The Necessary and Sufficient Condition for Glass Transition

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Abstract

The intrinsic nature of glass states or glass transitions has been a mystery for a long time. Recently, more and more studies tend to show that a glass has a relatively flat potential energy landscape (PEL). However, this only indicates that a flat PEL is a necessary condition to form a glass state or to induce a glass transition. What is a sufficient condition for glass formation or a glass transition? Here we demonstrate that a flat PEL is not only necessary but also sufficient for the formation of a glass. By adjusting the flatness of PELs, we show that: (1) no matter what the structural symmetry is, as long as a system is located in a region of PEL deep enough, it can undergo a first-order solid-liquid phase transition; and (2) if a system is located in a flat enough region of the PEL, it can undergo a glass transition, independent of its structural symmetry. Our molecular dynamics simulations uncover the direct transfer from one potential energy minimum to another below the glass transition temperature, which is a feature of flat PELs. This kind of transition is accomplished by a cooperative motion, which is a direct consequence of the assumption for transition in a metabasin and for chain-like motions of Adam-Gibbs’s entropy theory.
Introduction

Potential energy landscapes (PELs) provide a unique perspective and indispensable physical picture for exploring the nature of glass and glass transitions.[1-4] The concept of a PEL comes from Goldstein's seminal paper, in which he made a direct connection between glass transitions and PELs.[5] Later, by introducing the inherent structure, Stillinger and Weber further developed the concept of a PEL and established a statistical mechanics framework for a quantitative calculation of thermodynamic properties of glasses.[6] In the past half century, the PEL of some glasses has been investigated.[7-52] Scientists are trying to correlate the properties of glasses with the PEL.[53] For example, Angell explicitly proposes a connection between the topology of the PEL (namely the density of configurational states) and the fragility of the associated liquid.[54,55] Perhaps one breakthrough is the recognition that the glass transition is rooted in a specific PEL. The PEL of glasses is made up of many metabasins, which are separated by higher barriers.[20,23,39,56-61] In a metabasin, the PEL is relatively flat. It is suggested that β relaxation relates to the atomic motion in a metabasin, and α relaxation is the result of inter-metabasin motion.[62,63] With metabasins, the excess configuration entropy, as well as Adam-Gibbs’s chain-like motions,[64] may be given a reasonable explanation.[65,66]

With the help of the PEL viewpoint, it seems that we are approaching understanding the nature of glasses. Previous studies on PELs only show that glasses are in a relatively flat PEL of metabasins, indicating a sufficient condition for glassy states. However, whether a system located in a relatively flat PEL must undergo a glass transition (necessary condition for glass transitions), has not been well answered. If a relatively flat PEL is the necessary and sufficient condition for the glassy state and a glass transition, what role does the structural symmetry play? In other words, if a symmetrical structure is in a relatively flat PEL, can a glass transition occur? Similarly, if a disordered structure is in a deep PEL, can a first order solid-liquid phase transition occur?

The straightforward way to address these questions is to investigate the changes of thermodynamic behavior by directly adjusting the PEL. However, it is not easy to adjust PELs, especially in a controlled manner. There have been a few attempts to study the glass state by adjusting PELs. In these studies, PELs are mostly manipulated by changing a parameter of the model potentials.[67-70] One obvious disadvantage of the method lies in that the relationship between PELs and the potential parameters is elusive. Especially since the PEL is a complex function in high-dimensional phase space, it seems impossible to establish this kind of relationship. Even though previous studies still presented fruitful and instructive results.

To give a clear answer to the question of whether a relatively flat PEL is the necessary and sufficient condition for the glassy state and glass transition, we propose a controlled manner to adjust PELs. We systematically studied the glass transition of both ordered and disordered systems by adjusting them through various PELs. We established the
direct relationship between PELs and the glass transition, and we find that a relatively flat PEL is the key feature for a glass transition, rather than the structural issue.

Methodological Development

In order to adjust the PEL, we propose the following approach. Assuming $\varphi$ is the total interatomic potential of a system, a new potential $\varphi^*$ is defined as,

$$\varphi^* = \begin{cases} 
\varphi + \varepsilon(\varphi - \varphi_0)^m & \text{for } \varphi \leq \varphi_0 \\
\varphi & \text{for } \varphi > \varphi_0 
\end{cases}, \quad (1)$$

where $\varepsilon$, $\varphi_0$ and $m$ are adjustable parameters and $m$ is an even number ($m \geq 2$). It is easy to calculate the potential energy difference between $\varphi^*$ and $\varphi$ for all points in the phase space by directly using Eq. 1.

