Hierarchical aging pathways and signatures of thermodynamic transition in molecular glasses

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ABSTRACT When a liquid is supercooled, its structural equilibration time τ_{eq} increases sharply approaching the glass transition temperature T_g , below which it is kinetically arrested in the out of equilibrium glassy state. Upon annealing below T_g , such glassy state relaxes toward the equilibrium state. There is growing evidence that such relaxation process is quite complex, influenced by the complexity of the potential energy landscape. Here we report the observation of a hierarchical aging pathway in the process of the glass-to-supercooled liquid transition in various molecular glass forming systems. Differential scanning calorimetry reveals that the glassy state upon annealing below T_g firstly enters a transient metastable supercooled liquid state with slightly higher enthalpies than that of the equilibrium supercooled liquid state when extrapolated to below T_g . This observation is also confirmed by structural measurements *via* Raman scattering. The dynamics of the transient metastable-to-stable supercooled liquid transition exhibits characteristics of thermodynamic transition at spinodal temperature T_{sp} slightly above T_g , leading to anomalous behaviors such as the appearance of a transition-like behavior in the plot of fragility measurements. These observations imply that the free energy landscape of the supercooled liquid develops complexity with qualitative changes approaching T_g and could have strong influence on the process of the glass transition.

Keywords: glass transition, hierarchical aging pathways, thermodynamic transition, metastability

INTRODUCTION

Glass formation by cooling liquids below the melting point with thwarted crystallization is ubiquitous in nature and plays a prominent role in science and technology [1]. Upon supercooling, the viscosity of the supercooled li-

quid increases continuously and sharply, typically exceeding 14 orders of magnitude down to the laboratory glass transition temperature T_g , below which the system kinetically falls out of thermal equilibrium and forms a glassy solid [1]. The nature of glass and the glass transition remains one of the challenging fundamental problems in physics [1–6]. Studying the glassy state (GS) relaxation toward the equilibrium below T_g , called aging, is an important approach for understanding the GS and the glass transition [7]. For instance, theories focusing on the properties of the equilibrium (excluding referencing to the crystalline state) supercooled liquid state (SLS) predict a hidden thermodynamic phase transition from the SLS to an ideal glassy state at T_K ($<T_g$) with an associated divergence of the structural relaxation time τ_α (diverging viscosity of SLS) [3,6,8]. However, recent experiments of glasses with long aging times and theoretical analysis, including the examination of a 20-million-year-old amber, raised questions on the existence of the predicted τ_α divergence [9–11].

Aging from the GS to the SLS is commonly assumed to exhibit simple relaxation process determined by a single activation energy. This is reflected by the theory on the dependence of T_g on the heating rate q^+ described by an activated process with a constant activation enthalpy H^* [12]. This theory predicts a linear relationship between $\ln(q^+)$ and $1/T_g$, $\ln(q^+) = -H^*/(RT_g) + \text{const.}$, where R is the gas constant [13,14]. From the slope of the linear relationship, H^* can be determined. Furthermore, it is shown that the fragility m of the SLS near T_g , an important parameter of the SLS dynamics [15], can be evaluated by $m = H^*/(RT_g \ln 10)$ [13]. Recently, there is growing evidence suggesting that such single stage activated relaxation scenario cannot capture the complexity

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of the aging process both from thermodynamic and dynamic point of view. It was found that the volume recovery process of polycarbonate undergoes qualitative change after long aging time (10^7 s) [16]. Complex aging behaviors such as two-stage relaxation were also found in metallic glass systems [17]. Hierarchical aging pathways and fragile-to-strong transition were observed in Au-based metallic glass systems [18]. These complex aging behaviors point at the important role of the complexity of the potential energy landscape (PEL) where various dominant local minima control the various stages of the aging process [19].

Despite the influence of PEL, another important effect on the aging behaviors originates from the free energy landscape (FEL) which is the landscape of the thermodynamic function reflecting the combined role of enthalpy and entropy. Recent study shows that the FEL is much rougher than that is previously assumed and associates the glass dynamics with fractal change of free energy [8,20]. Further studies are needed to explore the effect of FEL on aging. In this work, we report the observation of a complex aging process in various molecular glasses. Systematic calorimetry and Raman spectroscopy investigations reveal that the GS, after annealing below (but near) T_g , firstly enters into a transient metastable supercooled liquid state (TMSLS). Here, metastable is with respect to the conventional SLS. Temperature dependences of enthalpy and structural changes and the temperature dependence of the transition rate from TMSLS to SLS all indicate the existence of a spinodal temperature T_{sp} which is only slightly above T_g . These results demonstrate that upon cooling the FEL of the SLS develops complexity with qualitative changes approaching T_g . Such complexity of the FEL could play an important role in the process of the laboratory glass transition.

