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Mean-Squared Energy Difference for Exploring Potential Energy Landscapes of Supercooled Liquids

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By extending the concept of diffusion to the potential energy landscapes (PELs), we introduce the mean-squared energy difference (MSED) as a novel quantity to investigate the intrinsic properties of supercooled liquids. MSED can provide a clear description of the "energy relaxation" process on a PEL. Through MSED analysis, we have obtained a characteristic time similar to that derived from structure analysis, namely τ_α^*. Further, we establish a connection between MSED and the feature of PELs, providing a concise and quantitative description of PELs. The relaxation behavior of energy has been found to follow a stretched exponential form. As the temperature decreases, the roughness of the accessible PEL changes significantly around a characteristic temperature T_x, which is 20% higher than the glass transition temperature T_g and is comparable to the critical temperature of the mode-coupling theory. More importantly, one of the PEL parameters is closely related to the Adam–Gibbs configurational entropy. The present research, which directly links the PEL to the relaxation process, provides avenues for further research of glasses.

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1. Introduction. Supercooled liquids exhibit complex dynamic processes, setting them apart fundamentally from normal liquids and solids. Unveiling the intrinsic physical mechanisms behind these relaxation processes is essential for demystifying the mysteries of glasses.[1–9] During the formation of glass, the relaxation time can span up to 12 orders of magnitude.[10–13] Such a large span of time not only poses a challenge to experimental measurement, but also brings great difficulty to theoretical research. For this reason, despite extensive studies on the relaxation process, its essence remains debated and continues to be a focal and challenging topic in glass research.

The two most important and widely studied relaxation processes in supercooled liquids are the α-relaxation and β-relaxation,[14–18] which were discovered in the loss modulus spectrum of glasses. Experimentally, the dynamical relaxation behavior of supercooled liquids and glasses is typically measured using dielectric spectroscopy or dynamic mechanical analysis depending on whether the sample has significant dielectric strength. These methods involve applying alternating electric fields (strain) at different frequencies and measuring the dielectric spectrum (dynamic modulus) of the sample. If a corresponding relaxation process exists at a given frequency, the dissipation intensity at that frequency increases. It has been observed that as temperature decreases, two broad peaks appear in the loss spectra of supercooled liquids, corresponding to two relaxation modes. The slow and fast modes refer to α-relaxation and β-relaxation, respectively.[14,19–23] In some materials, however, the loss spectra may exhibit a main peak and an excess wing instead of two peaks,[24–26] and the microscopic origin of the excess wing is still under debate.[19] Nevertheless, from a fundamental perspective, all relaxation processes should be determined by the morphology of the potential energy landscapes (PELs), i.e., the system navigating on a high-dimensional PEL. A widely adopted PEL picture is that β-relaxation corresponds to transitions between local minima (i.e., basins), while α-relaxation refers to transitions between meta-basins (MBs), which are large collections of basins separated by higher barriers.[27–33] As pointed out previously,[34,35] such a picture should carefully consider the spatial dynamic heterogeneity, especially for larger systems.

Despite substantial experimental and theoretical research on relaxations in supercooled liquids, many important issues remain unresolved. Especially, relaxation times from different theoretical methods can vary significantly, especially at high temperatures (e.g., Ref. [36]). In typical theoretical simulations, α-relaxation time (τ_α) and β-relaxation time (τ_β) are derived from specific structural correlation functions, with energy information entirely discarded. While in experiments, it is difficult to directly observe the micro-structure of glasses, so energy dissipation is often measured instead. However, the relaxation times derived from structural relaxation in computer simulations and energy dissipation in experiment lack direct connections, and it is unclear if they correspond to the same relaxation process. Especially, since α-relaxation is considered as the process that the system "walking" on

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a PEL, can one obtain valuable information about the PEL from α-relaxation? Is there a simple approach to directly calculate relaxation times from the information of energies? These questions motivate us to explore a faster, energy-based method for studying relaxation processes.

