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# A new threshold of uncovering the nature of glass transition: The slow $\beta$ relaxation in glassy states

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Received May 17, 2009; accepted August 8, 2009

The glass transition involves more than one dynamic relaxation mechanisms in supercooled liquids, such as  $\alpha$  relaxation, slow  $\beta$  relaxation and fast  $\beta$  relaxation and so on. For the traditional theoretical system,  $\alpha$  relaxation is believed mainly responsible for the nature of the glass transition as the beginning of the phenomenon. This idea, however, has been open to a big challenge since recent studies have indicated that slow  $\beta$  relaxation closely relates to  $\alpha$  relaxation. Slow  $\beta$  relaxation determines the characteristics of  $\alpha$  relaxation and is the precursor and the more microscopic base of glass transition behavior. In order to illuminate the significance of slow  $\beta$  relaxation in the fields of the glass transition and the structure of supercooled liquids, the accomplished progress is summarized from different aspects such as on the correlation between  $\alpha$  relaxation and slow  $\beta$  relaxation, on the manner of  $\alpha$ -slow  $\beta$  relaxation merging, on the energy landscape, on the excess wing and on the thermodynamically phenomenological models. The tendency of investigation in slow  $\beta$  relaxation is also evaluated.

**glass transition,  $\beta$  relaxation, liquid fragility, energy landscape, excess wing, boson peak**

**Citation:** Hu L N, Zhang C Z, Yue Y Z, et al. A new threshold of uncovering the nature of glass transition: The slow  $\beta$  relaxation in glassy states. Chinese Sci Bull, 2010, 55: 457–472, doi: 10.1007/s11434-009-0711-4

The nature of glass transition is one of the most focal and difficult points in the field of condensed matter physics, because the glass transition of complicated dynamic heterogeneity involves a dramatic slowing down of the structural relaxation, which ultimately brings the supercooled liquid into the glassy state. Correspondingly, the relaxation dynamics of supercooled liquids evolves with time from atomic vibrations, motion of cages, the  $\beta$  (secondary) relaxation, to finally the onset of fully cooperative  $\alpha$  (primary) relaxation process [1]. In different methods of measurements, the relaxations with different mechanisms generally have different performance. Figure 1 gives the schematic view of the frequency-dependent dielectric loss in non-conducting glass-forming materials at constant temperatures. It is seen that the  $\alpha$  relaxation peak at the lowest region of frequency is followed by another peak at a relatively high

frequency range, which is attributed to the  $\beta$  relaxation.

According to the classic theory of glass transition, the cooperative  $\alpha$  relaxation which occurs in the long or medium range is believed mainly responsible for the glass transition phenomenon, whereas the  $\beta$  relaxations that occur at shorter times or higher frequencies play no important role; the  $\alpha$  relaxation is the base of the glass transition. Based on this idea, a lot of theories (mainly from aspects of free volume [2] and the configurational entropy [3]) have been proposed, resulting in a general classical physicochemical picture of dynamic structural relaxation and thermodynamic glass transition. This idea, however, has been open to a big challenge since  $\beta$  relaxations, especially Johari-Goldstein type in rigid molecules, were introduced in 1970 [4]. More and more interest arouses further thinking about the roles of  $\beta$  relaxations, especially the type of slow  $\beta$  relaxations (the so-called Johari-Goldstein (JG) relaxation) [5,6]. It has been found that the JG relaxation determines the features of the

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following  $\alpha$  relaxation; the JG relaxation, as the precursor of the  $\alpha$  relaxation, in fact enters the material-specific characters of glass transition prior to the  $\alpha$  relaxation [7,8]. Therefore, in recent years the importance of the type of JG relaxation has been widely acknowledged, resulting in a new threshold of investigating glass transition.

## 1 Slow $\beta$ relaxation (JG relaxation)

Since the 1960s,  $\beta$  relaxations have been found in the group of polymers by dielectric [4], mechanical [9], NMR spectroscopy and sometimes photon correlation spectroscopy [10,11]. Some of these  $\beta$  relaxations, however, have no general dynamic properties and are attributed to different motions confined to only a part of the molecule, such as the side groups motion, the internal vibrations inside the molecule, the short chain portions, or even impurities [12]. These  $\beta$  motions are only intramolecular and play no important roles in glass transition, where the movement of cooperative rearrangement regions is demanded. By naming them fast  $\beta$  relaxations, they are attributed to a complex collective anharmonic cage rattling process [13].

Later, another type of secondary relaxation attracts people's attention, which is assigned to some motions of the entire molecules. The milestone work was reported by Johari and Goldstein [4,5,14], where the dielectric permittivity and dielectric loss curves were detected in a series of glasses of rigid molecules. They found that the dielectric behavior of these glasses showed a remarkable similarity to that of amorphous polymers, i.e. besides the  $\alpha$  relaxation peak, a distinct peak due to  $\beta$  relaxation can be observed at a relatively high frequency region (see Figure 1). Since there is no free space between molecules, i.e. lacking internal modes of motion in these rigid glasses, their results confirm the intermolecular, rather than intramolecular, origin of this kind of  $\beta$  relaxations. Their findings aroused the interests of the researchers in rethinking the features of slow  $\beta$  relaxations, in investigating its possible connection to the  $\alpha$  relaxation and its role in glass transition. In honor of Johari and Goldstein, these slow  $\beta$  relaxations are usually called

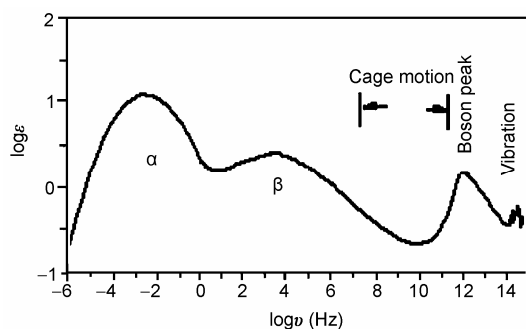
Johari-Goldstein (JG) relaxation. Indeed, the JG relaxation, which is attributed to the motions of whole structural unities in a certain range, is the closest behavior to the  $\alpha$  relaxation and in some cases its temperature location where it occurs is specified [15]. JG relaxations have been found in materials including not only polymers [16], but also ionic melts [17], small molecular organic materials [5,6].

Although the name of the JG relaxation is given arbitrarily, the most interesting thing is that, when studying this intrinsic relaxation in different materials, several common features show up [7,8,18,19]. Firstly, the JG relaxation has shown the feature of the precursor or a local step of the cooperative  $\alpha$  relaxation and it entails the motion of all parts of the molecule [7,20]. This dynamic property is well described by the correspondence between the average relaxation time of the secondary relaxation,  $\tau_\beta$ , and the primitive relaxation time,  $\tau_0$ , in the  $\alpha$  relaxation behavior described by VFT equation ( $\tau_\alpha = \tau_0 \exp[E_\alpha / R(T - T_g)]$ ) [21,22]. The investigated materials include ethyl benzene, 17.2% chlorobenzene in decalin, and 44% chlorobenzene. This feature indicates the close correlation underlying between the  $\alpha$  and the JG relaxations. The development of the JG relaxation finally determines the initial characteristics of the  $\alpha$  relaxation. Since the correspondence between  $\tau_\beta$  and  $\tau_0$  cannot be observed in fast  $\beta$  relaxations, it is generally used as a criterion to distinguish the genuine JG relaxation. Another well-known feature concerns a general relationship between the glass transition temperature  $T_g$  and the average activation energy of the JG relaxation  $E_\beta$ . The JG relaxation has Arrhenius temperature dependence in the glassy states,

$$\tau_\beta = \tau_\infty \exp[E_\beta / RT](T \leq T_g), \quad (1)$$

where  $\tau_\infty$  corresponds to the time per trial of surmounting the energy barrier  $E_\beta$  and equals to  $1/(2\pi f)$ , where  $f$  is the frequency of molecular vibration relevant to the relaxation process. The available value of  $\tau_\infty$  has been found in the range of  $10^{-16}$ – $10^{-13}$  s. By investigating more than 20 different glassy materials such as dimethyl phthalate, 1-propanol, and  $\text{CF}_4=\text{CClF}_3$ , Kudlik et al. found that the values of  $E_\beta$  centered on  $24RT_g$  [23,24]. This amazing finding implies that the temperature dependence of  $\log \tau_\beta$  is universal on the scale  $T/T_g$ . Although the empirical relationship of  $24RT_g$  is only approximate and there are deviations, it promises the physical fundamentals underlying this JG relaxation and suggests that the JG relaxation determines the key quantity of  $T_g$  in glass transition phenomenon. Notice that although eq. (1) is the same suitable for the fast  $\beta$  relaxation, the relationship between  $E_\beta$  and  $T_g$  cannot be observed there.

