



# Glass transition in disordered clusters

X.Y. Li<sup>a</sup>, D.Y. Sun<sup>a,\*</sup>, X.G. Gong<sup>b,c,\*</sup>

<sup>a</sup> Department of Physics, East China Normal University, No. 500, Dongchuan Road, Shanghai 200241, People's Republic of China

<sup>b</sup> Key Laboratory for Computational Physical Sciences (MOE), State Key Laboratory of Surface Physics, Department of Physics, Fudan University, Shanghai 200433, People's Republic of China

<sup>c</sup> Collaborative Innovation Center of Advanced Microstructures, Nanjing University, 210093, People's Republic of China

## ARTICLE INFO

### Article history:

Received 29 March 2019

Received in revised form 16 May 2019

Accepted 16 May 2019

Available online 22 May 2019

Communicated by R. Wu

### Keywords:

Glass transition

Cooperative diffusion

Configuration entropies

Molecular dynamics

## ABSTRACT

Using molecular dynamics simulations, the melting behavior of disordered aluminum clusters with 30 ~ 100 atoms has been systematically studied. We find that, all the disordered clusters undergo a glass transition before completely melting. We identify two characteristic temperatures, *i.e.*  $T_s$  and  $T_g$  (the glass transition temperature). When the temperature is higher than  $T_s$ , the cluster shape starts to change, accordingly the configurational entropy emerges. For temperatures between  $T_s$  and  $T_g$ , the disordered clusters show a remarkable cooperative diffusion, more importantly, the activation energy of cooperative diffusions below  $T_g$  is always lower than that of the liquid state. We have tried to understand such behavior from potential landscape and configurational entropies.

© 2019 Elsevier B.V. All rights reserved.

## 1. Introduction

Even now, glass and glass transitions are a mystery [1–8]. The mystery is manifold, but the dual characters of solid-like physical properties and liquid-like structures are likely key issues. Mechanically, a glass is rigid, like a crystalline solid; however structurally, a glass has disordered features, like a supercooled liquid. Incredibly, it remains unsolved whether or not from glass to liquid, or vice versa, is a true thermodynamic phase transition [9–15]. Thus, it is hard to give a clear definition for the glass transition within the framework of thermodynamics. It is safe to say that the scientific debate on the glassy state is still lively.

Although the thermodynamic features of a phase transition is ambiguous during glass transitions, some physical properties, such as viscosity [16–19], do change abruptly around the glass transition temperature ( $T_g$ ). The dramatic increase in viscosity is believed to deeply connect with the atomic dynamics. In fact, most thermodynamic theories on glass transitions hold that the dynamics behavior of atoms is involved. Especially, in Model-Coupling Theory (MCT) developed independently by Leutheusser [20], and Bengtzelius and coworkers [10], the dynamics process plays an essential role. The solution of MCT equations indicates that, there

exist at least three atomic relaxation time scales, which make a glass different from both liquids and crystals [21].

For a long time, many investigations focused on atomic level dynamics both experimentally and theoretically [22–27]. Among them, computer simulations, such as molecular dynamics (MD) and Monte Carlo simulations, which can give the most direct observation of atomic motions, were widely adopted in previous studies. In fact, recent progress in understanding glasses at the atomic level are largely due to computer simulations [7,17,24,26, 28–33]. Although great efforts had been made in studies of glasses, one of the key issues, namely atomic level diffusion around  $T_g$ , is much less understood. The reason is that, for most glasses atomic diffusion is almost frozen except for local vibrations around  $T_g$ , which makes computer simulations inefficient due to time scale limitations.

In 1998, two of the present authors (DY and XG) showed that an  $\text{Al}_{43}$  cluster in its most stable configuration has disordered character, and melts through a typical glass transition process [34]. This glass was identified as an ideal glass [35], which is defined as a glass state with zero configurational entropy [36,37]. Recent study on this nanoscale glass indicates that below  $T_g$ , although atomic diffusion definitely slows down, the diffusive motion of atoms can be obtained within affordable simulation times [38]. The natural question is then, is this unusual phenomenon universal in glass transitions, or just in this case? If this phenomenon is common in glassy states, what does it mean for glasses or glass transitions?

\* Corresponding authors.

E-mail addresses: dysun@phy.ecnu.edu.cn (D.Y. Sun), xggong@fudan.edu.cn (X.G. Gong).

In this paper, we report a MD study on melting of disordered nanoclusters. We find that before melting, all the disordered clusters show typical glass transition behavior, associated with a remarkable cooperative diffusion.

## 2. Computational methods

In this paper, disordered aluminum clusters in the range of 30 to 100 atoms are investigated. For comparison, two highly symmetric clusters ( $\text{Al}_{38}$  with  $D_{6h}$  symmetry and  $\text{Al}_{55}$  with  $I_h$  symmetry) are also studied. The glue potential [39], which is widely used in MD simulations, is adopted to describe the interatomic interaction of Al. The ground state of the clusters is taken from previous work [40]. The constant-temperature MD method with free boundary conditions is used in all calculations. The simulation spans the sub-microsecond scale in sub-picosecond steps. In whole simulations, the momentum of the center of mass and the total angular momentum of clusters are carefully eliminated from the calculations, thus the temperature refers only to the vibrational modes.