Undoubtedly, all processes of the system on the PEL should be reflected in the time series of potential energy. However, the valuable information for relaxations is usually obscured by random thermal fluctuations,[37] which is much more difficult to extract from a time series of potential energy. Simple thermodynamic averaging may remove thermal fluctuations, but it can also erase relaxation-related information. Conversely, simply considering the time variation of potential energy lacks statistical reliability. In this work, we introduce a method that provides sufficient time averaging without losing time information. Specifically, we analogize the "motion" of a system on the PEL to atomic motion in real space, treating the energy changes as a form of "diffusion" behavior. Through systematic analysis, we have established a description for the system's "walking" process on the PEL and obtain the α-relaxation time. Additionally, we can derive some quantitative information describing the morphology of PELs from the relaxation processes, which could be useful for calculating configurational entropy. This paper not only presents a simple algorithm for studying relaxation processes, but also provides a new perspective on the relationship between relaxations and the PEL of supercooled liquids.

2. Computational Details. In this study, we investigate supercooled liquids of the $Cu_{50}Zr_{50}$ and Kob–Anderson binary Lennard–Jones (KA-BLJ) systems. All molecular dynamics (MD) simulations were performed using the LAMMPS code.[38] The $Cu_{50}Zr_{50}$ alloy exhibits a strong glass-forming ability and remains stable throughout the supercooled temperature range. We simulated a bulk system containing 2048 atoms using the optimized EAM potential.[39] Initially, 10 different configurations were prepared at 2000 K, followed by cooling at a rate of 10^{10} K/s to 300 K. The entire cooling process was carried out using the NPT ensemble at zero external pressure. In our simulations, the glass transition temperature T_g for $Cu_{50}Zr_{50}$ is approximately 720 K, which is in agreement with previous studies.[40,41] At the temperatures of interest, the system underwent 1 ns NVT relaxation before changing to the NVE ensemble for sampling, with a sampling duration of up to 400 ns for each temperature. In contrast, the KA-BLJ system undergoes a glass transition without the need for rapid cooling. We simulated a KA-BLJ system containing 1000 atoms (with a ratio of $N_A : N_B = 80 : 20$) using the NVT ensemble, cooling from $T = 1.0$ to 0.1 at a rate of $1 \times 10^{-7}\,\tau^{-1}$. In this work, the glass transition temperature for KA-BLJ is $T_g = 0.39$. At each temperature of interest, long NVE ensemble simulations were conducted for up to $10^7\,\tau$. The simulations were carried out using reduced units, with parameters consistent with Ref. [42]. Since our study primarily focused on supercooled liquids, the entire simulation process was carefully monitored to ensure that no crystallization occurred.

We calculated the mean-squared displacement (MSD) for both systems at temperatures of interest. MSD is simply defined as $\langle \Delta r^2(t) \rangle = \langle [\boldsymbol{r}(t) - \boldsymbol{r}(0)]^2 \rangle$, in which $\boldsymbol{r}(0)$ and $\boldsymbol{r}(t)$ are the atom coordinates at time 0 and t. Similarly, we define ΔE as the difference of the total potential energy (E) per atoms, i.e., $\Delta E(t) = \frac{1}{N}[E(t_0) - E(t_0 + t)]$, with N being the number of atoms. The mean-squared energy difference (MSED) of total potential energies was then calculated by

$$\langle \Delta E^2(t) \rangle = \frac{1}{N^2} \langle [E(t) - E(0)]^2 \rangle. \tag{1}$$

Since the energy of the system is a one-dimensional variable, $\langle \Delta E^2(t) \rangle$ will eventually reach a certain value in equilibrium. From the definition of ΔE, we know that this value is related to both temperature and the specific heat,

$$\lim_{t \to \infty} \langle \Delta E^2(t) \rangle = \frac{1}{2} k_B T^2 C, \tag{2}$$

with C being the specific heat. According to the definition,

$$\Delta E(t) = \frac{1}{N} \sum_i^N \delta\varepsilon_i(t), \tag{3}$$

where $\delta\varepsilon_i(t) = [\varepsilon_i(t_0) - \varepsilon_i(t_0 + t)]$ is the potential energy difference of the i-th atom. $\langle \Delta E^2(t) \rangle$ can be expressed as

$$\begin{aligned} \langle \Delta E^2(t) \rangle &= \left\langle \left[\frac{1}{N} \sum_i^N \delta\varepsilon_i(t) \right]^2 \right\rangle \\ &= \frac{1}{N} \langle \delta\varepsilon_i^2(t) \rangle + \frac{2(N-1)}{N} \langle \delta\varepsilon_i(t) \delta\varepsilon_j(t) \rangle, \end{aligned} \tag{4}$$