Although the two features of the JG relaxation discussed above have been widely recognized, other features owned by the JG relaxation are still under controversy. For example, Richert [25] and Hansen [26] both found that for the JG relaxation, the  $\tau_\beta$  value was around  $10^{-6}$  s at the merging



**Figure 1** Schematic view of the frequency-dependent dielectric loss in non-conducting glass-forming materials.

temperature  $T_\beta$  where the  $\alpha$  and the JG relaxations merged. In some fast  $\beta$  relaxations, however, similar phenomenon has also been found (such as dimethyl phthalate) [27].

## 2 The progress in slow $\beta$ relaxations

Since both the slow  $\beta$  (JG) relaxation and the  $\alpha$  relaxation involve motions of the entire molecule in origin, it is reasonable for the initial researchers to expect some relationships between them. Up to now, however, accompanied with the achievements in this field and further insight into the JG relaxation, studies have indicated that the role of the slow  $\beta$  relaxation in glass transition is much more than expected. At present, the investigations on the JG relaxation have made great progress not only in the relationship between the JG relaxation and the  $\alpha$  relaxation, but also in the merging of them, the manifestation of the energy landscape, the nature of the excess wing and the Boson peak, as well as the establishment of the thermodynamic model. All the studies on these hot spots attempt to probe into the nature of the JG relaxation, and play important roles in solving other problems (such as the relationship between the thermodynamics and dynamics) in the field of condensed matter physics.

### 2.1 Correlations between the JG and the $\alpha$ relaxations

Although the JG relaxation as the nature of glasses and supercooled liquids was realized about three decades ago, the breakthrough concerning how the  $\alpha$  and the JG relaxations correlate was made only in the last ten years [18,19]. Based on the available experimental results of more than 50 different glasses, a strong correlation between  $\log\tau_\beta(T_g)$  and the Kohlrausch exponent  $(1-n)$ , as well as fragility parameter  $m$ , has been discovered: a large value of  $\log\tau_\beta(T_g)$  always corresponds to a small  $m$  or a large  $(1-n)$ . Here the liquid fragility  $m$  describes the tendency of the changes of  $\tau_\alpha$  (or the viscosity  $\eta_\alpha$ ) with temperature towards  $T_g$  in the supercooled region [28]. To describe the  $\alpha$  relaxation at constant temperature, Kohlrausch-William-Watts (KWW) function ( $\phi(t) = \exp[-(t/\tau_\alpha)^{1-n}]$ ) is generally used. We can see that both  $(1-n)$  and the liquid fragility  $m$  are important parameters involved in the  $\alpha$  relaxation of glass transition. The correlation between  $\log\tau_\beta(T_g)$  and the Kohlrausch exponent  $(1-n)$  indicates a close relation between the  $\alpha$  and the JG relaxations. The importance of this finding is the indication that the location of  $\tau_\beta$  in the relaxation map can be roughly fixed by the properties of the  $\alpha$  relaxation, since  $\tau_\infty$  in eq. (1) points to a vibrational frequency and the value of it usually concentrates in a narrow region. That is to say, the JG relaxation determines some dynamic features of the  $\alpha$  relaxation. Later, some researchers (such as Murthy [29], Peraz [30], Arbe [31] and Hansen [32]) further proposed that the

JG relaxation was intrinsically the basis of the  $\alpha$  relaxation.

The discussion above promoted the development of the theoretical models in this field. Among them, the most successful one is the coupling model (CM) developed by Ngai [21,33]. Notice that this theory is quite different from the model coupling theory (MCT) [34]. The latter has the prominence of considering the temperature dependence of the dynamic mechanism and introducing a new crossover temperature  $T_c$ . In contrast, the central idea of the CM is the existence of a temperature insensitive crossover time,  $t_c$ , which has been suggested by simple Hamiltonian models [20,35].  $t_c$  is around 2 ps for small molecular and polymeric glass formers [36,37]. According to the CM, the slow  $\beta$  and the  $\alpha$  relaxations correspond to the following stages with increasing time respectively:

$$\phi(t) = \exp[-(t/\tau_0)], \quad t \leq t_c; \quad (2)$$

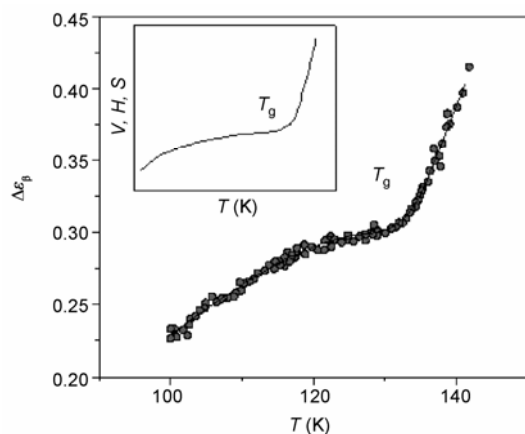
$$\phi(t) = \exp[-(t/\tau_\alpha)^{1-n}], \quad t \geq t_c. \quad (3)$$

Since the basic molecular units involved in the JG relaxation relax themselves independently corresponding to the nature of the local motion, the exponential description of eq. (2) is reasonable. Continuity of  $\phi(t)$  at  $t_c$  leads to the relation:

$$\tau_\alpha = [t_c^n \tau_0]^{1/(1-n)}. \quad (4)$$

This model gives perfect explanations for the feature owned by the JG relaxation, i.e.  $\tau_0(T,P) \approx \tau_\beta(T,P)$  [18]. The correspondence between  $\tau_0$  and  $\tau_\beta$  has been found in many glass formers, which exhibits genuine JG relaxations, indicating that the JG relaxation bears a strong resemblance to the primitive  $\alpha$  relaxation [33]. In plastic crystals particularly which are rigid molecules due to the indistinction of the volume changes, the relationship  $\tau_0(T,P) \approx \tau_\beta(T,P)$  also exists [38]. The resemblance can also be concluded by the correspondence between  $\tau_\beta(T)$  and  $\tau_0(T)$  with variable pressures. D-sorbitol [39] and 17.2% chlorobenzene in decalin [40] both show that  $\tau_{JG}(T)$ , as well as  $\tau_\alpha(T)$ , is pressure dependent, whereas the fast  $\beta$  relaxation is not the case, such as for diethyl phthalate (DEP) [41]. Besides, as shown in Figure 2, it has been found that the relative strength of the JG relaxation peak in dielectric curves,  $\Delta\epsilon_\beta$ , has similar temperature dependence with the entropy, enthalpy and volume of the system [8]. In Figure 2, the temperature dependences of  $\Delta\epsilon_\beta$ , entropy, enthalpy and volume are linear both in the high and in low temperature regions, while a distinct crossover presents at  $T_g$ . Since temperature, volume and entropy enter earlier into the JG relaxation than into the primary behavior, as a precursor of  $\alpha$  relaxation, it is emphasized that the new theory of glass transition needs reconsideration [42].