EXPERIMENTAL SECTION

Six molecular systems, *o*-terphenyl (OTP, Aladdin 99.0%), 5-hydroxytryptamine (serotonin, Aladdin 98.0%), glycerol (Aladdin 99.5%), ketoprofen (Aladdin 98.0%), indomethacin (Aladdin 98.0%), and (S)-(+)-ibuprofen (SIBP, Aladdin 98.5%) were measured without further purification.

The differential scanning calorimetry (DSC) experiments were carried out in a DSC Q2000 from TA instruments with a liquid nitrogen cooling systems LNCS90. The temperature of DSC system was calibrated by indium with the purity of 99.99%. 10 mg sample was enclosed in a hermetic aluminum pan under dry nitrogen

(at flow rate of 50.00 mL min⁻¹) to improve the thermal conductivity. The change of thermal lag after calibration was smaller than 0.1 K with the heating rate below 20.0 K min⁻¹.

The fragility measurements of different glass formers were performed by the DSC. The initial GS of each sample was acquired by cooling the sample from 10 K above its melting temperature to 30 K below T_K at a constant cooling rate $\dot{q}^- = 15.0$ K min⁻¹. Then the initial GS was reheated directly to above its melting temperature at a constant heating rate $\dot{q}^+$ and the T_g^{onset} was obtained from the heating curve of $C_{p,\text{norm}}(T)$ as shown in Fig. 1.

The normalized isobaric heat capacity $C_{p,\text{norm}}(T)$ curves can be obtained from the isobaric heat capacity $C_p(T)$ curves by the following equation:

$$C_{p,\text{norm}}(T) = \frac{C_p(T) - C_{p,\text{GS}}(T)}{C_{p,\text{SLS}}(T) - C_{p,\text{GS}}(T)}, \quad (1)$$

where $C_{p,\text{GS}}$ is the heat capacity of the glassy state and $C_{p,\text{SLS}}$ is the heat capacity of the supercooled liquid [21].

The numerical calculations of $C_{p,\text{norm}}(T)$ is based on the Tool-Narayanaswamy-Moynihan (TNM) model. The TNM model is a phenomenological model which can describe the $C_{p,\text{norm}}(T)$ based on the numerical calculation of relaxation time and fictive temperature T_f on condition that the nonequilibrium behavior of the GS is governed by an activated kinetic process [22–24]. According to the TNM model, the continuous cooling and heating procedure can be considered as a series of small temperature steps and isothermal periods [12,24], during which the relaxation time τ is mainly determined by the activation energy and fictive temperature T_f . After n temperature steps, the fictive temperature $T_{f,n}$ and the structural relaxation time τ_n can be calculated by the following equation:

$$\tau_n = \exp \left[\ln(A) + \frac{x\Delta h}{RT_n} + \frac{(1-x)\Delta h}{RT_{f,n}} \right], \quad (2)$$

$$T_{f,n} = T_0 + \sum_{i=1}^n \Delta T_i \left[1 - \exp \left[- \left(\sum_{j=1}^n \frac{\Delta T_j}{q\tau_j} \right)^{\beta_{\text{KWW}}} \right] \right], \quad (3)$$

where A is a constant, x are fitting parameters relating to the nonlinearity of structural relaxation process, Δh is related to the activation energy which is assumed to be unchanged with certain substance, R is the ideal gas constant, T_n is the temperature after n temperature steps, T_0 is the starting temperature well above T_g before cooling, and q is the cooling or heating rate. The normalized heat capacity can be calculated by the differential of fic-

Figure 1 The identification of the characteristic temperatures T_g^{onset} , T_p and T_g^{end} . T_g^{onset} is the onset temperature of glass transition and acquired by the intersection point of the baseline before the glass transition and the tangent line at the inflection point with the maximum slope of the $C_{p,\text{norm}}(T)$ curve. T_p is at the maximum of the $C_{p,\text{norm}}(T)$ curve. T_g^{end} is the intersection point of the baseline and the tangent line at the inflection point after the glass transition.

tive temperature:

$$C_{p,\text{norm}} = \frac{dT_f}{dT} = \frac{T_{f,n} - T_{f,n-1}}{T_n - T_{n-1}}. \quad (4)$$

The influences of q^- and q^+ on the peak height of overshoot of $C_{p,\text{norm}}(T)$ are discussed with all the other parameters fixed.