To characterize the shape of a cluster, the principal radii of gyration are calculated [41]. The principal radii of gyration ( $R_1$ ,  $R_2$ ,  $R_3$ ) of a cluster are calculated by  $R_i = \sqrt{I_i/N}$ , where  $I_i$  ( $i = 1, 2, 3$ ) is the principal moment of inertia of clusters. The volume of clusters is calculated based on the Wigner-Seitz primitive cell approximation [41]. Diffusion constants, which are an important thermodynamic quantity for identifying phases, are obtained through calculating the mean-square displacement of each atom.

To differentiate a cooperative diffusion from an individual diffusion, we have calculated the time-dependent displacement [38]

$$R_c(t) = \left( \frac{1}{N} \sum_{i=1}^N (r_i(t) - r_i(t + \Delta t))^2 \right)^{\frac{1}{2}},$$

where  $N$  is the number of atoms,  $r_i(t)$  denotes the position of the  $i$ th atom at time  $t$ , and  $\Delta t$  is a short duration, 5 ps in these studies. For a well-defined solid, the atoms only vibrate around their equilibrium positions, thus  $R_c(t)$  has a very small amplitude and a small variation with time. If diffusion is fast and less cooperative among atoms,  $R_c(t)$  will be very large and fluctuate uniformly with time, which corresponds to liquid states. On the contrary, if diffusion is intermittently triggered by strong cooperative motion among atoms,  $R_c(t)$  should show a remarkable variation with time.

## 3. Results and discussion

Fig. 1 depicts the average energy and volume per atom as a function of temperature for the ordered cluster  $\text{Al}_{38}$  (top panel). A jump occurs at around 580 K (melting temperature) in both energy and volume, indicating a typical first-order solid-liquid phase transition. Associated with the solid-liquid phase transition, the radii of gyration also have a jump as shown in the lower panel of Fig. 1. Before melting,  $\text{Al}_{38}$  keeps an almost ellipsoid shape due to its original symmetry, indicated by the two equal short and one long radii of gyration. After melting, the radii of gyration are equal, since a free-standing liquid droplet always has a spherical shape. A similar melting behavior is also found for an  $\text{Al}_{55}$  cluster, which accords with previous studies [42].

The disordered clusters behave differently than the first-order transition of the ordered clusters. Fig. 2 presents the average energy and volume per atom as a function of temperature for disordered  $\text{Al}_{46}$ ,  $\text{Al}_{62}$  and  $\text{Al}_{90}$  clusters. From Fig. 2, one can see that the melting behavior is totally different from that for ordered clusters (see Fig. 1). There is no abrupt change in either energy or volume, rather they change continuously over the entire temperature range. This is a typical glass transition behavior.  $T_g$  is estimated by

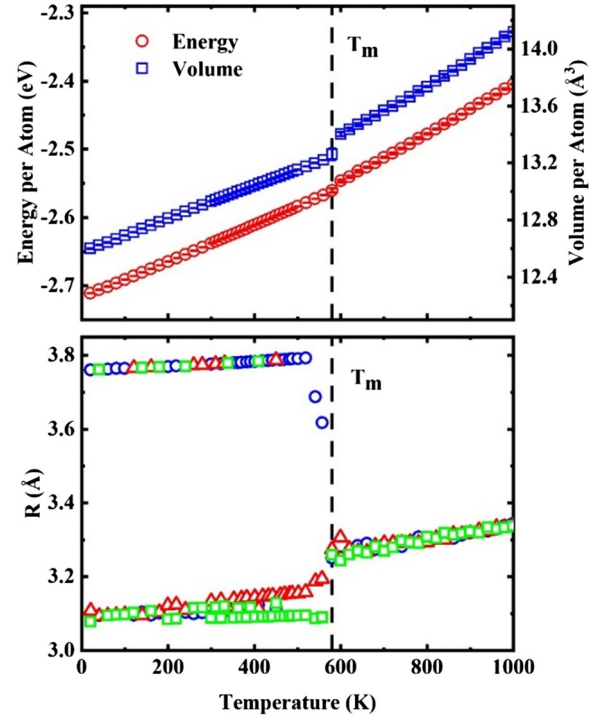
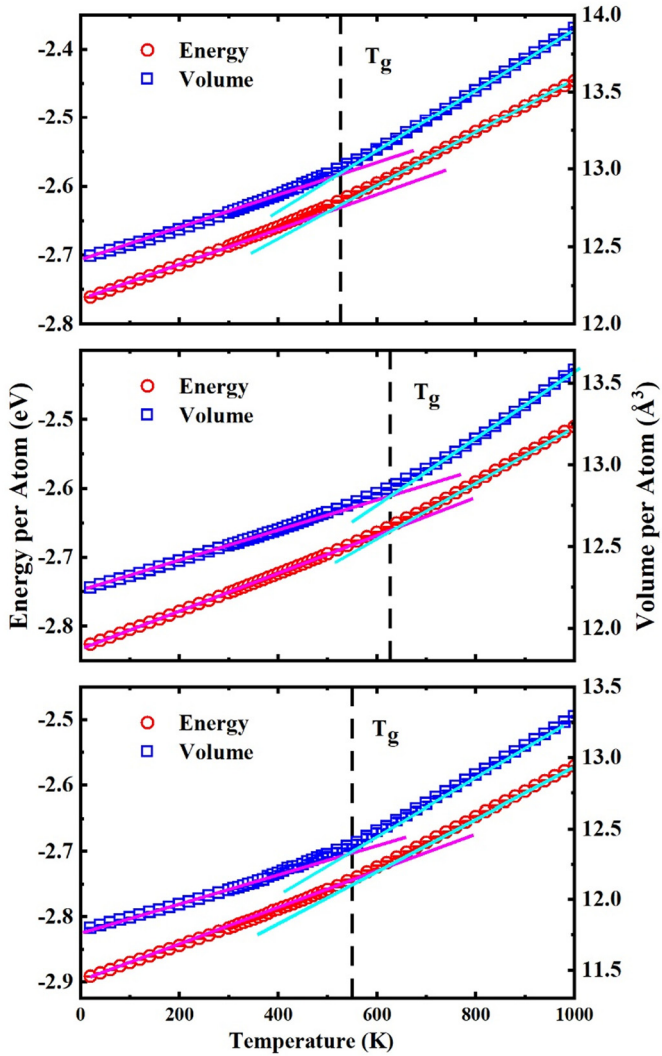