However, it should be noticed that  $\tau_{JG}(T)$  and  $\tau_0(T)$  cannot be exactly the same otherwise the JG relaxation will become the intermolecular cooperative motions with longer relaxation time, i.e. the  $\alpha$  relaxation. In order to explain



**Figure 2** Schematic view of the temperature dependence of the relative strength of the JG relaxation peak  $\Delta\epsilon_\beta$  and entropy, enthalpy and volume (the inset)

their different fates, possibilities have been proposed from the view of the glassy structure. Williams and Watts believed that the molecules (or the motions) involved in the JG relaxation were only a subset of the structural regions responsible for the primitive  $\alpha$  behavior and the former finally enters into the latter [43]. This picture accords with the nature of local motion and in some degree has got some experimental supports [44,45]. In silica glasses where both the medium-range-order and long-range-order structures have been found, Salmon's work verified that the latter structure was responsible for the  $\alpha$  relaxation, whereas the JG relaxation related to the former [44]. For metallic glasses, it seems that the JG relaxation arises from some small motions of atoms involved in its metastable islands [46]. This view seems to be reasonable when we look into the correlation of the separation between  $\tau_{JG}(T)$  and  $\tau_\alpha(T)$  with Kohlrausch parameter  $(1-n)$  [18,21]. The tendency can be easily seen from comparisons among sorbitol, xylitol, threitol and glycerol, which belong to the same polyalcohol family [47]: with the increase in the parameter  $n$ , the separation between  $\tau_{JG}(T)$  and  $\tau_\alpha(T)$  peaks becomes more distinct. Especially, the JG peak or even shoulder cannot be observed in strong glass formers with a small  $n$  value (such as glycerol and  $\text{GeO}_2$ ). In fact, from the equations given by the CM, the separation between  $\tau_\beta(T)$  and  $\tau_\alpha(T)$  can be described by

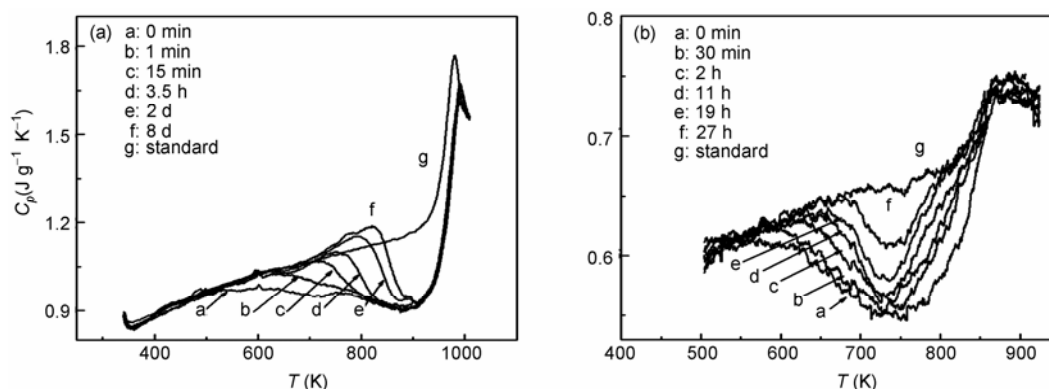
$$(\log \tau_\alpha - \log \tau_\beta) \approx n(\log \tau_\alpha - \log t_c). \quad (5)$$

This equation, in which a smaller  $n$  corresponds to a smaller value on the left side of eq. (5), accords quite well with the above empirical observation [18,19].

The other view used to explain the difference in nature between the  $\alpha$  and the JG relaxations concerns their difference in molecular environments. Johari proposed the concept of the islands of mobility in a rigid matrix due to the nonrandom distribution of local free volume, i.e. liquid-like

region to explain the JG relaxation [48,49]. Johari believed that the JG relaxation should be the essential attributes of the liquid, supercooled liquid and glassy solid. Opposite to the opinion of Johari, Tanata assumed that in the superheated liquid there was no JG relaxation which only occurred when the liquid was cooled to a particular temperature. The JG relaxation should attribute to the occurring of the solid-like region when the temperature is lowered [50]. Goldstein introduced the connecting tissues between the amorphous clusters [51]. In spite of the inherent differences of the opinions, all of them originate from the fact of the uneven micro-structure of the liquid and the supercooled liquid. It is just the uneven micro-structure that leads to the difference of the relaxation dynamic mechanism while the structure unit participating the JG relaxation only attributes to the  $\alpha$  relaxation partially. The existence of different micro-regions of different characteristics has been observed by  $C_p$  curves. Figure 3(a) shows the  $C_p$  curves of the hyperquenched glasses annealed at different temperatures and times below  $T_g$  [52]. Among them, the standard sample indicates the slow-cooled bulk glass (below 20 K/min) which has the zero excess entropy compared with the glass fiber. It is seen that there are three types of structural relaxation anomalies: the annealing-induced endothermic peaks which is called as the "pre-peak" or "sub- $T_g$ ", the non-equilibrium exothermal peaks, and then 'λ-shaped' peak attributed to the transformation from glass states to the supercooled regions [53,54]. It is generally thought that the presence of the sub- $T_g$  peak corresponds to some micro-regions with fast relaxation which reach the states with lower energy relative to the rest of glass during annealing. They are independent of other domains with slower relaxations and simple precursors of the annealing overshoot, since they can be reproducible. In contrast, the big area of exothermal peaks corresponds to the unreleased excess enthalpy trapped during cooling.

Although the unevenness of the microstructure of the supercooled liquid has been recognized, the relationship between the JG relaxation and the  $\alpha$  relaxation in the structural nature needs further studies. The typical strong glass  $\text{GeO}_2$  and the oxide glass with relatively large fragility are compared as shown in Figure 3(a) and (b). It is found that the thermal relaxation style of the typical strong glass is different from that of the fragile glass [55]. The annealing time has no influence on the  $C_p$  curve at heating above  $T_g$  in Figure 3(a). However, Figure 3(b) shows that the increase of the annealing time will separate the  $C_p$  curve at the whole heating process, indicating that the fast relaxation has remarkable influence on the  $\alpha$  process. Combining the recent research [56], the fragility has considerable influence on the relationship between the JG relaxation and the  $\alpha$  relaxation: the less the fragility, the closer the relationship. Therefore, here the liquid fragility is a factor which must be considered.



**Figure 3** Influence of annealing duration on the energy release of hyperquenched glasses. (a) Basaltic fibers annealed at 723 K for different durations [52]; (b) GeO<sub>2</sub> annealed at 565 K for different durations. The “standard” means the fully enthalpy-relaxed samples [55].

## 2.2 The merging region of the JG and the $\alpha$ relaxations

Accompanied with the deep investigation of the JG relaxation, more and more attention is paid to the manner by which the JG relaxation and the  $\alpha$  relaxation merge at the temperature  $T_\beta$  ( $T_\beta$  is also called the crossover temperature, about  $1.2T_g$ ). Figure 4 shows the general scenarios for the temperature dependences of the JG and the  $\alpha$  relaxations [57]. In Figure 4(a), at low temperatures or high frequencies, the relaxation behavior is mainly governed by the JG mode, reflected by the well resolved JG peak in dielectric loss curves. Upon approaching or above  $T_g$ , however, due to different temperature dependences of the JG and the  $\alpha$  relaxations, the  $\alpha$  process enters the experimental frequency window and finally their characteristic relaxation time becomes comparable at the temperature  $T_\beta$ . This range is usually referred to as the “merging region” (sometimes also called the “splitting region”). It has been found that the merging temperature  $T_\beta$  coincides with the temperature where the mechanism of the primary relaxation begins to deviate from the VFT equation [26], and it also relates to the departure of molecular dynamics from the temperature dependence expressed by the Adams-Gibbs model [25]. As a subject of great interest, the investigation of the dynamics in the merging region sheds light not only on the nature of both processes, but also on the complete picture of liquid-glass transition.