Since

$$\frac{\partial \varphi^*}{\partial r} = (1 + \varepsilon m (\varphi - \varphi_0)^{m-1}) \frac{\partial \varphi}{\partial r} \quad (2)$$

we see that all extreme and saddle points of $\varphi$ pass to $\varphi^*$ keep their location in phase space unchanged. In addition, $\varphi^*$ has another extreme point or saddle point determined by

$$1 + \varepsilon m (\varphi_s - \varphi_0)^{m-1} = 0. \quad (3)$$

To ensure these additional extreme or saddle points are far away from the temperature region of interest to us, the parameters ($\varphi_0, m, \varepsilon$) have been carefully selected (see below).

The adjustment on the flatness of PEL by Eq. 1 is reflected in two aspects. First, from the second derivatives of the potential energy with respect to atomic positions, namely

$$\frac{\partial^2 \varphi^*}{\partial r^2} = \frac{\partial^2 \varphi}{\partial r^2} + \varepsilon m (\varphi - \varphi_0)^{m-1} \frac{\partial^2 \varphi}{\partial r^2} + (\varepsilon m - 1)(\varphi - \varphi_0)^{m-2} \frac{\partial \varphi}{\partial r} \frac{\partial \varphi}{\partial r}, \quad (4)$$

one can see that, compared to that of $\varphi$, the PEL of $\varphi^*$ at extreme points can be adjusted to be more or less flat, based the choice of $\varepsilon$, $\varphi_0$ and $m$. Second, suppose $\varphi_a$ and $\varphi_b$ ($\varphi_a < \varphi_b \leq \varphi_0$) being adjacent minimum and saddle points at the PEL of $\varphi$ respectively, and $\varphi_a^*$ and $\varphi_b^*$ being the counterparts at the PEL of $\varphi^*$, we have $\varphi_b^* - \varphi_a^* = \varphi_b - \varphi_a + \varepsilon (\varphi_b - \varphi_0)^m - \varepsilon (\varphi_a - \varphi_0)^m$. Thus if $\varepsilon$ is negative (positive), the barrier in PEL becomes higher (lower).

It needs to point that, by adjusting the flatness of PELs, other than the additional extreme or saddle points determined by Eq. 3, we do not change either the number or position of extreme points in phase space, which is a remarkable feature of our method. We note that, similar ideas have been used to study the dynamics of polymers.[71-73] as a mechanism of accelerating molecular dynamic simulations.

Using molecular dynamics (MD) simulations, we have studied the melting behavior of two aluminum clusters ($\text{Al}_{43}$ and $\text{Al}_{55}$). For Al, $\varphi$ is the established glue potential. It is
known that at $\varepsilon=0$, Al$_{43}$ has a disordered ground state structure. The ground state of Al$_{55}$ has an ordered structure with high symmetry ($I_h$ symmetry). The melting of Al$_{55}$ is a typical solid-liquid phase transition, while Al$_{43}$ melts and solidifies with a typical glass-like transition, which has been suggested to be an ideal glass.

This choice of clusters to study glass transitions has at least two clear advantages. First, as demonstrated previously, some clusters can be considered to be a so-called ideal glass, i.e., the glass transition in these clusters can occur at any arbitrarily slow cooling rate. This point allows us to study the thermodynamic behavior of glass transitions independent of the cooling rate. Second, for clusters containing dozens of atoms, it is easy to extend the MD simulation time to microseconds or even longer. It becomes possible to explore the typically slow dynamics of glasses around the glass transition temperature. These two advantages are not available in bulk glass.

In current studies, for Al$_{43}$, $\varphi_0$ and $m$ are $-2.58 \times 43$ eV and 6, respectively, and $\varepsilon$ is chosen in the range of $[-4 \times 10^{-5}, 0]$. Since here $\varepsilon$ is negative, the PEL becomes steeper as $\varepsilon$ is decreased. For Al$_{55}$, $\varphi_0=-2.58 \times 55$ eV, $m=4$, and $\varepsilon$ is in the range $[0.0, 2.8 \times 10^{-4}]$. Since here $\varepsilon$ is positive, the PEL becomes flatter as $\varepsilon$ is increased. Our simulations confirm that for all chosen $\varepsilon$, the disordered structure and $I_h$ structure are still the stable configurations for Al$_{43}$ and Al$_{55}$, respectively.