Fig. 1. (Color online) Top panel: the energy (circle) and volume (square) as a function of temperature for an ordered cluster  $\text{Al}_{38}$ . Bottom panel: three principal radii of gyration ( $R_{1,2,3}$  indicated by different colors) for  $\text{Al}_{38}$ . A remarkable first order solid-liquid transition occurs at around 580 K.

linear extrapolation of the low temperature and high temperature dependence of energy or volume.

The radii of gyration of these disordered clusters also show a different trend from high symmetry clusters. Fig. 3 shows the corresponding radii of gyration for disordered clusters mentioned above. For these three disordered clusters, one can identify two characteristic temperatures ( $T_s$  and  $T_g$ ) as shown in Fig. 3. For temperature lower than  $T_s$  (290 K, 80 K and 380 K for  $\text{Al}_{46}$ ,  $\text{Al}_{62}$  and  $\text{Al}_{90}$ , respectively), the three radii of gyration can be distinguished from one another, and are much closer to 0 K value, with only slight thermal expansion. This reflects the fact that these clusters keep their initial structures or shapes before  $T_s$ . For temperatures above  $T_g$  (527 K, 627 K and 497 K for  $\text{Al}_{46}$ ,  $\text{Al}_{62}$  and  $\text{Al}_{90}$ , respectively), the cluster is completely melted. Accordingly, the three radii of gyration become equal. It is remarkable that, at temperatures between  $T_s$  and  $T_g$ , the shape of the disordered clusters changes, consequently, the three radii of gyration fluctuate dramatically. If the change in cluster shape is frequent, or simulations run long enough, the three radii of gyration should become much closer. In fact, the radii of gyration of  $\text{Al}_{62}$  are almost equal, since this cluster has much lower diffusion activation energies (see below). Thus,  $T_s$  can be considered the starting temperature of the glass transition, since at temperature higher than  $T_s$ , the shape or structure of these clusters begins to change remarkably. Although Fig. 3 only presents the data for the three disordered clusters, a similar glass transition behavior has been observed in all studied disordered clusters. Namely, two characteristic temperatures ( $T_s$  and  $T_g$ ) are universal in the melting process of disordered clusters.

Fig. 4 shows the diffusion constants versus temperatures for the disordered clusters, where the vertical axis is a logarithmic scale and the horizontal axis is the reciprocal temperature. For disordered clusters, there exists a remarkable non-negligible atomic diffusivity below  $T_g$ . The diffusion-temperature curve can be divided into two ranges higher or lower than  $T_g$ . Diffusions in both