Raman spectra were recorded in the 1,550–1,700 cm^{-1} range by a Horiba JobinYvon LabRAM HR800 Raman spectrometer using the 532 nm line of a mixed Nd:YAG laser equipped with 1,800 grooves/mm gratings. The spectrometer was equipped with a coupled device detector with liquid nitrogen cooled dewar. Temperature of the sample was controlled by a Linkam T95-PE temperature controller which kept temperature fluctuations within 0.10 K. Raman shift was calibrated by monocrystalline silicon before experiment.

RESULTS AND DISCUSSION

Fragility measurement

The kinetic behavior of the glass transition was investigated using DSC. Here, the standard fragility measurements of OTP, one of the most widely studied glass formers, indeed seemingly follows the anticipated linear behavior of $\ln(q^+)$ vs. $1000/T_g^{\text{onset}}$ (Fig. 2a inset). The measured fragility $m = 72$ is identical to the previously reported value [25]. However, to our great surprise, when

we substantially increased the density of the observation points in q^+ , a transition-like behavior emerges in the $\ln(q^+)$ vs. $1000/T_g^{\text{onset}}$ plot of OTP (Fig. 2a). As shown in Fig. 2b–f, similar transition-like behavior is also observed in other molecular glass formers including serotonin, glycerol, (S)–(+)-ibuprofen, ketoprofen, and indomethacin. These results show that high density data points are needed to reveal whether such transition-like behavior are also present in other small molecule systems [26].

Heat capacity measurement

To study the nature of this transition-like behavior, SIBP is selected for further systematic investigations for the following reasons. Its melting point of 324.2 K is low and presents no thermal stability issue for organic molecules. The SLS of SIBP is extraordinarily stable against crystallization, persisting at least for days over the entire supercooled liquid region (Fig. S1), opening the window for a systematic investigation of the transition-like behavior. In the stable crystalline phase of SIBP, all molecules are in the form of cyclic dimers *via* intermolecular hydrogen bonding (Fig. S2) [27]. The liquid phase consists of monomers and multimers *via* intermolecular hydrogen bonding, including dimers, trimers and tetramers where the cyclic dimer is the most energetically favorable structure with the strongest intermolecular hydrogen bonding [28]. Here, the change of the strength and the population of hydrogen bondings provide a sensitive measure for detecting the change of the liquid structure.

The calorimetry signature of the glass transition upon heating is the sharp increase of the normalized isobaric specific heat $C_{p,\text{norm}}(T)$ and emergence of an overshoot around T_g under the employed heating rate. This overshoot is due to a rapid recovery of the lost enthalpy through the relaxation process [12]. The upper panel of Fig. 3a shows a set of representative $C_{p,\text{norm}}(T)$ curves for q^+ ranging from 1.0 to 15.0 K min^{-1} . The initial GS is prepared by cooling the liquid from 333.2 K down to 193.2 K under the constant cooling rate $q^- = 15.0 \text{ K min}^{-1}$. It is very interesting to note that the peak height at T_p of the $C_{p,\text{norm}}(T)$ overshoot firstly decreases with increasing q^+ in the low- q^+ range, reaching a minimum at $T = 230.6 \text{ K}$ under $q^+ = 3.0 \text{ K min}^{-1}$. In contrast, the peak height at T_p of the $C_{p,\text{norm}}(T)$ overshoot increases with increasing q^+ in the high- q^+ range above $q^+ = 3.0 \text{ K min}^{-1}$. The passage time $\tau_{\text{avg}} \equiv (T_g^{\text{end}} - T_g^{\text{onset}}) / q^+$ from the GS to the SLS reflects clearly this abrupt change [15]. The lower panel of Fig. 3a plots τ_{avg} vs. $1000/T_p$ by varying q^+ from 1.0 to 20.0 K min^{-1} and the abrupt

Figure 2 Calorimetry measurements of glass transition in molecular liquids. (a) Plot of $\ln(q^+)$ vs. $1000/T_g^{\text{onset}}$ acquired by sixteen observation points for OTP. Plot of $\ln(q^+)$ vs. $1000/T_g^{\text{onset}}$ acquired by five observation points are shown in the inset with the sixteen observation points shown as faded background. Plots of $\ln(q^+)$ vs. $1000/T_g^{\text{onset}}$ acquired by sixteen observation points for serotonin (b), glycerol (c), (S)-(+)-ibuprofen (d), ketoprofen (e), and indomethacin (f).