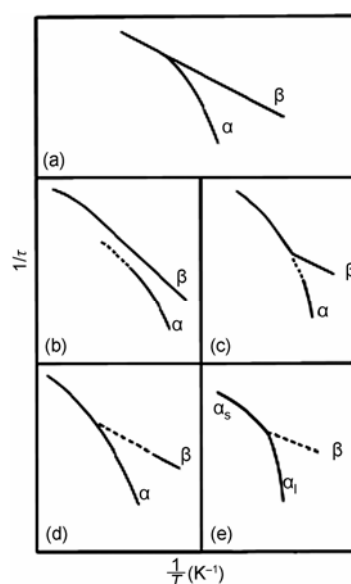
In Figure 4(a), if we extrapolate the temperature dependence of the JG relaxation and the  $\alpha$  relaxation below  $T_\beta$  to the high temperature region, both of the relaxation processes should exist in the high temperature region. What's more, the characteristic relaxation time of the JG process would become shorter than that of the  $\alpha$  relaxation. However, in reality the JG relaxation curve and the  $\alpha$  relaxation curve always merge into one [58]. In order to explain the paradox, a molecular model was proposed by Williams and Watts (WW) more than 20 years ago which is called as WW model (convolution ansatz) [58,59]. In the model, the  $\alpha$  and the slow  $\beta$  processes are assumed to own independent re-

laxation mechanisms and all the relaxation motions will be finished by the  $\alpha$  process. A simplification of the general idea in this model is described as

$$\phi(t) = \phi_\alpha(t)[f_\alpha + (1 - f_\alpha)\phi_\beta(t)], \quad (6)$$

where  $\phi_\alpha$  and  $\phi_\beta$  correspond to the normalized relaxation functions of the  $\alpha$  and the slow  $\beta$  processes, respectively, and  $1 - f_\alpha$  accounts for the fraction of the relaxation involved in the slow  $\beta$  process. According to this model, the relaxation behavior in the merging region is only the natural consequence of the extrapolation of the low-temperature relaxation behavior, and accordingly, there are no changes of the  $\beta$  relaxation mechanism in the merging region.

WW ansatz has been successfully used for the analysis of the high-temperature dynamics of polymers and molecular glass formers, which mostly corresponds with the experimental results [23,60,61]. With  $\phi_\alpha$  and  $\phi_\beta$  built at low



**Figure 4** General scenarios suggested for the merging region in the Arrhenius diagram. (a) Conventional; (b) PnBMA type; (c) PEMA type; (d) PPG type; (e) OTP type.

temperatures, the whole dielectric relaxation data at high temperatures, as well as neutron scattering data, can be well obtained according to eq. (6). Furthermore, the work on poly-(methyl methacrylate) shows that WW ansatz seems suitable to different conditions, no matter the dielectric response in the merging region is dominated by the slow  $\beta$  or the  $\alpha$  process [62]. Considering the difficulty in the quantitatively performance during the treatment of the dielectric data, using a neutron spin echo combined with dielectric study, Arbe and Richter further substantiated the appropriation of WW ansatz for the merging region [31]. It has been found that for poly(epichlorohydrin), toluene, and D-sorbitol, the relaxation part involved in the slow  $\beta$  relaxation becomes larger with increasing temperature, i.e. the  $f_\alpha$  value in eq. (6) becomes smaller [8,63,64]. The case is denoted by the L-type JG relaxation [65]. In contrast, the JG process in other glass formers such as *o*-terphenyl belongs to G-type, since it seems that no JG relaxation is observed in the equilibrium liquid state and it only appears in the glassy state [66].

Besides the simplified WW ansatz, another phenomenological description called superposition (or addition) ansatz also arouses a lot of interest [63]:

$$\phi(t) = f_\alpha \phi_\alpha(t) + (1 - f_\alpha) \phi_\beta(t). \quad (7)$$

In some cases of a series of polymers, this model has also been verified successfully [67,68]. The central mind of this view is that the dielectric spectra can be described by the addition of the contributions corresponding to the  $\alpha$  and JG processes. Although eqs. (6) and (7) have similar forms, the physical meaning of the two ansatzs is distinctly different from each other. In the framework of superposition ansatz, there usually exists a change in the temperature dependence of the  $\beta$  characteristic relaxation time, i.e. a change of the mechanism of the secondary relaxation in the temperature range where the  $\alpha$  and the slow  $\beta$  processes merge. It has been interpreted theoretically as a signature of the dynamic cooperativity missing above  $T_\beta$ . As an important experimental support to the superposition ansatz, the dynamics of the slow  $\beta$  relaxation begins to change from Arrhenius to non-Arrhenius temperature dependence in the range of  $T_g - 1.2T_g$  in the materials of sorbitol and *m*-fluoroaniline [69,70], which is further verified by Paluch's work [71], where the high-pressure dielectric measurements were used to resolve the JG relaxation from the nearby  $\alpha$  process. The region where the JG relaxation changes its dynamic mechanism is attributed by the authors to the half-soft of cages, accompanied by the observed mechanism change of the  $\alpha$  process. Another interesting description which seems to support the superposition ansatz is the Mode Coupling Theory (MCT) [34,72], the central idea of which is based on a nonlinear feedback mechanism for the density correlations in a fluid. The most important contribution of this model is the introduction of a critical temperature,  $T_c$ , where a

high-temperature relaxation mechanism begins to change. By associating  $T_c$  to  $T_\beta$ , this model deals with the slow  $\beta$  relaxation process between the microscopic relaxation at short times and the primary relaxation at long times. The  $\beta$  relaxation dynamics can be well described in a simple glass former with a Lennard-Jones system [73]. Recent experiments also indicate the changes in the mechanism of translational diffusion about  $T_\beta$  [74,75]. However, the MCT appears more appropriate to fragile liquids than to strong glasses and the weakness of this theory is the inability to describe real systems below the crossover at  $T_c$  and to provide a molecular interpretation [76–78].

In accordance with the superposition ansatz, Donth and the coworkers have proposed several possible scenarios for the possible  $\alpha$ - $\beta$  merging manner through careful examination of the dielectric loss curves of PEMA, PnBMA and so on. As shown in Figure 4, (b)–(e) correspond with PnBMA type, PEMA type, PPG type and OTP type respectively [57]. In the case of PnBMA and PEMA, above  $T_g$  the  $\alpha$  process usually dies out and the JG motion is totally responsible for the relaxation. The JG relaxation of PPG and OTP cannot be identified because of the low strength in the merging region, while the  $\alpha$  relaxation changes continually in the whole temperature interval. The difficulty in detecting whether the superposition ansatz is more reasonable than the WW ansatz or not lies in the fact that the different merging scenarios proposed by Donth can also be rationalized by the WW theory, which has been observed by assuming that both the  $\alpha$  and JG processes have the same KWW equations [63].