in which $\langle \delta\varepsilon_i^2(t) \rangle$ is the MSED of the potential energy of the i-th atom, and $\langle \delta\varepsilon_i(t) \delta\varepsilon_j(t) \rangle$ is the correlation in the energy evolution between the i-th and j-th atom. In most cases, the number of atoms $N \gg 1$, so $\frac{2(N-1)}{N} \langle \delta\varepsilon_i(t) \delta\varepsilon_j(t) \rangle \approx 2 \langle \delta\varepsilon_i(t) \delta\varepsilon_j(t) \rangle$. From Eq. (3), one can see that, MSED of total potential energies $[\langle \Delta E^2(t) \rangle]$ not only encompasses MSED for individual atoms $[\langle \delta\varepsilon_i^2(t) \rangle]$, but also reflects the correlation of the potential energy of each atom $[\langle \delta\varepsilon_i(t) \delta\varepsilon_j(t) \rangle]$.

To obtain the conventional α-relaxation time τ_α, we computed the self-intermediate scattering function (SISF) $F_s(q = q_{max}, t) = \langle \exp\{-i\boldsymbol{q} \cdot [\boldsymbol{r}(0) - \boldsymbol{r}(t)]\} \rangle$, in which q_{max} is the wave vector where the static structure factor $S(q)$ reaches its first maximum.[43,44] In previous studies, τ_α is usually defined as the duration required for SISF to decay from 1 to e^{-1}.

3. Results and Discussion. Figure 1 shows $\langle \Delta r^2(t) \rangle$ and $\langle \Delta E^2(t) \rangle$ in $Cu_{50}Zr_{50}$ system. Based on previous analyses about MSD and the SISF, atomic motion in supercooled liquids can generally be divided into three stages: free motion, confined motion within a local "cage", and diffusive motion.[6,45–48] $\langle \Delta E^2(t) \rangle$ perfectly reflects these stages of structural evolution. It can be seen that $\langle \Delta E^2(t) \rangle$ exhibits a peak in a very short time (around 0.05 ps),

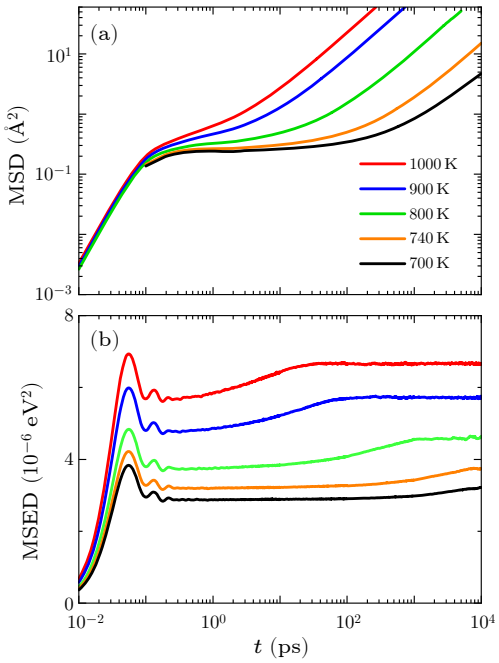

Fig. 1. Mean-squared displacement [$\langle\Delta r^2(t)\rangle$] (a) and mean-squared energy difference [$\langle\Delta E^2(t)\rangle$] (b) for $Cu_{50}Zr_{50}$ at several temperatures. The information about atomic vibration [the regular oscillation within 1 ps in (b)] was eliminated in MSD while kept in MSED. Both functions show plateau in intermediate time, corresponding to the cage breaking regime in real space and intra-meta-basin hopping in potential energy landscapes, respectively. Over time, MSD eventually increases proportional to t in diffusion regime, while MSED grows and reaches platform after the system "sees" all the accessible areas on potential energy landscapes.

followed by a decay to the first plateau around 0.2 ps. This peak actually corresponds to oscillations in the total energy with a period of 0.1 ps [the regular oscillations seen within 1.0 ps in Fig. 1(b)]. This time period is almost independent of temperature and corresponds to the characteristic time of atomic vibrations. For $t < 0.05$ ps, the change in $\langle\Delta E^2(t)\rangle$ reflects the vibrations of the system near the potential energy minima. Thus, for $t < 0.05$ ps, both $\langle\Delta r^2(t)\rangle$ and $\langle\Delta E^2(t)\rangle$ are proportional to t^2.