change of τ_{avg} occurs at $T_p = 230.6$ K. These experiments are also repeated with different initial GS, including using $q^- = 0.5$ K min $^{-1}$ instead of $q^- = 15.0$ K min $^{-1}$ used in the above experiments (Fig. 3b). As the overshoot of C_p curve is closely related to the kinetics of the relaxation process, the abnormal changes of the peak height of the overshoot are directly related to the abnormal behavior of τ_{avg} versus T , where a rapid decrease of τ_{avg} , far exceeding that of an activated behavior, is observed as T increases approaching $T_p = 230.6$ K.

Also evaluated is the case of $q^- = q^+$ where each $C_{p,\text{norm}}(T)$ curve is obtained with the heating rate q^+ equal to the cooling rate q^- under which the initial GS is prepared (Fig. 3c) [12]. In all these cases, there is always an overshoot minimum occurring at the same temperature of $T = 230.6 \pm 0.3$ K and an abrupt change of τ_{avg} versus $1000/T_p$ at the same T_p . These results indicate that the equilibration time τ_{eq} decreases abruptly at $T = 230.6 \pm 0.3$ K, denoted as T_{sp} , which is independent of the employed cooling/heating rates. The above mentioned $C_{p,\text{norm}}(T)$ are very different from what are expected by the conventional activated kinetic process [29]. In such theory, the conventional $C_{p,\text{norm}}(T)$ behavior can be cal-

culated numerically based on the TNM model, which describes the nonequilibrium behavior of the GS governed by a single stage activated kinetic process [13,22,23,30]. Fig. 3d-f show the corresponding calculated $C_{p,\text{norm}}(T)$ curves and the τ_{avg} versus $1000/T_p$ under various conditions. Here, the overshoot minimum and the abrupt change of τ_{avg} are completely absent. Moreover, it is of note that the overshoot minimum and the abrupt change of τ_{avg} should be absent even considering dynamic heterogeneity [31]. These results are characteristic behaviors of a purely kinetic process with no abrupt change of activation energies over the involved temperature range. Clearly, the relaxation process cannot be described by the simple process with constant activation enthalpy.

Enthalpy measurement

Since the observed abnormal dynamic behaviors cannot be explained qualitatively by a purely kinetic process, possible thermodynamic origin was investigated. Here, the GS prepared under $q^- = 15.0$ K min $^{-1}$ down to 193.2 K was heated with $q^+ = 15.0$ K min $^{-1}$ from 193.2 K to a chosen T and held there isothermally for a time period of

Figure 3 Calorimetry measurements of SIBP glass transition and numerical calculations. (a) The set of $C_{p, \text{norm}}(T)$ curves with q^+ from 1.0 to 15.0 K min^{-1} with the initial GSs prepared under cooling rate $q^- = 15.0 \text{ K min}^{-1}$ (upper panel). The corresponding τ_{avg} versus $1000/T_p$ (lower panel). (b) The set of $C_{p, \text{norm}}(T)$ curves with q^+ from 1.0 to 15.0 K min^{-1} with the initial GS prepared under the cooling rate $q^- = 0.5 \text{ K min}^{-1}$ (upper panel). The corresponding τ_{avg} versus $1000/T_p$ (lower panel). (c) The set of $C_{p, \text{norm}}(T)$ curves with q^+ from 1.0 to 15.0 K min^{-1} with the initial GSs prepared under cooling rate $q^- = q^+$ (upper panel). The corresponding τ_{avg} versus $1000/T_p$ (lower panel). Also shown are the corresponding results from numerical calculations with the initial GSs prepared under cooling rate $q^- = 15.0 \text{ K min}^{-1}$ (d), $q^- = 0.5 \text{ K min}^{-1}$ (e), and $q^- = q^+$ (f).

t_{isotherm} (Fig. S3); the enthalpy $H_{\text{isotherm}}(T)$ was obtained by integrating the heat flow over the entire heating and isothermal time period (Fig. S3). This experiment is possible because of the extraordinary stability of SIBP against crystallization.