### 2.3 Potential energy landscape (PEL)

How the features of the PEL evolve around  $T_g$  during the  $\alpha$  relaxation process has been investigated widely in the past three decades. For example, Gibbs [78] pointed out that the fewer was the number of the energy minima on the landscape, the larger the resistance for the system to attain the potential energy minima was. Later, Angell demonstrated the correlation between the number of the energy minima in the PEL and the liquid fragility [79], which has been verified by a compilation of the heat capacity jump values at the glass transition for different glass formers with fragility [80]. Experiments suggest that the behavior of glass-forming liquids tends to present two different dependences: on entropy or on free volume [81]. How the basic landscape features depend on the details of particle interactions and how they arise from the nature of real particles involved in (molecular or atom) architecture of the systems hold the key to understanding the relationship between dynamics and thermodynamics in deeply supercooled liquids.

Although some progress has been made in the PEL, it is only in the past decade that how to build the PEL involved in the secondary or JG process was taken into account. Furthermore, the problems concerning the dynamic behaviors

in the merging region of the JG and the  $\alpha$  relaxations, such as controversies between the WW ansatz [60–63] and the addition ansatz [67–69], also arouse the reconsideration of this topographic picture. For example, the WW ansatz means that at high temperature above  $T_g$ , both  $\alpha$  and JG processes exist with no changes of relaxation mechanism, whereas, if the case is addition ansatz, the JG relaxation will take over the whole relaxation behavior. Consequently, the question of heterogeneity in the  $\alpha$  and the JG relaxations is addressed, and how to clarify these questions from the viewpoint of the PEL is of great importance [49].

The PEL view involved in the JG relaxation was firstly mentioned by Johari [82], and then described in detail by Stillinger in 1995 [83]. In this picture, the JG relaxation corresponds to transitions between inherent structures (IS) within the mega-basin while the  $\alpha$  relaxation corresponds to transitions between mega-basins. Based on this simple description, more works attempt to further the studies concerning the correlation of the JG and the  $\alpha$  relaxations. By assuming that the  $\alpha$  relaxation is promoted by coherent excitations of a minimum number of  $\beta$  processes within a co-operational rearrangement region, a mesoscopic model well depicts how the slowdown of relaxation in fragile liquids evolves, considering the combined effect of an entropic bottleneck and the energy constraint [84]. It seems that there is no diverging length scale needed. The apparent decoupling of rotational and translational diffusion near the calorimetric glass transition [85] suggests that two different relevant time scales exist. Some other experimental results, such as from four-dimensional nuclear magnetic resonance [86], seem to accord with this view, where the concept of “environmental fluctuation” or “rate memory” is introduced. The evolution of the high-frequency motion from the excess wing to the resolved JG peak in propylene carbonate seems indicating that it is only in the deeper minima of the potential energy surface that sufficient substructure within the minima develops for the high frequency features to be resolved as differentiable features [87]. It makes a contrast with other cases. One case is the example of OTP, for which the annealing causes the JG relaxation to disappear [66]. Another case is that sufficiently fast quenching causes the JG relaxation to appear [88]. It embodies that the JG relaxation has difference in types (as shown above, L-type and G-type).

In another view called two-site jump angular model [89], the complex reorientational motion in supercooled liquids is considered as a composite process of two distinct motions: “fast” restricted angular fluctuations (but still much slower than any microscopic time scale) inside an energy minima associated with the JG relaxation, and the large-angular  $\alpha$  transitions among the states corresponding to the megaminima in the energy landscape. It is assumed that the molecular reorientation is coupled intrinsically to the transitions among an extensive number of free-energy minima. When the model is used for dielectric response, the scenario

obtained agrees with the WW ansatz, since at high temperatures the  $\alpha$  relaxation seems dominant according to the model. The influence of  $\alpha$  relaxation on JG dielectric peak derived from the model is also in accordance with Arbe et al.’s work [31,60].

The controversy in the experimental supports concerning the WW and addition ansatzs comes from the big influence of an even slight extrapolation of dielectric JG peak values. However, the mechanism underling the WW ansatz is the statistical independence of the two relaxations (JG and  $\alpha$ ). That means, in the WW ansatz, no influence of the rearrangements of the local structure involved in the transitions among different energy minima on the local fluctuations involved in  $\beta$  relaxation. In accordance with this idea, Vogel and Rössler [90] gave their description of the energy landscape of glass formers. In this model, each configuration of the  $\alpha$  relaxation involving the arrangement of a certain number of molecules corresponds to energy minima and, and at the same time, the corrugated bottom of each of these minima contains another landscape of the JG relaxation minima which also involve the same number of molecules as that in the  $\alpha$  process. According to it, all molecules in the system contribute to the JG relaxation, and consequently, the JG process is not heterogeneous anymore. Johari and his coworkers demonstrated their different views on this point [49]. They pointed out that, if the JG process was the case as described above, the entire landscape would also change due to the decrease in temperature of the equilibrium liquid. Another model, so-called minimal model [91], assumes that the JG relaxation involves two levels characterized by one parameter of barrier potential,  $U$ , and one parameter reflecting the asymmetry,  $\Delta$ . According to this definition, it rationalizes the contrasts observed between the JG relaxation in liquids and in glasses. Besides, the correspondence between the temperature where  $\Delta$  equals zero and the merging temperature  $T_\beta$  is also observed. This model, however, is too oversimplified. More concrete explanations of JG motion are depicted by Marqués and his coworkers [92]. In this model, based on the relationship found between diffusive processes and the number of accessible paths in the multidimensional energy landscape, the JG relaxation time is attributed to a “search” for diffusive directions which occur at the saddle points of the PEL [93,94]. This description concerning the JG and the  $\alpha$  relaxations correlates the two theoretical methods in the field of glass transition, i.e. the PEL approach and the MCT theory.

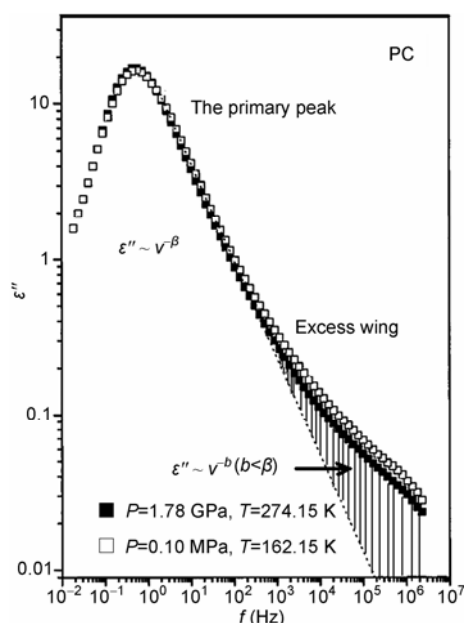
## 2.4 The excess wing and the boson peak

Among all the dynamic processes observed in glassy dynamics, the unusual processes beyond the slow secondary and primary relaxations, such as the excess wing, have attracted considerable interest in recent years, stimulated by further understanding the JG relaxation. The research on the excess wing shows significance to discover the nature and



the characteristics of the JG relaxation behavior.