After the ballistic regime, the motion of atoms in real space becomes constrained by their neighboring atoms, causing $\langle\Delta r^2(t)\rangle$ reaches a local maximum (though not very pronounced), then enters an almost plateau. The time that $\langle\Delta r^2(t)\rangle$ reaches the local maximum is defined as τ_β in literatures (e.g., Ref. [16]). At low temperatures, atoms remain trapped in a "cage" for longer periods (this may originate from the tendency of atoms moving more cooperatively [6,49,50]), which extends the plateau. From the PEL perspective, this timescale corresponds to the system's motion between different local minima, commonly referred to as the β regime. Unlike the thermal vibration, no obvious oscillation was observed in the β regime. The absence of the β-relaxation signal in $\langle\Delta E^2(t)\rangle$ may stem from the fact that β events are localized, with no significant correlation or cooperation among them. [19,51,52] Since β-relaxation involves local motion of only a small number of atoms and occurs over short timescales, multiple β-relaxation events can exist simultaneously in the system. [53,54] This randomness causes different β-relaxation processes to cancel each other out in terms of their impact on the total energy.

On longer timescales, $\langle\Delta E^2(t)\rangle$ enters a region where it first increases steadily and then approaches saturation. In the early stage of this process, as the system explores larger and larger regions of the PEL, $\langle\Delta E^2(t)\rangle$ continues to grow slowly. Eventually, when the system "sees" the full extent of the accessible PEL, $\langle\Delta E^2(t)\rangle$ stabilizes at a certain value, consistent with our earlier analysis. During this time window, the atomic motion in real space transitions into the diffusion stage, where $\langle\Delta r^2(t)\rangle$ shifts from the plateau to proportionality with t. At this timescale, the slow change in $\langle\Delta E^2(t)\rangle$ indicates that the involved relaxation times are long. Based on this, we can preliminarily conclude that the system begins transitioning between MBs, which likely corresponds to the α-relaxation process. We will verify this conclusion in the following analysis.

Recently, Yu *et al.* proposed an order parameter, i.e., the inherent structures minimal displacement (IS $D_{\min}$), which could rationalize relaxation dissipation in a unified scaling. [55] They found that IS $D_{\min}$ of glass-forming liquids increases monotonically, and eventually reaches a constant value in sufficiently long time. We believe IS $D_{\min}$ and MSED may share some fundamental connections. Since IS $D_{\min}$ depicts the exploration of the accessible IS space, and MSED describes how the system evolves in the energy space, they are both designed to explore the features of the accessible PEL.

Unlike thermal vibration and β-relaxation, α-relaxation corresponds to the transition between MBs, and the associated relaxation time is sufficiently long. In this case, the change in total potential energy mainly reflects the difference in the average energy of each MB. When the system is confined within one MB, and only the background strength provided by thermal vibrations is considered, $\langle\Delta E^2(t)\rangle$ can be approximated as $\langle\Delta E^2(t)\rangle = \Delta E_0^2 = U_0^2$. Assuming the average energy difference between MBs is $U_{\rm m}$, and the characteristic transition time is τ_α^*. Once a transition occurs, the energy difference becomes $\Delta E^2(t) = \Delta E_0^2 + U_{\rm m}^2$, while the probability that the system remains in the same MB after time t can be written as $P(t) = {\rm e}^{-t/\tau_\alpha^*}$. Considering that structural relaxation is often characterized by a stretched exponential function due to its heterogeneous nature, [49,56] the overall $P(t)$ is reasonably replaced by ${\rm e}^{-(t/\tau_\alpha^*)^\beta}$. Clearly, the time evolution of $\langle\Delta E^2(t)\rangle$ can be expressed as

$$\begin{aligned}\langle\Delta E^2(t)\rangle &\cong \Delta E^2(0) + U_{\rm m}^2[1 - P(t)] \\ &= U_0^2 + U_{\rm m}^2(1 - {\rm e}^{-(t/\tau_\alpha^*)^\beta}).\end{aligned} \tag{5}$$