For both clusters, $\varphi_0=-2.58$ eV times the number of atoms, corresponds to the potential energy above the melting temperature at $\varepsilon=0$. It is easy to calculate that the additional extreme or saddle points determined by Eq. 3 are far away from the potential range of interest. The value of $\varphi_s$ is easily gotten from Eq. 3. For Al$_{43}$, $\varphi_s > \varphi_0$, and the corresponding $\varphi_s$ for all $\varepsilon$ is higher than 900 K, which is irrelevant to any phase or glass transition in the current studies. For Al$_{55}$, $\varphi_s < \varphi_0$, for all studied $\varepsilon$, and the corresponding temperature is less than ~200K, which is much lower than the melting point or glass transition temperatures. In fact, the extra extreme or saddle points at $\varphi_s$ have essentially no effect on the thermodynamic properties.

**Result and Discussion**

The basic difference between a glass transition and a solid-liquid phase transition lies in how the energy and volume change. In a glass transition process, both energy and volume change continuously over the whole range of temperatures. While in a solid-liquid phase transition, both energy and volume have a jump at the melting temperature. Figs. 1 and 2 depict the change of energies, volumes and specific heats with temperature for different PELs adjusted by different parameters. The melting behavior is closely related to the flatness of the PEL regardless of the structural symmetry. For the disordered Al$_{43}$, with the increase of $\varepsilon$, for which the PEL becomes steeper and steeper, the melting behavior changes accordingly from a typical glass transition to a first order solid-liquid phase transition. For the ordered Al$_{55}$, when the PEL gets progressively flatter by increasing $\varepsilon$, the melting behavior changes from a
A typical first order solid-liquid phase transition to a glass transition. These results indicate that the glass transition is not intrinsically dependent on the structural symmetry, but on the flatness of the PEL. When the PEL becomes steeper, a first order solid-liquid phase transition occurs; when the PEL becomes flatter, a glass transition occurs.

At \( \varepsilon = 0 \), the melting of \( Al_{43} \) is a typical glass transition, indicated by the continuous change in energy (black circles in upper panel of Fig. 1) and volume (black circles in upper panel of Fig. 2), as we have demonstrated several times in our previous work.[79,80] The glass transition temperature, which is around 520K, can be estimated by a linear extrapolation of the low temperature and high temperature dependence of energies. As \( \varepsilon \) decreases from zero to negative, which means the PEL gets steeper and steeper, the melting of \( Al_{43} \) shows a typical first order solid-liquid phase transition of finite systems, as shown in Fig. 1 (upper panel). For \( \varepsilon = -2 \times 10^{-5} \), the melting of \( Al_{43} \) has begun to deviate from the glass transition behavior. For \( \varepsilon = -4 \times 10^{-5} \), the energy changes rapidly, and a significant latent heat appears. The step around melting is not very sharp, which is a remarkable feature of the finite size effect of melting.[81] The clear fact beyond question is that a typical first-order phase transition does occur in this disordered glass-like \( Al_{43} \) after the PEL is adjusted, i.e., if the PEL of glass becomes deeper, it shows a typical solid-liquid transition.

![Figure 1](image_url)

**Figure 1**: (Color online) The energy as a function of temperature for ordered \( Al_{55} \) (lower panel) and disordered \( Al_{43} \) (upper panel). For \( Al_{43} \), with the increase of \( \varepsilon \), the continuous change in energy is gradually replaced by a step, while for \( Al_{55} \), with the increase of \( |\varepsilon| \), a step in energy is gradually replaced by a continuous change.
The lower panel of Fig. 1 shows the energy as a function of temperature for the ordered Al$_{55}$ with a range of $\varepsilon$. The energy has a clear step for $\varepsilon=0.0$ and $1 \times 10^{-4}$ at the melting temperature, a typical feature of a first-order phase transition. However, for $\varepsilon=2 \times 10^{-4}$, the energy step disappears, resulting in a typical glass transition process. This indicates that, if an ordered configuration is trapped in a steep PEL, a glass transition can occur.

The change of volume with temperature further supports our conclusions drawn from energy changes. Fig. 2 shows the volume as a function of temperature for Al$_{43}$ (upper panel) and Al$_{55}$ (lower panel). For the disordered Al$_{43}$, when $\varepsilon=0$, the volume changes continuously with typical glass transition characteristics. When $\varepsilon=-5 \times 10^{-5}$, the volume jumps obviously at the melting point, showing characteristics typical of a solid-liquid phase transition in finite systems. For ordered Al$_{55}$, the volume clearly jumps for $\varepsilon=0$ and $1 \times 10^{-4}$ around the melting temperature. This is a typical feature of a first-order phase transition. When $\varepsilon=2 \times 10^{-4}$, the step has disappeared, reflecting a typical glass transition process.