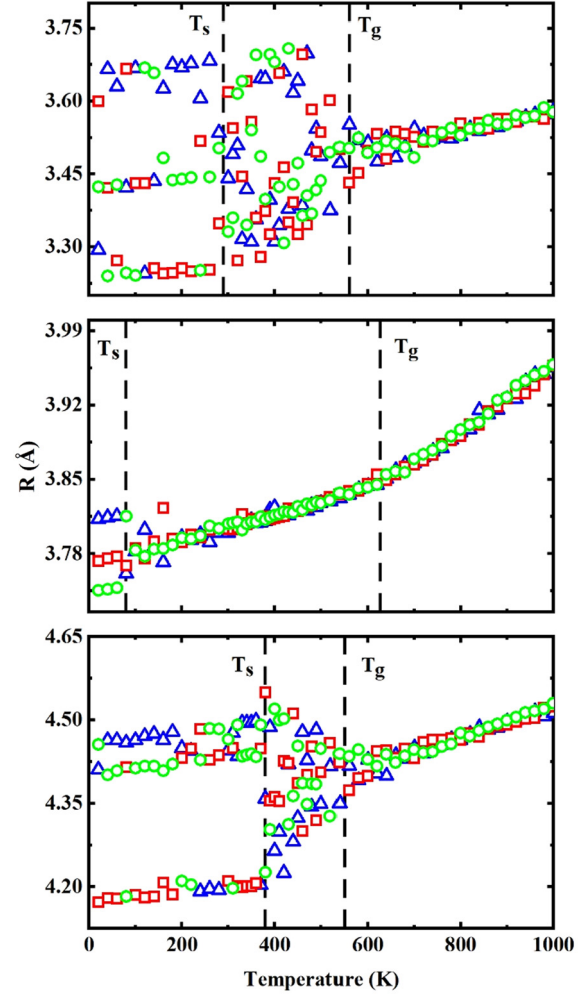


**Fig. 2.** (Color online) The energy (circle) and volume (square) per atom as a function of temperature for disordered clusters  $\text{Al}_{46}$ ,  $\text{Al}_{62}$  and  $\text{Al}_{90}$ . Both energy and volume continuously change with temperature, indicating a glass transition behavior. The glass transition temperature ( $T_g$ ) is identified by extrapolation of the low temperature and high temperature dependence of energy or volume (solid lines).

ranges can be well fitted with the Arrhenius relationship, but with different diffusion activation energies.

The activation energy of diffusion can be obtained by Arrhenius fitting to the diffusion constant-temperature data, namely the slope of the fitted lines. Fig. 5 shows the diffusion activation energy of glasses and liquids for all disordered clusters. Surprisingly, the diffusion activation energy of glasses is always less than that of the liquid state. The lower activation energy of glassy state is also obtained in one previous experiment [43].

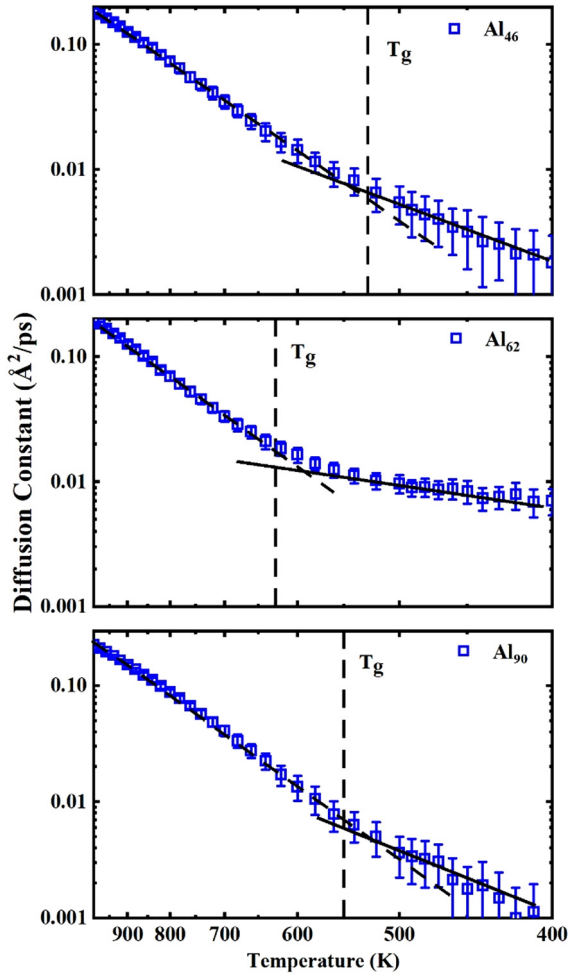
The low activation energy of diffusion in glassy states is not due to the well-known pre-melting of surface atoms. To illustrate this, we calculated the diffusion constant of each atom versus its average position, which we defined as the average distance from the mass center of the cluster. Obviously, if only surface atoms melt, the average position of each atom will be almost unchanged. Fig. 6 depicts the data for  $\text{Al}_{46}$ ,  $\text{Al}_{62}$  and  $\text{Al}_{90}$ . It can be seen that, for clusters in liquid state (760 K, 760 K and 800 K for  $\text{Al}_{46}$ ,  $\text{Al}_{62}$  and  $\text{Al}_{90}$ , respectively), the diffusion constant of each atom is almost independent of atom position. Surprisingly, for disordered clusters below  $T_g$  (450 K, 200 K and 460 K for  $\text{Al}_{46}$ ,  $\text{Al}_{62}$  and  $\text{Al}_{90}$ , respectively), inner atoms also have non-negligible diffusion, comparable to that of surface atoms.



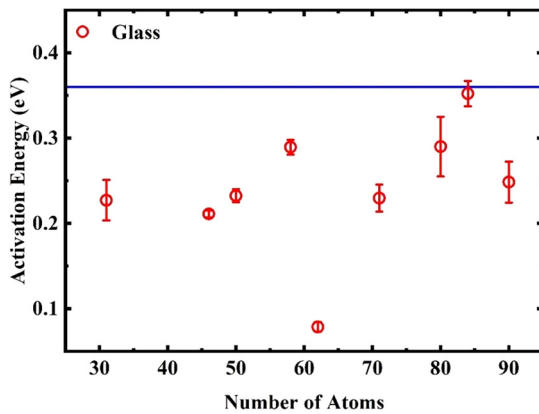
**Fig. 3.** (Color online) Three principal radii of gyration ( $R_{1,2,3}$  indicated by different colors) for  $\text{Al}_{46}$ ,  $\text{Al}_{62}$  and  $\text{Al}_{90}$  (from top to bottom).