From this equation, we can see that α-relaxation does not cause $\langle\Delta E^2(t)\rangle$ to exhibit the regular oscillatory behavior. There are two main reasons: 1) The relaxation time of α-relaxation follows an exponential distribution, indicating significant temporal heterogeneity of dynamic processes. [37,57] This means that α-relaxation events are much less correlated in time, and thus, we do not observe oscillations in $\langle\Delta E^2(t)\rangle$; 2) The characteristic timescale for

movement between MBs is much longer, and the time the system spends in the saddle point is negligible compared to the time it spends near the minima. As a result, information about barrier heights is effectively averaged out over long time and does not manifest in total potential energy fluctuations.

Figure 2(a) shows the MSED of $Cu_{50}Zr_{50}$ alloy at $T = 820\,\mathrm{K}$ (black curve), the results of the stretched exponential fitting using Eq. (5), and the standard exponential fitting. It can be seen that the stretched exponential form (red curve) fits the MSED almost perfectly, which contrasts with the fitting results of the standard exponential form (blue curve). Figure 2(b) depicts the temperature dependence of the shape parameter β in $Cu_{50}Zr_{50}$ and KA-BLJ. In comparison to SISF, we believe that, the smaller value of β corresponding to a growing temporal heterogeneity of the energy relaxation. It can be seen that β decreases with decreasing temperature in both systems, which is consistent with previous studies.[37,58] To the best of our knowledge, all reported results on β have been obtained by fitting the structural correlation functions.[4,13,49,56] It is the first time that the energy relaxation of the supercooled liquid is found to exhibit a stretched exponential form. More importantly, as the temperature approaches T_g, the shape parameter β for energy relaxation gradually decreases to the value predicted by the trap model, i.e., $\beta = d/(d+2) = 0.6$,[4] while β from SISF does not always exhibit such trend.[59,60]

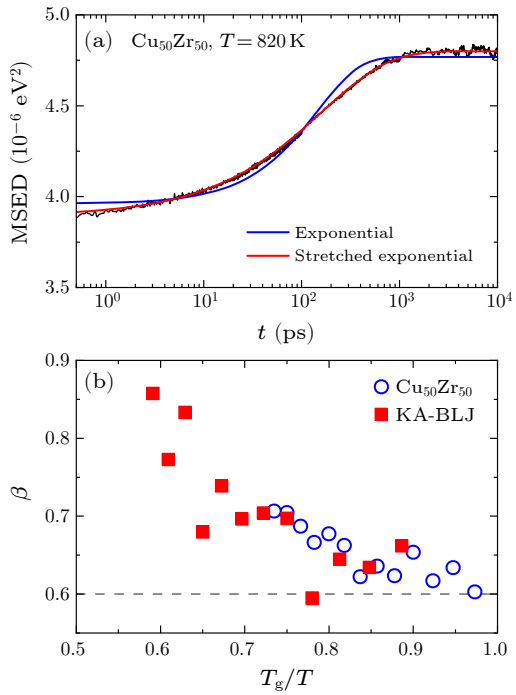

Fig. 2. (a) $\langle \Delta E^2(t) \rangle$ of $Cu_{50}Zr_{50}$ at 820 K. The stretched exponential function can almost perfectly fit $\langle \Delta E^2(t) \rangle$ (red line), which forms a stark contrast to the simple exponential fit (blue line). For both $Cu_{50}Zr_{50}$ and KA-BLJ, the stretched exponential form provides an excellent fit to $\langle \Delta E^2(t) \rangle$. (b) The fitted β in $Cu_{50}Zr_{50}$ and KA-BLJ decrease with decreasing temperature. β tends towards 0.6 at the glass transition temperature (T_g), which is precisely the value predicted by the trap model.[4]