The change in melting behavior for different PELs can also be found from specific heat, as shown in Fig. 3. For Al$_{43}$ (lower panel of Fig. 3), for $\varepsilon=0$ the specific heat does not exhibit any peak or discontinuity, indicating a typical glass transition. With $\varepsilon=-2 \times 10^{-5}$, the peak in specific heat becomes sharp, which is a distinct feature of melting in finite-size systems. The appearance of a peak instead of a discontinuity is due to the existence of the solid-liquid coexistence for finite-size systems. For Al$_{55}$ (upper panel of Fig. 3), we have identified a change from the first-order solid-liquid phase transition to the glass transition as the PEL flattens. One can see that, for $\varepsilon=0$ and $1 \times 10^{-4}$, the specific heat has a step at the melting point, which is a hallmark of solid-liquid phase transitions. While it becomes a continuous change and does not show any peak in the entire temperature range for $\varepsilon=2 \times 10^{-4}$, implying a glass transition.
Figure 2: (Color online) The volume as a function of temperature for ordered Al₅₅ (lower panel) and disordered Al₄₃ (upper panel). The change in volume is similar to that shown in Fig. 1.

Figure 3: (Color online) The specific heat as a function of temperature for disordered cluster Al₄₃ (lower panel) and ordered cluster Al₅₅ (upper panel). For Al₄₃, with the decrease of ε, i.e., the PEL becomes deeper, the peak in specific heat becomes sharper and sharper, indicating evolution from a glass transition to a first order phase transition. For Al₅₅, with the increase of |ε|, i.e., the PEL becomes flatter, the jump in specific heat disappears gradually, indicating evolution from a first order phase transition to a glass transition.

Principal radii of gyration, in addition to indicating a change of cluster shape, also identify the type of phase transition. We find that the difference between the maximum and minimum radius of gyration (ΔR=R_max−R_min) gives clear information about structural changes and melting behavior. Fig. 4 shows ΔR as a function of temperature. For a first order solid-liquid phase transition (Al₄₃ with ε=−3.4×10⁻⁵, Al₅₅ with ε=1.0×10⁻⁴), the clusters keep their original structure before completely melting, indicated by an approximately constant value of ΔR. A jump in ΔR around the melting temperature can be clearly seen for these clusters. For a typical glass transition (Al₄₃ at ε=−0.4×10⁻⁵, Al₅₅ at ε=2.0×10⁻⁴), far below T_g, ΔR has already begun to change. With the increase of temperature, in contrast to the first solid-liquid phase transition, ΔR gradually changes, spanning temperatures over a range of about 200K. We can define the temperature at which clusters begin to change shape as the starting temperature (T_s), which represents a characteristic temperature, above which configurational entropies emerge in glassy states.

According to Fig. 4, three characteristic temperatures, T_s, T_g and T_m, can be determined.
T_m is the obvious one without any ambiguity. It is defined as the temperature, at which \( \Delta R \) jumps, which is in accordance with abrupt changes in the volume and energy as shown in Figs. 1 and 2. T_s can be easily defined as the temperature at which \( \Delta R \) obviously begins to change. In contrast, it is not easy to determine T_g, which is a well-known difficulty. However, Fig. 4 shows us that the glass transition is much more clearly reflected on the \( \Delta R \)-T curve. In the current work, T_g can be estimated by linear extrapolation of the low temperature and high temperature dependence of \( \Delta R \), as illustrated by dash lines in Fig. 4. Two issues need to be emphasized: 1) T_g is consistent with that determined by other thermodynamic quantities, energies, volumes, etc; and 2) It is inevitable that there can be large errors, as is also the case in other methods.

![Figure 4. (Color online) The difference between the maximum and minimum radius of gyration.](image)

There seems to be a consensus that cooperative diffusion within a few atoms exists in a glass. This perspective comes from Adam-Gibbs entropy theory and Goldstein's PEL picture.[5,64] Recently, it has become generally believed that this cooperative diffusion may correspond to a transition in a metabasin. We show that the atomic diffusion in a glass below T_g can indeed be considered as a transition from one potential energy minimum to another, for which the transition is accomplished by cooperative diffusion.[82-86].