Diffusion below  $T_g$  is attributed to cooperative diffusion among atoms, namely solid-solid structure-like transformations. To give evidence for the cooperative diffusion, we calculated time-dependent displacement ( $R_c(t)$ ) at three different temperatures as shown in Fig. 7. It can be seen that, at high temperatures,  $R_c(t)$  is large and varies uniformly with time, which is typical behavior for atomic diffusion in liquids with single atom behavior. At low temperatures, the atoms vibrate around their equilibrium positions, thus,  $R_c(t)$  has a very small amplitude and a small variation with time, indicating the cluster is in a well-defined solid-like state. However, at intermediate temperatures between  $T_s$  and  $T_g$ ,  $R_c(t)$  shows a remarkable variation with time. During some short intervals,  $R_c(t)$  is large, but these are interspersed with periods for which  $R_c(t)$  exhibits solid behavior. When  $R_c(t)$  suddenly becomes very large in a short interval, there are always a few atoms that diffuse quickly simultaneously. Thus, we suggest that, this kind of diffusion is intermittently triggered by strong cooperative motion among atoms. Recall that at this temperature the cluster is in the glassy state, which implies that atom diffusion is induced by a cooperative motion in a short time, i.e., a solid-solid structural transformation. Recent experimental and theoretical results also suggest cooperative motion in other glasses or supercooled liquids [44–51]. Similar behavior has been found for all studied disordered clusters.

Fig. 8 presents  $T_s$  and  $T_g$  for all the studied disordered clusters ranging from 30 to 100 atoms. With increasing cluster sizes, both  $T_s$  and  $T_g$  fluctuate. There is no significant correlation between

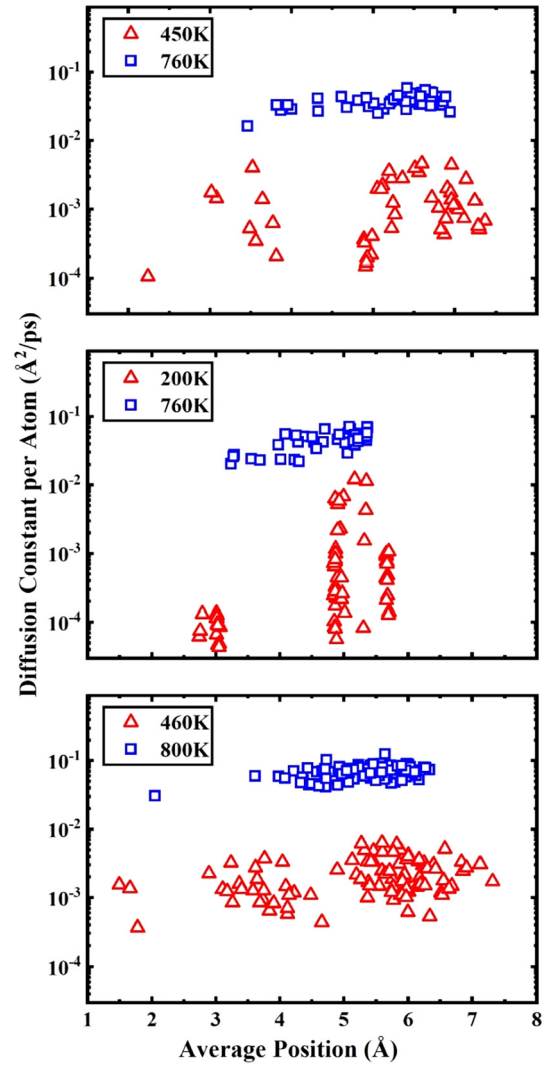


**Fig. 4.** (Color online) Temperature dependence of the diffusion constant for  $\text{Al}_{46}$ ,  $\text{Al}_{62}$  and  $\text{Al}_{90}$  (from top to bottom), where the vertical axis is logarithmic and the horizontal axis is reciprocal temperature. The solid lines are the Arrhenius fits to the data. The slope of the fitted lines indicates the activation energies of diffusions.