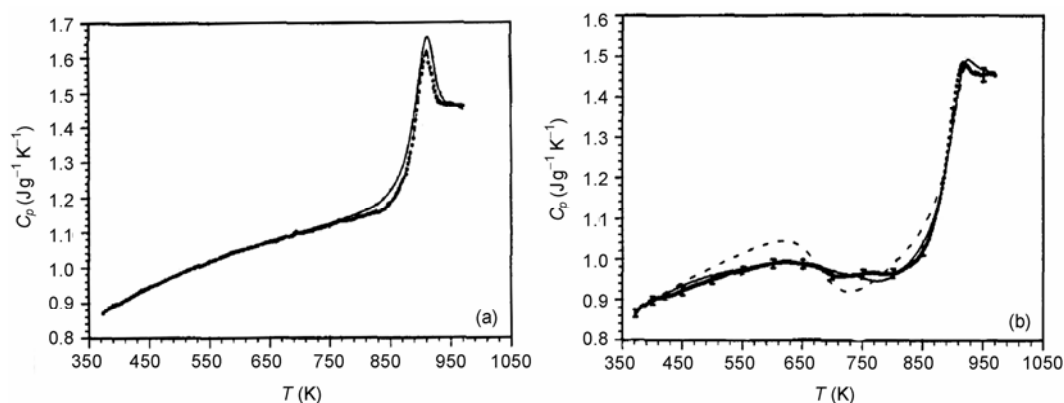
Figure 5 gives the definition of the excess wing intuitively [7]. In the measurement of glass formers by broadband dielectric spectroscopy, the excess wing usually points to an excess contribution to the high-frequency flank of the  $\alpha$  peak and is described by a second power law,  $\varepsilon'' \sim \nu^{-b}$  ( $b < \beta$ ), with respect to the power law,  $\varepsilon'' \sim \nu^{-\beta}$ , of the  $\alpha$  relaxation peak. An intriguing phenomenon is that the glass formers with the observed excess wing usually have no observed JG peaks (type-A, such as glycerol and propylene carbonate), and in the opposite way, the glass formers with JG peaks have no excess wing (type-B, such as toluene and sorbitol, as shown in Figure 1) [7]. This phenomenon leads to different understandings. Dixon et al. [95], Leheny and Nagel [96] believe that the excess wing, as an inseparable part of the  $\alpha$  relaxation, is an intrinsic feature of all glass formers. Using “time-temperature superposition”, they succeeded in putting the imaginary part of the dielectric data of both the main peak and the excess wing detected at different temperatures and frequencies into a single master curve. It suggests that the shapes, positions and relative amplitudes of the main peak and the excess wing are determined by a single parameter, the  $\alpha$  peak position. Moreover, the difference in the effects of either temperature or pressure on the excess wing in cresolphthalein dimethylether and phenolphthalein dimethylether and the JG relaxation in diisobutyl phthalate and bis(methoxyphenyl) cyclohexane [97] has been observed, in accordance with the observation from Schneider [98]. It shows that the JG relaxation and the excess wing do not have the same origin. In accordance with the opinions above, for type-B materials the excess wing is hidden by the JG peak. Therefore, they suggested



**Figure 5** The dielectric spectra of propylene carbonate at different combinations of pressure and temperature.

that, during the quantitative line-shape analysis, i.e. the fitting procedure to separate the  $\alpha$  and the JG peaks, the excess wing should be considered even in the case of well resolved JG peak, which seems successfully used in a benzyl chloride-toluene glass [99]. Theoretically, the asymptotic  $\alpha$  relaxation peak can be recovered by a thermodynamic model with a Gaussian distribution of independently relaxing domains in liquids [100]. In defect diffusion model, the excess wing is explained by the tendency of forming isolated mobile single defects (MSDs) in the glass formers [101].

However, the belief given above is at odds with other dominant views, especially when the CM has been verified by a series of experimental results [18,19,47]. As shown in eq. (5), in more fragile glass formers with a larger value of  $n$ , i.e. a broader dispersion of  $\alpha$  relaxation, the difference between  $\tau_{JG}(T)$  and  $\tau_{\alpha}(T)$  becomes more distinct. That means the JG peak is not well resolved from the main peak (even overlap) if  $n$  is small (such as approximate to zero). Notice that the glass formers of type A all have smaller  $n$ , compared with type B including the JG peak. The predicted values of  $\tau_{JG}(T)$  for these materials by CM model always fall within the excess wing. Although only empirically, the trend indeed presents that the dielectric strength of the resolved JG peak decreases with the decreasing  $n$  [7,18,55]. Based on these findings, it is reasonable to believe the correspondence between JG peak and the excess wing. That is to say, for type A, the JG peak is so close to the primary peak or with so low amplitude, that only its high-frequency tail remain visible and the other part is hidden by the  $\alpha$  peak, resulting in the phenomenon called the excess wing observed. The reason why the  $\alpha$  and the JG peaks cannot decouple has been suggested by both experimental and simulation observation [102,103]. In a general way, the stronger glass formers have smaller microregions responsible for the  $\alpha$  relaxation and consequently have stronger influence on the JG motions involved in certain size of cages. Here the excess wing in nature is the JG relaxation. One strong support is the phenomenon that the excess wing is gradually developed into a shoulder during aging procedure on glasses, such as glycerol and propylene carbonate and propylene glycol [104]. According to Cummins, this evolution is a consequence of rotational and translational (RT) coupling [105]. The coincidence of the peak frequencies measured by disparate probes shows that the translation-aided diffusion is governed by the same relaxation time as the molecular reorientations in many glass formers [106]. Another support is given by the dielectric data of the plastic crystals such as cyclooctanol, where due to the existence of glass-like transition and the lack of the complexity of true glasses, only the rotational and conformational degree of freedom contributes to the dynamic behavior [38]. This kind of crystals has quite similar shapes of relaxation curves to the usual glass-formers. Notice that one strong proof for the other view proposed by Dixon et al., i.e. the common nature



**Figure 6** Heat capacity relaxation data with a heating rate of 40 K/min for a bulk sample cooled at 20 K/min (a) and the rapidly cooled fibers cooled at about  $10^6$  K/min (b). Solid line and dashed line represent simultaneous fits by the TC and TN models, respectively. The dots are the experimental data.

of the excess wing and the  $\alpha$  relaxation, is that the relaxation time of the excess wing has non-Arrhenius temperature dependence in some type A materials, different from the Arrhenius form owned by a typical JG relaxation found in type B [95–98]. To explain it, Lunkenheimer pointed out no principal reason that the JG relaxation should always obey Arrhenius behavior [107]. Indeed, the temperature dependence of  $\tau_{JG}(T)$  for *m*-fluoroaniline and sorbitol has been found to undergo a transition from Arrhenius to non-Arrhenius behavior in the vicinity of  $T_g$  [70]. Theoretically, this view is explained by a recent extension of the Weiss mean-field theory, where the excess wing is ascribed to a superposition of peaks or shoulders, in addition to the  $\alpha$  peak [108]. At the same time, even the Nagel scaling to get a master curve can be explained by the CM view [109]. Although some glass formers show, besides an excess wing, another relaxation peak at higher frequencies, it has been found that this higher frequency relaxation is not the true JG motion [110].

Besides the excess wing, another additional contribution to the liquid dynamic properties such as the viscosity, is the boson peak, the fast process in the ns-ps regime. The boson peak, due to the increase in the density of vibrational states, over the Debye value, caused by localized excitations, is usually associated with the existence of medium-range order structures in glass formers [111]. It is usually detected by neutron scattering measurement and low-frequency Raman spectroscopy, as well as computer simulations. There exist a number of models for describing and interpreting the boson peak, namely, the Debye [112], soft-potential [113], fractal [114] and Einstein localized oscillator models [115]. Compared with the quantitative description given by the last one, the other models tend to be phenomenological. For example, the model of Einstein oscillators has been used to determine the location, width and intensity of the boson peak in alkali borate glasses [116]. In the PEL term, the boson peak is a remnant of the softening of the free energy landscape at the dynamical temperature and it is composed

by modes that migrate at imaginary frequency  $\omega$  at  $T > T_c$  [117].