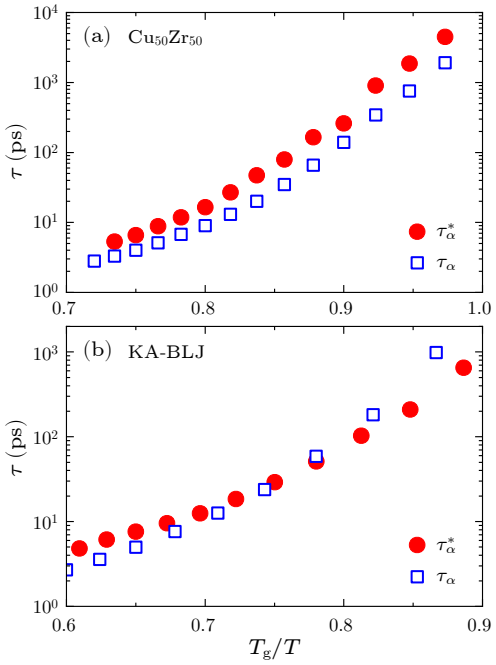

Fig. 3. Relaxation time in $Cu_{50}Zr_{50}$ (a) and KA-BLJ (b). τ_α^* (filled circle) is the relaxation time obtained by fitting $\langle \Delta E^2(t) \rangle$ with Eq. (5), and τ_α (open square) stands for the structural relaxation time obtained from self-intermediate scattering function. τ_α and τ_α^* are similar in value and share the same tendency, which proves the feasibility of obtaining relaxation time from energy correlation function.

Our fitting results indicate that the long-time behavior in $\langle \Delta E^2(t) \rangle$ indeed corresponds to the α-relaxation process in the system. The obtained relaxation time τ_α^* is plotted in Fig. 3, where (a) corresponds to $Cu_{50}Zr_{50}$ and (b) to KA-BLJ. For comparison, τ_α obtained from the SISF based on structural correlation are also shown in the figure. It is clearly shown that τ_α^* obtained from $\langle \Delta E^2(t) \rangle$ and τ_α from SISF exhibit the same trend and are very close in magnitude. This is in agreement with the work of Baity-Jesi *et al.*, in which they investigated the typical escape time of MBs by studying inherent structures.[61] Such a difference may arise from the fact that $\langle \Delta E^2(t) \rangle$ is more sensitive to relaxation processes that cause significant energy changes, whereas SISF is more sensitive to the process that causes structural changes. This aligns with the nature of α-relaxation, which has a broad distribution and involves complex relaxation processes.

Our theoretical analysis [Eq. (5)] not only provides a model for relaxation time but also gives quantitative information about the PEL. Figure 4 shows the fitted U_0 and U_m as a function of scaled temperatures for $Cu_{50}Zr_{50}$ [(a) and (b)] for KA-BLJ [(c) and (d)], with lines being the linear fitting. Here, U_0^2 represents background fluctuations excluding the α-relaxation process, which includes contributions from thermal vibrations and short-term relaxation processes. U_m, on the other hand, is the average energy difference between MBs, and its square corresponds to the potential energy fluctuations caused by α-relaxation. Based on the definition, we expect $U_0 \propto k_B T$. It is clear that U_0 is proportional to T, which aligns perfectly with our expectations.

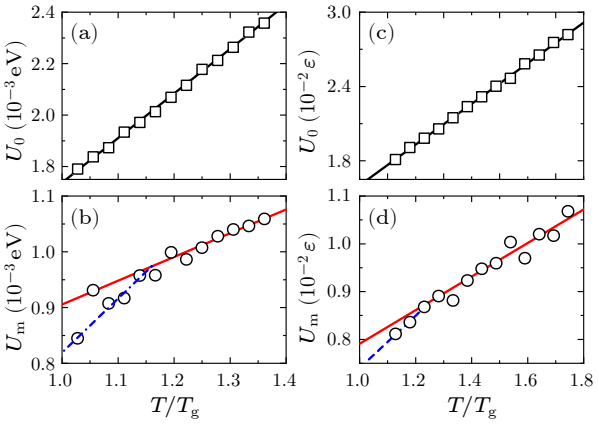

Fig. 4. The fitted U_0 and U_m as a function of scaled temperatures for $Cu_{50}Zr_{50}$ (a) and (b), and KA-BLJ (c) and (d). The lines are results of the linear fitting. U_0 is the background fluctuation intensity provided by fast processes and is proportional to temperature, while U_m is the average energy difference between meta-basins. When temperature approaches T_x (defined at the intersection of the red line and the blue line), U_m of $Cu_{50}Zr_{50}$ shows a significant turning and decreases faster (dashed blue line), which indicates the system moving in a flatter area on potential energy landscapes. For both $Cu_{50}Zr_{50}$ and KA-BLJ, T_x is around $1.2T_g$.