We have calculated the diffusion coefficient, which is shown in Fig. 5 for Al_{43} (upper panel) and Al_{55} (lower panel). If clusters melt through a solid-liquid phase transition, the atomic diffusivity becomes negligible below the melting point, indicating a normal solid state. For both Al_{43} and Al_{55}, if a glass transition occurs, the atoms have obvious
diffusivity below $T_g$. This is a typical feature for glassy clusters suggested recently.[79,80]

The diffusion activation energy can be obtained by fitting the diffusion coefficient via temperatures. For glass transitions, diffusion activation energies are clearly different below and above $T_g$. In particular, the glass state (low temperature) has lower activation energy than that in the liquid state (high temperature), in agreement with previous studies.[26,87,88] As we have pointed out previously, this is a typical characteristic of diffusion in glasses.[79,80] It is well known that the diffusion of atoms in liquids is mainly determined by thermal collisions. The change in activation energy around $T_g$ implies a change of diffusion mechanism. As discussed in detail in our previous works, this diffusion is a kind of collective diffusion, and the diffusion barrier is even lower than that in the liquid.[80]

Obviously, this cooperative diffusion is the result of a flat PEL, because it only occurs with a sufficiently flat PEL, i.e., $\epsilon \geq -1 \times 10^{-5}$ for Al$_{43}$ and $\epsilon \geq 2 \times 10^{-4}$ for Al$_{55}$. One can conclude that the relatively flat potential energy surface is the essence of the glassy state, and results in cooperative diffusion at low temperature.

![Figure 5](image_url)

Figure 5. (Color online) Temperature dependence of the diffusion constant for Al$_{43}$ (upper panel) and Al$_{55}$ (lower panel), where the vertical axis is logarithmic and the horizontal axis is reciprocal scale. For Al$_{43}$ at $\epsilon=0.0$ and Al$_{55}$ at $\epsilon=2 \times 10^{-4}$, there is the evident diffusivity below the glass transition temperature. The arrows, with the same color as data points, roughly indicate the corresponding $T_g$ or $T_m$. 
Figure 6. (Color online) The short-time average of potential energy ($E_c$) and displacement ($R_c$) for $Al_{43}$ at $\varepsilon=0.0$ (upper panel) and $Al_{55}$ at $\varepsilon=2 \times 10^{-4}$ (lower panel), where the temperature is 400K.

This cooperative diffusion corresponds to a jump from one local minimum to a neighboring local minimum, still in the relatively flat PEL. The direct way to show this is to calculate the evolution of potential energies and atomic displacements. In order to separate the thermal fluctuation from the energy and atomic displacements, the short-time average of the energy ($E_c(t)$) and atomic displacement ($R_c(t)$) are calculated by averaging over a certain time interval. More concretely, the short-time average of displacement is

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

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 current studies. Our previous study has shown that $R_c(t)$ can be used to identify the cooperative motion.\cite{80} The short-time average of the energy is

$$E_c(t) = \frac{1}{\Delta t} \int_0^{\Delta t} E(t + \tau)d\tau,$$

where $E(t)$ is the instantaneous potential energy, and $\Delta t$ is again 5 ps. If $E_c(t)$ takes a certain value at one time period and is a different value during another time period, the system can be considered to be at different local minimum of the PEL. If $E_c(t)$ is synchronized with a notable change in $R_c(t)$, we can conclude that the cooperative diffusion corresponds to the jump from one PEL minimum to another.
Fig. 6 shows the evolution of $R_c$ and $E_c$ over time. The upper panel of Fig. 6 corresponds to Al$_{43}$ at $\varepsilon = 0.0$, the lower panel of Fig. 6 corresponds to Al$_{55}$ at $\varepsilon = 2 \times 10^{-4}$, both at $T=400K$. Both $E_c$ and $R_c$ maintain relatively small values over many time periods, which corresponds to one or more equilibrium states with similar energy. However, in some short periods of time, $R_c$ has a rapid increase. By carefully observing the atomic trajectory, we find that the rapid increase of $R_c$ is always associated with a larger displacement of a few atoms at the same time. The size of displacement is comparable to the average distance between atoms, indicating that diffusion occurs. This process can be considered as a cooperative diffusion. At the same time, a rapid increase of $E_c$ occurs simultaneously, which should relate to the activation process of this cooperative diffusion. After a rapid increase, $R_c$ quickly returns to the smaller value, then $E_c$ equilibrates to a new state. Perhaps it corresponds to a transition from one inherent structure to another. Since the two equilibrium states are very close in energy, which is precisely what people speculate or assume about a metabasin. Although only a few cooperative diffusion events are shown, such behaviors are common in glassy states.

Combining the current result with our previous work,[80] we can present a general phase behavior of a glass. Thermodynamically, a solid, glass and liquid mainly differ in two aspects, internal energies and configurational entropies. The difference in energies is obvious and easily understood. However, the difference in configurational entropies is ambiguous. A solid is in a deep potential well, in which the vibrational entropy is important, while the configurational entropy is neglectable. In liquids, the atoms diffuse quickly, the configurational entropy reaches a maximum compared to solids and glasses. In glasses, the atom vibrates at a local potential minimum for most of the time. As we have demonstrated, the remarkable feature of glasses is the existence of collective diffusion, thus the configurational entropy should play a role on the thermodynamical behavior of glasses.