Notice that the JG relaxation also occurs in some micro-regions within certain sizes. Using different anions and the same BMIM (1-butyl-3-methyl imidazolium) cation, Alberto found that the fast  $\beta$  relaxation existed in all the supercooled liquids, whereas the JG relaxation only occurred with the presence of dipolar moments [17]. It suggests that the JG relaxation is due to a long, not quite short, range Coulomb interaction in ionic melts. Investigation in a series of strong glasses discovered the existences of two order structures, one with medium range and the other with longer size [44]. It is also found that the latter is responsible for the  $\alpha$  relaxation, whereas the JG relaxation is caused by the former. Since the view of the medium-range order structure nature of the JG relaxation becomes more and more accepted, the relationships between the boson peak and this secondary relaxation behavior is naturally expected. On the other hand, it has been found that the strength of boson peak closely correlates to the  $\alpha$  relaxation [118,119]. The competition between the strength of the boson peak and the structural relaxation contributes to the fragility strength of glass formers; the relaxation behavior in supercooled liquid promises to be predicted by some parameters of the vibrational properties in solid glasses. Taking account of the close relationship between the JG and the  $\alpha$  relaxation, there seems to be big possibility that the key characteristics of the JG relaxation might be predicted from proper determinations of the characteristic dynamics in the first few picoseconds. In contrast to the JG relaxation, the boson peak is attributed to quasilocal vibrations (QLVs), which can be traced to local irregularities of the amorphous structure [120].

## 2.5 Phenomenological models

According to Scherer's classification, besides rheological and kinetic relaxational approaches, phenomenological ap-

proach is also an aspect of great importance [121]. A phenomenological model seeks to predict the structural recovery event of glass in an arbitrarily thermal history using a small set of parameters derived from limited experimentation. That means monitoring the time-dependent variation of physical quantities after quenching the sample to below  $T_g$ . This slow, far-from-equilibrium dynamics, the so-called “physical aging”, is not only of fundamental interest for statistical mechanics but also of great practical interest since so many amorphous materials are used in everyday life for times exceeding their preparation time.

For slow cooling rates, the residual stresses reflected by the excess enthalpy in glasses relative to that in well-annealed glasses can be calculated by the Tool-Narayanaswamy (TN) equation [122,123]. This model contains a relaxation function, which is traditionally assumed to have a stretched exponential characteristic (such as the KWW function). The TN-equation containing the KWW function is widely applied by glass technologists to advanced numerical modeling, which calculates the properties of glasses after thermal history and heat treatment and helps to design large glasses with specific properties [124]. Figure 6 gives the comparison between the simultaneous and experimental results of TN equation [125]. It can be seen that the correspondence of the TN model with the experimental value of the glass under a slow cooling condition is better than that with the heat scanning curve of the glass under fast cooling condition. TN model is only suitable for a narrow temperature region (down to about 20 K below  $T_g$ ), since it treats glassy materials as thermorheologically simple (TS), which means that the shape of the relaxation function is invariant with respect to temperature. When a broader temperature interval is probed, the TN model fails [125]. Later, a model involved in thermorheological complex (TC) was introduced by Rehson and Ducroux in 1992 [126] and further developed in 1994 [127]. The advantage of this model is that the temperature dependences of both the shape of the equilibrium relaxation function and the distribution of characteristic relaxation time are considered. Structural relaxation is treated as a multi-relaxation process, for which each mechanism is assigned to its own energy barrier and Kauzmann temperature. As a consequence, the TC model gives a fit not only to the  $C_p$  data of bulk samples during reheating, but also to that of rapidly cooled fibers.

However, TC model cannot well simulate the heat capacity curve of the hyperquenched glass after the heat treatment (such as the sub- $T_g$  peak or shoulder as shown in Figure 3) [126,128–130]. The lack of success in both TN and TC modeling in some extreme conditions roots in the unclearness of several important fundamental questions concerning the JG relaxation. One is that no consensus exists about the effect of thermal history on the JG relaxation. For example, Bershein et al. [131,132] believe that the sub- $T_g$  relaxation that has been widely observed by mechanical and dielectric spectroscopy is in fact the JG relaxation. The distinct influ-

ence of thermal history on the JG relaxation in non-equilibrium rigid molecules has been observed by Wagner and Richert [88,133]. They reported that the hyperquenching method makes the JG relaxation more distinct and separate from the  $\alpha$  motion, and the changes of the JG relaxation peak can be observed by annealing. However, some researchers have different viewpoints. Based on the finding that the Adam-Gibbs temperature dependence of characteristic relaxation time below  $T_g$  in rapidly cooled glassy glycerol, Yamamuro pointed out that the relaxation below  $T_g$  is mainly associated with the  $\alpha$  relaxation [134]. The same view was also owned by Muzeau when some poly (methyl methacrylate) was investigated [135]. He owned that the JG relaxation was not affected by physical aging and only that the  $\alpha$  relaxation spread out in the  $\beta$  relaxation temperature domain. Noticing these controversies, Lunkenheimer pointed that the aging dynamics was finally dominated by the  $\alpha$  process, no matter whether the aging affected the JG relaxation or not [136]. This idea supports the local step nature of the JG relaxation and the long-range nature of the  $\alpha$  relaxation. There have been some evidence that the volume and the enthalpy evolve toward equilibrium differently, either manifesting different times to attain equilibrium or different rates of approach to equilibrium [137–139]. It is observed that enthalpy recovers into equilibrium faster than the mechanical response does, whereas the mechanical response is faster than the volumetric response. It suggests different activation energies for different processes.

We notice that the recently developed composite relaxation function (CRF) modeling can well describe the features of DSC curves [140] in a qualitative degree. Take the hyperquenched E glass fiber for example, which is isothermal annealed for different time, the heat capacity curve from the CRF as shown in Figure 7(a) basically corresponds with that from experiments as shown in Figure 7(b). All sub- $T_g$  peaks, the exothermic peak and the glass-transition peak are well described by the CRF model; however, the traditional TN model fails in this case. Some physical meaning should be underlying the new factor introduced into the CRF with respect to TN model. Indeed, a phenomenological model in a good quantitative way will contain valuable information about the structural development of the liquid during cooling and unquestionably accelerate our understanding in the JG relaxation. For example, if we know in glasses the relation between enthalpy or volume relaxation on the one hand, and shear and field relaxation on the other, it will help us decide whether the JG relaxation is attributed to the motions of molecules between clusters or controlled by the relaxation within clusters. The complete modeling can also give some hints on how the JG relaxation behaves in the merging region which is urgently waiting to be dealt with. Figure 2 is helpful for correct description of the JG relaxation behavior. The relationship between the parameters of the JG relaxation peak (such as strength, width and position) and those of the main peak can be analyzed by the systematic dielectric

data for different kinds of materials. To some degree, it promises to improve our model to predict the relaxation curve of trapped enthalpy in hyperquenched glasses quantitatively, with only the cooling rate available.

### 3 The work in the future

All in all, great interest has been attracted in the JG relaxation in the field of glasses. Since more and more investigations in aspects such as temperature dependence, pressure-dependence and activation energy verify that this slow  $\beta$  relaxation induces the glass transition instead of the  $\alpha$  relaxation, many questions involved in glass transition phenomenon, as a consequence, need reconsiderations [141]. We must admit that the whole picture of glass transition composed of the JG relaxation and the  $\alpha$  relaxation is still a big challenge. The main problems which exist in this field, as well as the key aspects of the glass transition phenomenology, have been reviewed in detail by Craves, Angell and Murthy with different interest and emphasis [1,28,29]. Besides, one method is often suggested to resolve a certain problem, such as Tanaka's discussion concerning the spatial nature of the JG relaxation [142]. All of those have provided valuable information for the further research of the slow  $\beta$  relaxation and the glass transition. Here, we do not seek to point out the controversy in this field again, which in fact has been reflected by the development in this area. Rather, we prefer to expound the trend in this field from the standpoint of general characteristics of the JG relaxation.