Since U_m is proportional to the average energy difference between MBs, as the temperature decreases, configurations with higher energies become inaccessible due to reduced kinetic energy. Consequently, we observe a decrease in U_m with decreasing temperature. Interestingly, as the temperature drops, U_m first decreases slowly until it reaches a turning point, after which it declines more rapidly [dashed line in Figs. 4(b) and 4(d)]. This transition occurs near $T_x \sim 1.2T_g$, which is close to T_c predicted in the mode-coupling theory.[44] This change suggests that below T_x, the accessible configuration space shrinks more quickly with the decease of temperatures. From the perspective of the PEL, this corresponds to a significant reduction in the system's likelihood of accessing MBs with large energy differences after T_x, resulting in the system being trapped in a relatively flatter region. These results are in agreement with previous studies that the typical energy difference between MBs decreases with temperature, and the relaxation is governed by the rare low-energy paths at lower temperature.[56]

The structural correlation function SISF is widely used to calculate the structural relaxation time in supercooled liquids. However, the direct connection between SISF and the topography of PELs is elusive. Our results demonstrate that MSED does provide richer information about the energy relaxation. Since MSED is computed from the evolution of energy and directly related to PEL, it is capable of giving a qualitative description about PEL. More importantly, MSED is able to distinguish energy fluctuations contributed by fast and slow dynamic processes, i.e., U_0^2 and U_m^2. This provides a new idea to establish connections between dynamic and thermodynamic properties in supercooled liquids.

Among various theoretical models for α-relaxations,[62–66] the Adam–Gibbs model stands out as the most influential one and plays a pivotal role in the study of α-relaxation.[67–69] The key point in the AG model lies in that τ_α is governed by the configurational entropy (labeled as S_{AG}). The present study may provide a connection between the PEL and S_{AG}. Considering the excess specific heat $C_{ex} = \frac{2\langle \Delta E^2 \rangle}{k_B T^2}$ (where the specific heat only reflects contributions from potential energies), we can obtain the excess entropy S_{ex} using $S_{ex} = \int \frac{C_{ex}}{T} dT$. According to Eq. (5), for sufficiently long time, the MSED can be expressed as the sum of two components: $\langle \Delta E^2(t) \rangle = U_0^2 + U_m^2$. Therefore, the excess specific heat and entropy can be written as: $C_{ex} = \frac{2U_0^2}{k_B T^2} + \frac{2U_m^2}{k_B T^2}$, and $S_{ex} = S_1 + S_2$, where

$$S_1 = \int \frac{2U_0^2}{k_B T^2} dT, \quad S_2 = \int \frac{2U_m^2}{k_B T^2} dT. \tag{6}$$

Since U_0^2 mainly reflects contributions from thermal vibrations and short-term relaxations, S_1 mainly corresponds to vibrational entropy and the configurational entropy induced by short-time and short-range atomic rearrangements. While U_m^2 primarily reflects energy fluctuations due to long-time α-relaxation, S_2 mainly corresponds to configurational entropy induced by long-time and long-range atomic rearrangements. Thus, S_2 could be the configurational entropy discussed in the Adam–Gibbs model, i.e., S_{AG}. It needs to be pointed out that, although MSD and MSED are somewhat comparable in their own right, the ideas of computing configurational entropy derived from the two methods are different.[70]