**Fig. 5.** (Color online) Diffusion activation energy of glass state for different disordered clusters. The value is obtained by Arrhenius fitting to the diffusion constant-temperature data. The activation energy of the liquid state (solid line) is averaged over all clusters. From the figure, it is obvious that the activation energy of glass is always less than that of liquid.

the characteristic temperatures and cluster sizes, which is different from high symmetry clusters, for which  $T_m$  usually increases with the increase of cluster size [42]. Interestingly, an approximated anti-correlation between  $T_s$  and  $T_g$  can be seen in Fig. 8,

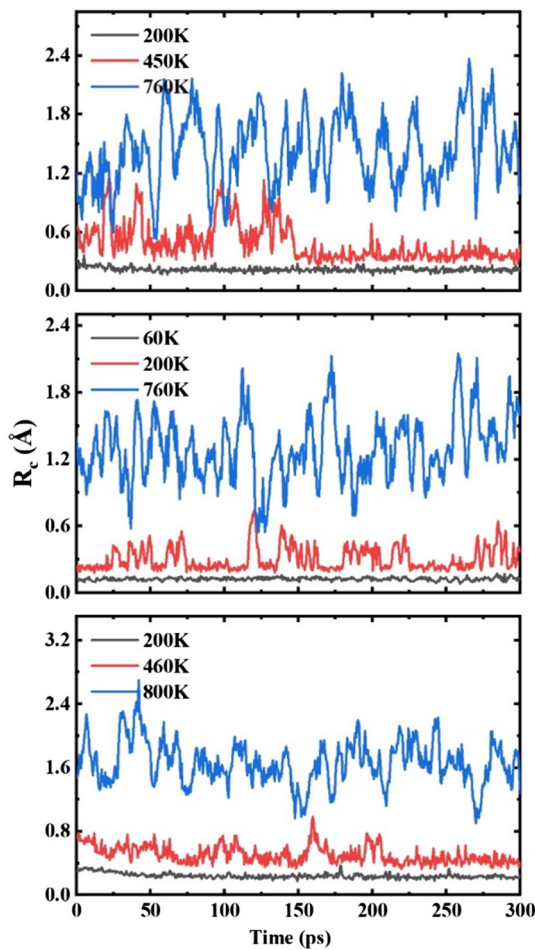


**Fig. 6.** The diffusion constant of each atom in two different temperatures for  $\text{Al}_{46}$ ,  $\text{Al}_{62}$  and  $\text{Al}_{90}$  (from top to bottom respectively). Here the average position is defined as the average distance from the mass center of the cluster over the simulation times. In the glass state (below  $T_g$ ), inner atoms also have non-negligible diffusion compared to surface atoms.

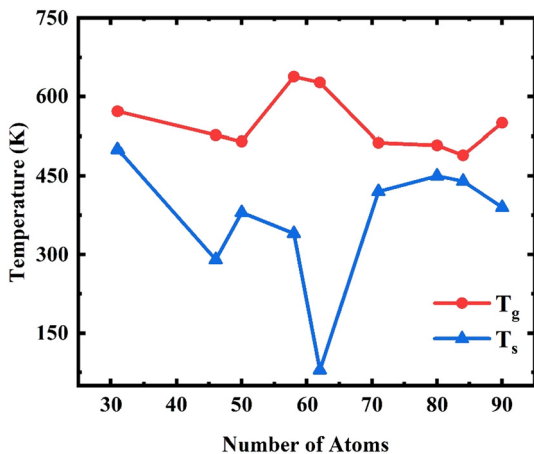
namely the lower  $T_s$  is, the higher  $T_g$  is. Looking again at Fig. 5, it is seen that there is another positive correlation between  $T_s$  and activation energies of diffusion.

As previously asserted [38], the free energy of a glass before melting should involve a contribution from the configuration entropy. As we have pointed out, between  $T_s$  and  $T_g$ , the configurational transformation dominates the long-range diffusivity of atoms. Considering the contribution of the configuration entropy, a glassy cluster should further lower its free energy, which will affect its glass transition temperature. Although precisely calculating of the configuration entropy is out of our current scope, the correlations between  $T_s$  and  $T_g$ , as well as  $T_s$  and activation energies of diffusion, may support this kind of contribution. The lower  $T_s$  reflects the fact that the configurational transformation can be staggered at low temperature. Lower activation energies of diffusion make the system visit more configurations. Both factors should tend to a higher configuration entropy, thus leading to a higher  $T_g$ . The data shown in Figs. 5 and 8 seemingly supports this conclusion. It needs to point out that, since  $T_g$  is not solely dependent on entropies but also on energies, the exact calculation of  $T_g$  is extremely difficult.





**Fig. 7.** (Color online) The time-dependent displacement ( $R_c(t)$ ) at three temperatures for  $\text{Al}_{46}$ ,  $\text{Al}_{62}$  and  $\text{Al}_{90}$  (from top to bottom respectively). At intermediate temperatures between  $T_s$  and  $T_g$ ,  $R_c(t)$  shows a remarkable variation with time, indicating a cooperative motion.



**Fig. 8.** (Color online)  $T_g$  and  $T_s$  versus the number of atoms for all the studied disordered clusters.  $T_g$  is obtained through extrapolation of temperature dependence of energy or volume.  $T_s$  is determined from the change of radii of gyration with temperature.

#### 4. Summary

We have found that the glass transition is universal behavior in disordered clusters. During the transition, energies and volumes of clusters change continuously. For all the disordered clusters, the shape or structure starts to change at a characteristic temperature

( $T_s$ ) lower than the glass transition temperature ( $T_g$ ). Atoms in the disordered clusters exhibit clear cooperative diffusion between  $T_s$  and  $T_g$ , which has smaller activation energy than that of liquid state. Diffusion below the glass transition temperature indicates the emergence of configuration entropies.

