ;  $T_g$ —a glass transition temperature at which a large amount of liquid-like atoms occurs and system transforms into the supercooled liquid region, in which there is a competition between liquid-like and solid-like domains in the region while the formers grow fast with temperature;  $T_m$ —a total melting point at which all atoms in the system become liquid-like. Note that  $T_{li} < T_g < T_m$ .
- (iii) Our calculations show that glass-to-liquid transition in our LJG glass with free surfaces exhibits a reversible behavior at a relatively low computational cooling rate, i.e., the system almost repeats the states observed during a liquid-to-glass transition obtained upon cooling system from the melt. Reversibility of glass-liquid transition indicates a high stability of the obtained glass.<sup>5</sup>
- (iv) Since systems with LJG interatomic potential are adequate for metallic glasses,<sup>21,22</sup> the same atomic mechanism of melting as described above can be suggested for melting of metallic glasses with free surfaces.

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