Fig. 4a shows the measured $H_{\text{isotherm}}(T)$ with $t_{\text{isotherm}} = 3,600 \text{ s}$. Above 230.2 K, $H_{\text{isotherm}}(T)$ shows a linear temperature dependence as expected from a SLS [32]. Interestingly, from 223.2 to 227.2 K, $H_{\text{isotherm}}(T)$ also shows a linear temperature dependence with a comparable slope as $H_{\text{isotherm}}(T)$ above 230.2 K but slightly shifted upward.

Further, the features of $H_{\text{isotherm}}(T)$ above 223.2 K change very little with t_{isotherm} varying from 1,200 to 3,600 s (Fig. 4b). This is very different from the typical GS where $H_{\text{isotherm}}(T)$ changes continuously with increasing t_{isotherm} . Above results suggest that the system firstly enters a transient metastable state in the temperature range from 223.2 to 227.2 K. Here, the metastability is referred to the SLS which is itself metastable with respect to the crystalline state. The linearity of the enthalpy versus temperature curve, $H_{\text{isotherm}}(T)$, the independence of this curve on t_{isotherm} from 1,200 to 3,600 s, and the similar

Figure 4 Enthalpy measurements of SIBP glass transition. (a) Enthalpy at T after held isothermally for 3,600 s represented by $H_{\text{isotherm}}(T)$. (b) $H_{\text{isotherm}}(T)$ acquired with t_{isotherm} varying from 1,200 to 3,600 s.

Figure 5 Raman measurements of SIBP glass transition. (a) A typical Raman spectrum acquired at 223.2 K. (b) The temperature dependence of the Raman shift of the band around 1,649.00 cm^{-1} .

slope of this curve to that of the supercooled liquid state indicate that the system enters a transient metastable state with established thermal equilibrium in the transient metastable state. Thus, the system enters a well-defined liquid (TMSLS) state after 1,200 s annealing and remains there at least for 3,600 s in the temperature region from 223.2 to 227.2 K [33]. It is of note that the TMSLS merges to the SLS at 230.2 ± 0.5 K, identical to $T_{\text{sp}} = 230.6 \pm 0.3$ K within experimental uncertainties. Such dynamic and thermodynamic signatures are characteristics of a spinodal transition at $T_{\text{sp}} = 230.6$ K where the free energy barrier separating TMSLS and SLS disappears [34].

Raman measurement

The possible structural origin of the TMSLS to SLS transition was investigated by Raman spectroscopy. Here, the SIBP liquid was firstly cooled from 333.2 to 153.2 K at a rate of 15.0 K min^{-1} , then heated step by step to 235.2 K with an interval of 5.0 K in the temperature range of 213.2 to 223.2 K and an interval of 1.0 K above 223.2 K. At each

step after equilibrating the system for 10 min, ten Raman spectra were taken isothermally with exposure time of 10 s and accumulation number was 6. The experiments were repeated three times to eliminate the statistical error. A typical Raman spectrum acquired at 223.2 K is shown in Fig. 5a. There are three characteristic bands at 1,576.31, 1,613.15, and 1,648.95 cm^{-1} . Here, the broad band around 1,649.00 cm^{-1} corresponds to the vibration mode involving the carboxylic C=O group [35,36], and an upshift of this Raman band reflects the weakening of the hydrogen bonding [37]. The temperature dependence of this Raman shift is shown in Fig. 5b, exhibiting a similar behavior as that of $H_{\text{isotherm}}(T)$ with the two straight lines merging at 230.2 ± 0.5 K.

The Raman results reveal that the hydrogen bonding is weaker in the TMSLS than that in the SLS. This is fully consistent with results of the previous study showing the increase of hydrogen bonding population upon cooling in the supercooled liquid [28]. TMSLS corresponds to the state with higher monomer population and insufficient

Figure 6 Illustration of the free energy landscape. Upon heating, the GS firstly enters the TMSLS at an intermediate free energy minimum. The transition from TMSLS to SLS speeds up dramatically at $T_{sp} \sim T_g$ above which the free energy local minimum disappears.

conversion from multimers to cyclic dimers compared with the equilibrium SLS.

Discussion

What could be the mechanism and the structural basis underlying the emergence of metastable states? In structural glasses where disorders are self-induced, geometrical factors could lead to frustrations [38,39]. Metastable states could arise from such geometrical frustration mechanism depending on the degree of frustration [40]. One of the frustration mechanisms is proposed by Tanaka [41]. Here, the growth of local crystalline bond orientational ordering (CBOO) provides the incompatibility with liquid structure and frustration, leading to energetic and/or entropic frustration and sharp slowdown in dynamics [41]. This scenario can be envisioned in the SLS of SIBP.