#### Conflicts of interest

There are no conflicts to declare.

#### Acknowledgements

Project supported by the National Natural Science Foundation of China (Grant No. 11874148). The computations were supported by ECNU Multifunctional Platform for Innovation.

#### References

- [1] P.G. Debenedetti, F.H. Stillinger, Supercooled liquids and the glass transition, *Nature* 410 (2001) 259.
- [2] J.C. Dyre, Colloquium: the glass transition and elastic models of glass-forming liquids, *Rev. Mod. Phys.* 78 (2006) 953.
- [3] A. Cavagna, Supercooled liquids for pedestrians, *Phys. Rep.* 476 (2009) 51–124.
- [4] L. Berthier, G. Biroli, Theoretical perspective on the glass transition and amorphous materials, *Rev. Mod. Phys.* 83 (2011) 587.
- [5] V.V. Hoang, D. Ganguli, Amorphous nanoparticles – experiments and computer simulations, *Phys. Rep.* 518 (2012) 81–140.
- [6] P. Charbonneau, J. Kurchan, G. Parisi, P. Urbani, F. Zamponi, Glass and jamming transitions: from exact results to finite-dimensional descriptions, *Annu. Rev. Condens. Matter Phys.* 8 (2017) 265–288.
- [7] O. Adjaoud, K. Albe, Microstructure formation of metallic nanoglasses: insights from molecular dynamics simulations, *Acta Mater.* 145 (2018) 322–330.
- [8] Y. Ivanisenko, C. Kubel, S.H. Nandam, C.M. Wang, X.K. Mu, O. Adjaoud, K. Albe, H. Hahn, Structure and properties of nanoglasses, *Adv. Eng. Mater.* 20 (2018) 16.
- [9] C.A. Angell, K.J. Rao, Configurational excitations in condensed matter, and the bond lattice model for the liquid-glass transition, *J. Chem. Phys.* 57 (1972) 470–481.
- [10] U. Bengtzelius, W. Gotze, A. Sjolander, Dynamics of supercooled liquids and the glass transition, *J. Phys. C, Solid State Phys.* 17 (1984) 5915.
- [11] C.A. Angell, The amorphous state equivalent of crystallization: new glass types by first order transition from liquids, crystals, and biopolymers, *Solid State Sci.* 2 (2000) 791–805.
- [12] B. Coluzzi, G. Parisi, P. Verrocchio, Thermodynamical liquid-glass transition in a Lennard-Jones binary mixture, *Phys. Rev. Lett.* 84 (2000) 306–309.
- [13] L. Santen, W. Krauth, Absence of thermodynamic phase transition in a model glass former, *Nature* 405 (2000) 550.
- [14] C. Cammarota, B. Giulio, Ideal glass transitions by random pinning, *Proc. Natl. Acad. Sci. USA* 109 (2011) 8850–8855.
- [15] L. Berthier, R.L. Jack, Evidence for a disordered critical point in a glass-forming liquid, *Phys. Rev. Lett.* 114 (2015) 1.
- [16] C.A. Angell, K.L. Ngai, G.B. McKenna, P.F. McMillan, S.W. Martin, Relaxation in glass-forming liquids and amorphous solids, *J. Appl. Phys.* 88 (2000) 3113.
- [17] M. Wyart, E.C. Michael, Does a growing static length scale control the glass transition?, *Phys. Rev. Lett.* 119 (2017) 195501.
- [18] B. Ruta, E. Pineda, Z. Evenson, Relaxation processes and physical aging in metallic glasses, *J. Phys. Condens. Matter* 29 (2017).
- [19] P. Luo, et al., Ultrastable metallic glasses formed on cold substrates, *Nat. Commun.* 9 (2018) 1389.
- [20] E. Leutheusser, Dynamical model of the liquid-glass transition, *Phys. Rev. A* 29 (1984) 2765.
- [21] S.P. Das, Mode-coupling theory and the glass transition in supercooled liquids, *Rev. Mod. Phys.* 76 (2004) 785–851.
- [22] Z.W. Wu, M.Z. Li, W.H. Wang, K.X. Liu, Hidden topological order and its correlation with glass-forming ability in metallic glasses, *Nat. Commun.* 6 (2015) 6035.
- [23] T. Salez, J. Salez, K. Dalnoki-Veress, E. Raphael, J.A. Forrest, Cooperative strings and glassy interfaces, *Proc. Natl. Acad. Sci. USA* 112 (2015) 8227–8231.
- [24] S.S. Schoenholz, E.D. Cubuk, D.M. Sussman, E. Kaxiras, A.J. Liu, A structural approach to relaxation in glassy liquids, *Nat. Phys.* 12 (2016) 569.
- [25] S. Bernini, D. Leporini, Cage effect in supercooled molecular liquids: local anisotropies and collective solid-like response, *J. Chem. Phys.* 144 (2016) 144505.
- [26] R. Miyazaki, T. Kawasaki, K. Miyazaki, Cluster glass transition of ultrasoft-potential fluids at high density, *Phys. Rev. Lett.* 117 (2016) 165701.
- [27] G. Biroli, C. Cammarota, Fluctuations and shape of cooperative rearranging regions in glass-forming liquids, *Phys. Rev. X* 7 (2017) 011011.