By adjusting the PEL, we are able to make some comprehensive comparisons. Fig. 7 shows the change of $T_s$, $T_g$ and $T_m$ as a function of $\varepsilon$. It can be seen that, $T_g$, for either Al$_{43}$ or Al$_{55}$, shows a significant jump when the melting behavior of the cluster changes from a first-order solid-liquid phase to a glass transition. This jump should be caused by the emergence of configuration entropies.

The last question we want to answer is, under what conditions is the glassy state thermodynamically stable rather than metastable? This question mainly involves three thermodynamic quantities: the depth of the potential well of the ground state, the free energy of the glass ($F_G$) and the free energy of the liquid ($F_L$). Assuming $T_c$ refers to the critical temperature at which the system escapes from the initial potential well, if $F_G<F_L$ at $T_c$, the glass will be thermodynamically stable, and the glass transition will occur. In contrast, if $F_G>F_L$, the system will melt via a solid-liquid phase transition, and the glass will be thermodynamically unstable. Generally, these three thermodynamic quantities, except $T_c$, are very difficult to calculate, especially $F_G$. Fortunately, the current calculations provide strong support for the above statements. Obviously, $T_s$ and $T_m$ can
be considered as $T_c$, because above this temperature, the system is no longer in the ground or initial state. By adjusting the PEL, however the potential barrier is decreased or increased, $T_s$ and $T_m$ should share the same function of $\varepsilon$, which is strongly supported by the data in Fig. 7. For Al$_{43}$, $T_s$ increases as the potential barrier increases. At a critical value of the potential barrier, the glass becomes metastable, and the glass transition disappears from the melting process. For Al$_{55}$, $T_m$ decreases as the potential barrier decreases. When passing through a critical value of potential barrier, the glass becomes thermodynamically stable, thus the melting process is a glass transition. The above discussion is the core value of this work.

![Figure 7](image)

**Figure 7.** (Color online) $T_s$, $T_g$ and $T_m$ as a function of $\varepsilon$. For Al$_{43}$, $\varepsilon<1 \times 10^{-5}$, the disordered clusters begin to exhibit a first-order solid-liquid phase transition. For Al$_{55}$, $\varepsilon>2 \times 10^{-4}$, the ordered clusters begin to undergo a glass transition.

**Summary**

In this paper, we have systematically studied the glass transition of nanoclusters by molecular dynamics. We have proposed a method to adjust the flatness of a potential energy surface. This method can adjust the height of potential barriers without changing the number or position in phase space of the potential energy extremal points. By adjusting the flatness of the potential energy surface, we have found that the clusters can undergo either a first-order solid-liquid phase transition or a glass transition, which is independent of the structural symmetry. This makes it possible for us to demonstrate for the first time that a flat potential energy landscape is a sufficient and necessary condition for glass transitions. Because these clusters undergo an ideal glass transition, *i.e.* under an arbitrarily slow cooling rate, it allows study of the dynamic processes at
any long time. We find that, even under the glass transition temperature, the system can frequently transfer from one potential surface minimum to another, and this process is achieved by a collective diffusion, which is completely different from the thermal collision process in liquids. Our study provides, for the first time, a microscopic version of atomic motion below the glass transition temperature, as well as a physical picture of the potential energy landscape.