Upon cooling, the growth of CBOO can be identified with the increase of the number of cyclic dimers which are the only building blocks for periodic space filling of SIBP (Fig. S2). Although cyclic dimers are by far the most energetically favorable local configurations, linear dimers are also present with significant population [28], perhaps driven by entropy and interactions such as CH/ π bonds [42]. Upon cooling, the energetically driven growth of the number of cyclic dimers n_{cycdim} has to compete with linear dimers and other configurations which are incompatible with periodic space filling. This could then lead to frustration and the formation of TMSLS in the FEL, $G(T, n_{\text{cycdim}})$, where the number of cyclic dimers $n_{\text{cycdim}}(\text{TMSLS})$ is lower than what it should be in the SLS,

$n_{\text{cycdim}}(\text{SLS})$, at the given temperature. Such scenario is fully consistent with the Raman results where an increase of hydrogen bond strength is observed in the TMSLS to SLS transition. As the cooling process eventually becomes non-quasistatic, SIBP with increasing n_{cycdim} firstly enters the TMSLS below T_{sp} , and the emergence of TMSLS causes a significant increase of the equilibration time τ_{eq} for establishing the SLS. The emergence and the growth of free energy barriers below T_{sp} could contribute significantly to the glass transition.

The hierarchical relaxation process reveals the complexity of the FEL below T_{sp} . Upon heating, as illustrated in Fig. 6, the annealed GS firstly enters the TMSLS with closer resemblance in structural order such as n_{cycdim} . Longer time annealing would eventually lead to structural relaxation to the SLS. The last stage of relaxation becomes much faster when the temperature reaches the spinodal point T_{sp} .

CONCLUSIONS

This work reports the observation of a two-stage hierarchical aging process in molecular glasses. It reveals that the glassy state, after annealing below T_g , firstly enters into a TMSLS. The TMSLS then undergoes a transition to the SLS above T_g . Moreover, it is shown that there is a spinodal temperature T_{sp} associated with the TMSLS-to-SLS transition. Here, $T_{sp} > T_g$ but is found to be close to T_g . The transition time τ from TMSLS to SLS decreases steeply at the spinodal temperature. This steep decrease of τ is evidenced by several anomalous behaviors. In dynamic properties, an anomalous transition-like behavior is observed in the plot of the fragility measurement, unlike the expected linear behavior of simple aging process; the overshoot in the specific heat C_p vs. T associated with the glass transition exhibits a minimum at a given heating rate corresponding to T_{sp} , unlike the behavior of monotonic increase (or unchanged) as expected from single stage aging process. This is further supported by measurements of enthalpy vs. T after aging as well as structural changes vs. T after aging, both showing a transition at T_{sp} . These results show that the FEL of the supercooled liquid could develop important complexity with qualitative changes below the spinodal temperature T_{sp} . Such complexity in FEL below T_{sp} could facilitate the onset of the laboratory glass transition.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information See supplementary material for specific details about the crystalline structure of SIBP, the stability of supercooled liquid, and the method of enthalpy measurement. All the supporting data are available in the online version of the paper.

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小分子玻璃中的分层老化路径和热力学转变迹象

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摘要 当液体被过冷, 液体的结构平衡时间 τ_{eq} 在接近玻璃化转变温度 T_g 附近时迅速增加, 使得液体在温度降到 T_g 以下时从动力学角度看束缚在非平衡的玻璃态中. 当在 T_g 以下退火时, 这个玻璃态逐渐弛豫到平衡态. 越来越多的证据表明这个弛豫的过程非常复杂, 而且受到势能景图的影响. 本文通过研究不同的小分子玻璃形成系统发现从玻璃转变到过冷液体的过程中出现了一个分层的老化路径. 通过差示扫描量热仪实验发现在 T_g 以下退火时, 玻璃态先进入到一个暂时的亚稳态过冷液体. 在 T_g 以下, 这个液体的焓值稍微比平衡态过冷液体高. 通过拉曼散射测量结构的实验同样证实了这个发现. 这个暂时的亚稳态到稳态过冷液体的转变动力学在温度 T_{sp} 处表现出了热力学转变的特征, 并且导致了一系列反常现象比如在脆性指数图上出现的类相变行为. 这些发现暗示了过冷液体的自由能景图在接近 T_g 的时候变得复杂而且具有质的变化, 同时对玻璃化转变过程有很明显的影响.