- [28] H.B. Yu, R. Richert, R. Maaß, K. Samwer, Unified criterion for temperature-induced and strain-driven glass transitions in metallic glass, *Phys. Rev. Lett.* 115 (2015) 135701.
- [29] Y. Jin, P. Urbani, F. Zamponi, H. Yoshino, A stability-reversibility map unifies elasticity, plasticity, yielding, and jamming in hard sphere glasses, *Sci. Adv.* 4 (2018) eaat6387.
- [30] A. Ninarello, L. Berthier, D. Coslovich, Models and algorithms for the next generation of glass transition studies, *Phys. Rev. X* 7 (2017) 021039.
- [31] H. Mizuno, H. Shiba, A. Ikeda, Continuum limit of the vibrational properties of amorphous solids, *Proc. Natl. Acad. Sci. USA* 114 (2017) E9767–E9774.
- [32] P. Cao, M.P. Short, S. Yip, Understanding the mechanisms of amorphous creep through molecular simulation, *Proc. Natl. Acad. Sci. USA* 114 (2017) 13631–13636.
- [33] Y.C. Hu, F.X. Li, M.Z. Li, H.Y. Bai, W.H. Wang, Five-fold symmetry as indicator of dynamic arrest in metallic glass-forming liquids, *Nat. Commun.* 6 (2015) 8.
- [34] D.Y. Sun, X.G. Gong, Structural properties and glass transition in Al N clusters, *Phys. Rev. B* 57 (1998) 4730.
- [35] E.G. Noya, J.P.K. Doye, F. Calvo, Theoretical study of the melting of aluminum clusters, *Phys. Rev. B* 73 (2006) 125407.
- [36] J.H. Gibbs, E.A. DiMarzio, Nature of the glass transition and the glassy state, *J. Chem. Phys.* 28 (1958) 373–383.
- [37] M.H. Cohen, D. Turnbull, Molecular transport in liquids and glasses, *J. Chem. Phys.* 31 (1959) 1164–1169.
- [38] D. Sun, C. Shang, Z. Liu, X. Gong, Intrinsic features of an ideal glass, *Chin. Phys. Lett.* 34 (2017) 026402.
- [39] F. Ercolessi, J.B. Adams, Interatomic potentials from first-principles calculations: the force-matching method, *Europhys. Lett.* 26 (1994) 583.
- [40] J.P. Doye, D.J. Wales, F.H. Zetterling, M. Dzugutov, The favored cluster structures of model glass formers, *J. Chem. Phys.* 118 (2003) 2792–2799.
- [41] D.Y. Sun, X.G. Gong, A new constant-pressure molecular dynamics method for finite systems, *J. Phys. Condens. Matter* 14 (2002) L487.
- [42] F. Baletto, R. Ferrando, Structural properties of nanoclusters: energetic, thermodynamic, and kinetic effects, *Rev. Mod. Phys.* 77 (2005) 371–423.
- [43] B. Cai, L.Y. Shang, P. Cui, J. Eckert, Mechanism of internal friction in bulk  $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$  metallic glass, *Phys. Rev. B* 70 (2004) 184208.
- [44] M. Philipp, C. Nies, M. Ostermeyer, W. Possart, J.K. Krüger, Thermal glass transition beyond kinetics of a non-crystallizable glass-former, *Soft Matter* 14 (2018) 3601–3611.
- [45] M. Arutkin, E. Raphael, J.A. Forrest, T. Salez, Cooperative strings in glassy nanoparticles, *Soft Matter* 13 (2017) 141–146.
- [46] S. Tatsumi, S. Aso, O. Yamamuro, Thermodynamic study of simple molecular glasses: universal features in their heat capacity and the size of the cooperatively rearranging regions, *Phys. Rev. Lett.* 109 (2012) 045701.
- [47] T. Bauer, P. Lunkenheimer, A. Loidl, Cooperativity and the freezing of molecular motion at the glass transition, *Phys. Rev. Lett.* 111 (2013) 225702.
- [48] N. Xu, V. Vitelli, A.J. Liu, S.R. Nagel, Anharmonic and quasi-localized vibrations in jammed solids—modes for mechanical failure, *Europhys. Lett.* 90 (2010) 56001.
- [49] M.L. Manning, A.J. Liu, Vibrational modes identify soft spots in a sheared disordered packing, *Phys. Rev. Lett.* 107 (2011) 108302.
- [50] A. Widmer-Cooper, P. Harrowell, Predicting the long-time dynamic heterogeneity in a supercooled liquid on the basis of short-time heterogeneities, *Phys. Rev. Lett.* 96 (2006) 185701.
- [51] C. Brito, M. Wyart, Heterogeneous dynamics, marginal stability and soft modes in hard sphere glasses, *J. Stat. Mech. Theory Exp.* 2007 (2007) L08003.