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References

Uncategorized References

[1] P. G. Debenedetti and F. H. Stillinger, Nature 410, 259 (2001).
[2] F. Sciortino, Journal of Statistical Mechanics: Theory and Experiment 2005, P05015 (2005).
[3] A. Heuer, Journal of Physics: Condensed Matter 20, 373101 (2008).
[4] U. Buchenau, Journal of Physics: Condensed Matter 15, S955 (2003).
[5] M. Goldstein, Journal of Chemical Physics 51, 3728 (1969).
[6] F. H. Stillinger and T. A. Weber, Physical Review A 25, 978 (1982).
[7] A. Heuer, Physical Review Letters 78, 4051 (1997).
[8] O. M. Becker and M. Karplus, Journal of Chemical Physics 106, 1495 (1997).
[9] S. Sastry, P. G. Debenedetti, and F. H. Stillinger, Nature 393, 554 (1998).
[10] G. Diezemann, H. Sillescu, G. Hinze, and R. Böhmer, Physical Review E 57, 4398 (1998).
[11] M. A. Miller, J. P. K. Doye, and D. J. Wales, Journal of Chemical Physics 110, 328 (1999).
[12] G. Dalldoss, O. Pilla, G. Viliani, C. Brangian, and G. Ruocco, Physical Review B 60, 3200 (1999).
[13] F. Sciortino, W. Kob, and P. Tartaglia, Physical Review Letters 83, 3214 (1999).
[14] S. Büchner and A. Heuer, Physical Review Letters 84, 2168 (2000).
[15] S. Sastry, Nature 409, 164 (2001).
[16] D. J. Wales and J. P. K. Doye, Physical Review B 63, 214204 (2001).
[17] I. Saika-Voivod, P. H. Poole, and F. Sciortino, Nature 412, 514 (2001).
[18] T. F. Middleton and D. J. Wales, Physical Review B 64, 024205 (2001).
[19] F. H. Stillinger and P. G. Debenedetti, Journal of Chemical Physics 116, 3353 (2002).
[20] G. Fabricius and D. A. Stariolo, Physical Review E 66, 031501 (2002).
[21] T. S. Grigera, A. Cavagna, I. Giardina, and G. Parisi, Physical Review Letters 88, 055502 (2002).
[22] L. Angelani, G. Ruocco, M. Sampoli, and F. Sciortino, Journal of Chemical Physics 119, 2120 (2003).
[23] B. Doliwa and A. Heuer, Physical Review Letters 91, 235501 (2003).
[24] J. Chowdhary and T. Keyes, Journal of Physical Chemistry B 108, 19786 (2004).
[25] A. Saksaengwijit, J. Reinisch, and A. Heuer, Physical Review Letters 93, 235701 (2004).
[26] S. A. Trygubenko and D. J. Wales, Journal of Chemical Physics 121, 6689 (2004).
[27] M. Vogel, B. Doliwa, A. Heuer, and S. C. Glotzer, Journal of Chemical Physics 120, 4404 (2004).
[28] Y. V. Fyodorov, Physical Review Letters 92, 240601 (2004).
[29] A. J. Moreno, S. V. Buldyrev, E. La Nave, I. Saika-Voivod, F. Sciortino, P. Tartaglia, and E. Zaccarelli, Physical Review Letters 95, 157802 (2005).
[30] A. Heuer, B. Doliwa, and A. Saksaengwijit, Physical Review E 72, 021503 (2005).
[31] T. Odagaki, T. Yoshidome, A. Koyama, and A. Yoshimori, Journal of Non-Crystalline Solids 352, 4843 (2006).
[32] R. K. Bowles and I. Saika-Voivod, Physical Review E 73, 011503 (2006).
[33] C. Wang and R. M. Stratt, Journal of Chemical Physics 127, 224503 (2007).
[34] J. A. Rodríguez Fris, G. A. Appignanesi, E. La Nave, and F. Sciortino, Physical Review E 75, 041501 (2007).
[35] D. V. Matyushov, Physical Review E 76, 011511 (2007).
[36] V. K. De Souza and D. J. Wales, Journal of Chemical Physics 130, 194508 (2009).
[37] C. Rehwald, N. Gnan, A. Heuer, T. Schröder, J. C. Dyre, and G. Diezemann, Physical Review E 82, 021503 (2010).
[38] J. Smiatek and A. Heuer, Journal of Computational Chemistry 32, 2084 (2011).
[39] N. Xu, D. Frenkel, and A. J. Liu, Physical Review Letters 106, 245502 (2011).
[40] T. Akimoto, T. Kaneko, K. Yasuoka, and X. C. Zeng, Journal of Chemical Physics 138, 244301 (2013).
[41] P. Charbonneau, J. Kurchan, G. Parisi, P. Urbani, and F. Zamponi, Nature Communications 5, 3725 (2014).
[42] D. Jacobson and R. M. Stratt, Journal of Chemical Physics 140, 174503 (2014).
[43] A. Zaccone, P. Schall, and E. M. Terentjev, Physical Review B 90, 140203(R) (2014).
[44] X. Du and E. R. Weeks, Physical Review E 93, 062613 (2016).