We have noticed an interesting feature in Fig. 1, namely that the first maximum value of $\langle \Delta E^2(t) \rangle$ (around $t = 0.05$ ps) is even larger than its equilibrium value at long time. As the final piece, we briefly discuss the reason why the peak at short times in $\langle \Delta E^2(t) \rangle$ is even higher than the long-time values. This is, in fact, a manifestation of the correlation of potential energies between atoms. As shown in Eq. (3), $\langle \Delta E^2(t) \rangle - N^{-1} \langle \delta \varepsilon^2(t) \rangle$ gives the overall correlation of potential energies between atoms, $2\langle \delta\varepsilon_i(t) \delta\varepsilon_j(t) \rangle$. To illustrate this issue, we plot $\langle \Delta E^2(t) \rangle$ and $N^{-1} \langle \delta \varepsilon^2(t) \rangle$ in Fig. 5(a), and their difference $[2\langle \delta\varepsilon_i(t) \delta\varepsilon_j(t) \rangle]$ in Fig. 5(b). One can see that, the peak at short times does not appear in $\langle \delta \varepsilon^2(t) \rangle$, which indicates the peak in $\langle \Delta E^2(t) \rangle$ does associate with the correlation of potential energies between different atoms. From Fig. 5(b), we find that, in the initial period, the positive correlation prevails and peaks around $t = 0.04$ ps. In this timescale, the motion of atoms shows a strong positive correlation. Thereafter, the negative correlation progressively gains dominance. One can see that the correlation decays as time further increases, indicating a growing degree of negative correlation. At sufficiently long time, the overall correlation between all atoms vanishes, thus the curve reaches a plateau. The coexistence of positive and negative correlations is actually the requirement of the fluctuation-dissipation theorem. If there is only one correlation mode, the energy will either change monotonically (only positive correlation) or dramatically reduce the magnitude of fluctuations (only negative correlation). The coexistence of positive and negative correlations makes the total energy remain in a balanced state.

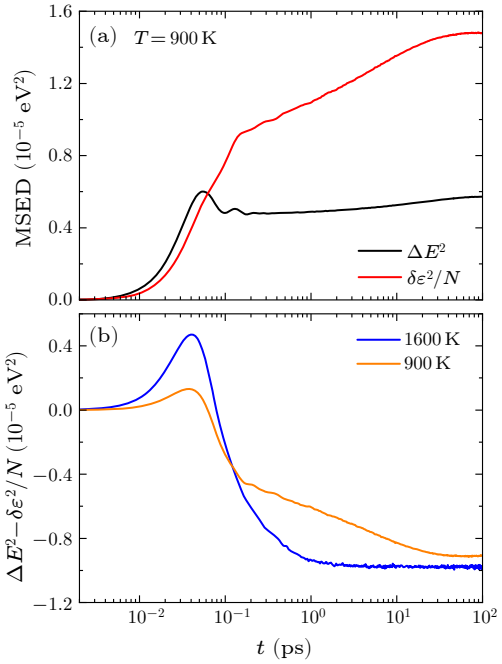

Fig. 5. (a) MSED of the total potential energy $[\langle \Delta E^2(t)\rangle]$ and MSED of induvial atom $[\langle \delta\varepsilon^2(t)\rangle]$ of $Cu_{50}Zr_{50}$ at $T = 900\,\mathrm{K}$. (b) Difference between $\langle \Delta E^2(t)\rangle$ and $N^{-1}\langle \delta\varepsilon^2(t)\rangle$, which gives the correlation of the potential energy between atoms, $2\langle \delta\varepsilon_i(t)\delta\varepsilon_j(t)\rangle$. In the initial period, the positive correlation prevails and peaks around $t = 0.04\,\mathrm{ps}$. Thereafter, the negative correlation progressively gains dominance.

At higher temperatures, e.g., 1600 K, the correlation between atoms is relatively weak, so $\langle \delta\varepsilon_i(t)\delta\varepsilon_j(t)\rangle$ decays very fast. While in the supercooled liquid regime, $\langle \delta\varepsilon_i(t)\delta\varepsilon_j(t)\rangle$ shows a two-step decay behavior, similar to the SISF curves.

4. Conclusion. This study introduces the mean-squared energy difference (MSED) as a novel tool for analyzing the relaxation processes in supercooled liquids. By extending the notion of diffusion to potential energy landscapes (PELs), MSED enables a clear and experimentally relevant depiction of how a system "walking" on PELs, and further gives a relaxation time (τ_α^*). τ_α^* shares similar values and tendency with structural relaxation time (τ_α). We demonstrate that MSED offers insights comparable to structural correlation functions but with a more direct connection to energy fluctuation. Finally, the present study successfully establishes a relationship between MSED and the PEL, and reveals a significant change from a rough PEL to a relatively flat PEL before the glass transition.

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