[45] H. J. Hwang, R. A. Riggelman, and J. C. Crocker, Nature Materials 15, 1031 (2016).
[46] Y. Jin and H. Yoshino, Nature Communications 8, 14935 (2017).
[47] Z.-Y. Wei, C. Shang, X.-J. Zhang, and Z.-P. Liu, Physical Review B 95, 214111 (2017).
[48] S. P. Niblett, V. K. De Souza, R. L. Jack, and D. J. Wales, Journal of Chemical Physics 149, 114503 (2018).
[49] M. Blank-Burian and A. Heuer, Physical Review E 98, 033002 (2018).
[50] V. Ros, G. Ben Arous, G. Biroli, and C. Cammarota, Physical Review X 9, 011003 (2019).
[51] P. Cao, M. P. Short, and S. Yip, PNAS 116, 18790 (2019).
[52] C. Scalliet and L. Berthier, Physical Review Letters 122, 255502 (2019).
[53] Z. Raza, B. Alling, and I. A. Abrikosov, Journal of Physics: Condensed Matter 27, 293201 (2015).
[54] C. A. Angell, Journal of Physics and Chemistry of Solids 49, 863 (1988).
[55] C. A. Angell, Journal of Non-Crystalline Solids 131, 13 (1991).
[56] R. A. L. Vallée, M. Van Der Auweraer, W. Paul, and K. Binder, Physical Review Letters 97, 217801 (2006).
[57] G. A. Appignanesi, J. A. Rodríguez Fris, and M. A. Frechero, Physical Review Letters 96, 237803 (2006).
[58] Y. Yang and B. Chakraborty, Physical Review E 80, 011501 (2009).
[59] T. Oppelstrup and M. Dzugutov, Journal of Chemical Physics 131, 044510 (2009).
[60] T. Okushima, T. Niiyama, K. S. Ikeda, and Y. Shimizu, Physical Review E 97, 021301 (2018).
[61] F. Despa and R. S. Berry, Journal of Chemical Physics 115, 8274 (2001).
[62] M. Goldstein, Journal of Non-Crystalline Solids 357, 249 (2011).
[63] A. S. Keys, L. O. Hedges, J. P. Garrahan, S. C. Glotzer, and D. Chandler, Physical Review X 1, 021013 (2011).
[64] G. Adam and J. H. Gibbs, Journal of Chemical Physics 43, 139 (1965).
[65] G. P. Johari and J. Khouri, Journal of Chemical Physics 138, 12A511 (2013).
[66] M. Ozawa, C. Scalliet, A. Ninarello, and L. Berthier, Journal of Chemical Physics 151, 084504 (2019).
[67] P. Jund, M. Ravomanantsoa, and R. Jullien, Journal of Physics Condensed Matter 12, 8777 (2000).
[68] Z. Shi, P. G. Debenedetti, F. H. Stillinger, and P. Ginart, Journal of Chemical Physics 135, 084513 (2011).
[69] S. Sengupta, F. Vasconcelos, F. Affouard, and S. Sastry, Journal of Chemical Physics 135, 194503 (2011).
[70] Y.-C. Hu, J. Schroers, M. D. Shattuck, and C. S. O'Hern, Physical Review Materials 3, 85602 (2019).
[71] J. Duncan, Q. Wu, K. Promislow, and G. Henkelman, Journal of Chemical Physics 140, 194102 (2014).
[72] S. Bonfanti and W. Kob, Journal of Chemical Physics 147, 204104 (2017).
[73] Y. Miao, Journal of Chemical Physics 149 (2018).
[74] D. Sun and X. Gong, Physical Review B 57, 4730 (1998).
[75] J. P. K. Doye, Journal of Chemical Physics 119, 1136 (2003).
[76] E. G. Noya, J. P. K. Doye, and F. Calvo, Physical Review B 73, 1 (2006).
[77] L. Berthier and G. Biroli, Reviews of Modern Physics 83, 587 (2011).
[78] V. V. Hoang and D. Ganguli, Physics Reports 518, 81 (2012).
[79] X. Y. Li, D. Y. Sun, and X. G. Gong, Physics Letters A 383, 2604 (2019).
[80] D. Sun, C. Shang, Z. Liu, and X. Gong, Chinese Physics Letters 34, 026402 (2017).
[81] J. Jellinek, T. L. Beck, and R. S. Berry, Journal of Chemical Physics 84, 2783 (1986).
[82] N. Mousseau, G. T. Barkema, and S. W. De Leeuw, Journal of Chemical Physics 112, 960 (2000).
[83] N. Giovambattista, S. V. Buldyrev, F. W. Starr, and H. E. Stanley, Physical Review Letters 90, 085506 (2003).
[84] T. Bauer, P. Lunkenheimer, and A. Loidl, Physical Review Letters 111, 225702 (2013).
[85] S. Karmakar, C. Dasgupta, and S. Sastry, Physical Review Letters 116, 085701 (2016).
[86] H. B. Yu, R. Richert, and K. Samwer, Journal of Physical Chemistry Letters 7, 3747 (2016).
[87] K. Trachenko, M. T. Dove, K. D. Hammonds, M. J. Harris, and V. Heine, Physical Review Letters 81, 3431 (1998).
[88] B. Cai, L. Y. Shang, P. Cui, and J. Eckert, Physical Review B 70, 184208 (2004).