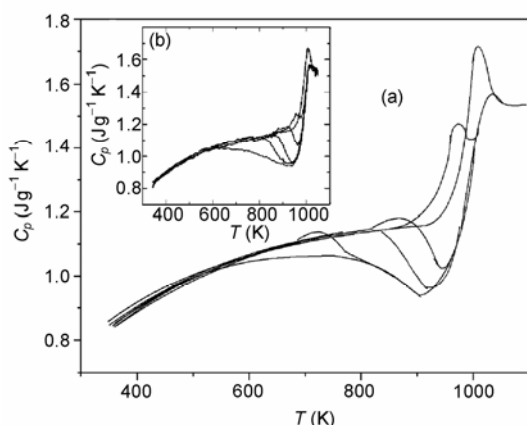
Firstly, we should realize the importance of the studies on kinds of materials. At the beginning, the research on the JG relaxation mainly centered on the polymers, and then it was extended into molecular glasses with covalent bond, electrovalent bond and so on. Now we should arouse the acknowledgement to the importance of strong glasses in this

field, since as noticed, when we tried to get some judgments, fragile glasses are usually regarded as the best cases for investigation, due to the distinct  $\alpha$  and the JG peak separation, while strong liquids such as  $\text{SiO}_2$  and  $\text{GeO}_2$  are seldom concerned. The investigation on strong glasses is becoming more and more important, which is reflected by the following representative examples.

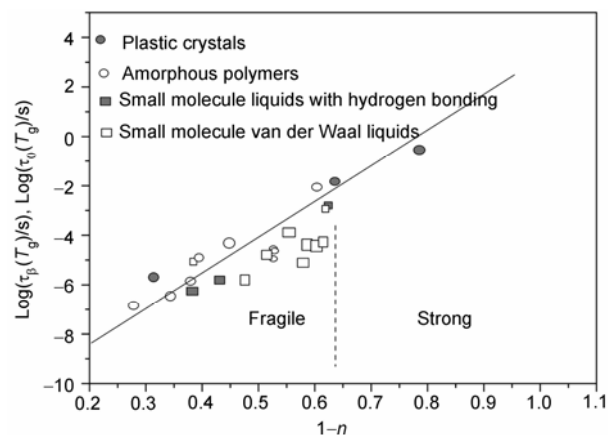
The first example concerns the argument about the nature of "liquid-like" region or "solid-like" region of the JG relaxation. According to the view owned by Johari et al. and the CM [18,19,48,49], where the JG relaxation is believed intrinsic in the "liquid-like" regions, strong glasses have JG relaxations with much longer characteristic relaxation time than fragile glasses, resulting in the overlapping between the  $\alpha$  and the JG dielectric peaks. However, the idea that no JG relaxation exists in typical strong glasses is owned by other researchers, where JG motion is due to the local orientational fluctuations in "solid-like" regions [50,102,142]. It can be found that whether the JG relaxation exists in strong glasses or not is the key point of this argument.

The second example concerns whether the JG relaxation is dynamic homogenous or heterogeneous [49]. The controversies between the view of Williams and Watts and that of other researchers come from the fact that both the views have been supported to some degree by different experimental results [43,48–50]. In fact, it is possible that there is a trend of spatial nature of JG relaxation to change from strong to fragile glasses according to the relationship between fragility strength and the boson peak [118], the relationship between fragility strength and the distribution spectrum of the  $\alpha$  relaxation [143] as well as eq. (5). The settlement of this controversy needs comprehensive consideration including both fragile and strong glasses, rather than only the discussion on the fragile system where the JG relaxation is easy to be observed.

The third example concerns the Coupling Model. Although the CM has been verified by more and more ex-



**Figure 7** Systematic annealing of hyperquenched E glass at  $T=800$  K. The annealing was carried out for the following time periods: 0, 15 min, 3.5 h, 1 d and 2 d. (a) The results of the CRF model; (b) the results of the measurements.



**Figure 8** Solid line represents the calculated  $\tau_0(T_g)$  from CM model, i.e.  $\tau_0(T_g)$ . Single points show the experimental data from dielectric test [18].

perimental results from fragile glasses, direct verification seldom comes from strong glasses. As shown in Figure 8, the  $\tau_{\beta}(T_g)$  of the JG relaxation in strong glass formers is difficult to be measured directly, except the special plastic crystal. Strong glasses are regarded as a predictive part [18] and its  $\tau_{\beta}(T_g)$  is obtained from the extrapolation of the data of the fragile glass formers. It can be imagined that whether the CM fits the extreme case of strong glasses is paramount to understanding the key points involved in JG relaxations, as well as the judgment of the CM.

Accordingly, most of the controversies concerning the JG relaxation result from (at least relate to) the unavailable data of the JG relaxation in strong glasses [7]. For strong glasses, neither the peak nor the shoulder indicating the presence of the JG relaxation has been observed experimentally either by isochronal or isothermal measurement in a usual way (such as dielectric mechanical, NMR spectroscopy and photon correlation spectroscopy). Besides, the network structure in typical strong glasses relaxes around the temperature dependent on the basis of the measuring frequencies usually used and the data on the breadth of the relaxation time spectrum in strong glasses is unavailable [4,5,14,49,144,145]. It is just these factors that bring difficulties to the studies of strong glasses. Therefore, it is urgent to find applicable means to investigate the JG relaxation in strong glasses. Recently, the hyperquenching-annealing-calorimetry approach has been applied to  $\text{GeO}_2$  strong glasses [55]. The basic idea of the attempt is to utilize the hyperquenching technology to frozen in the structural and energetic states at some imaginary temperature  $T_f$  (far above  $T_g$ ) and then the gradual change of the structural and energetic states from  $T_f$  to  $T_g$  will be observed during the heating process. For extremely strong glasses, we can imagine that, based on the typical Arrhenius behavior of viscosity in the whole temperature range as shown in Angell plot, the activation energy of the structure relaxation in the hyperquenched states should be the same with the activation energy of the  $\alpha$  relaxation exhibited by the standard glasses, if there is no distinguishable influence coming from secondary relaxations. Otherwise, this method will present us a window to find the characteristics of  $\beta$  relaxations with respect to the  $\alpha$  relaxation.

Secondly, besides strong glasses, metallic glasses are another type of materials which need more attention in the future investigation. Different from other non-metallic systems, metallic liquids are composed of metallic-bond interacting atoms with arrangements similar to dense random packing of spheres. Its index  $(1-n)$  representing the dispersion of the relaxation time for different series of metallic glass liquids centers about 0.5 [146], while that of the molecular liquids varies a lot from 0.3 to 0.75. One typical characteristic of metallic glass formers is that the reorientations of the spheres around their axis will not contribute to the reorientation of the elastic dipole. With the research field of the JG relaxation becoming more deeply, this char-

acteristic of metallic glass liquid becomes more important. For instance, only the excess wing is observed in the dynamic and mechanical relaxation spectra for  $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$  and  $\text{Ce}_{70}\text{Al}_{10}\text{Cu}_{20}$  glasses instead of obvious JG relaxation peak or shoulder [147,148]. The excess wing observed in metallic glasses, as proposed by the authors, is then due to the small-scale translational motions of atoms. At this point, the system of metallic glasses can be regarded as a special case. During the research of the JG relaxation, studies on some systems having special structures or properties play positive roles in discovering the nature of the JG relaxation. The successful examples include plastic crystal and rigid molecule. It is just from the characteristic of no free volume between atoms in rigid molecule that one of the characteristics of the JG relaxation, i.e. the cooperative motion of the whole molecule (not motion of any part of the molecule) was understood and accepted [4,5]. The recent report on  $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$  has suggested that the type of metallic glasses is ideal for investigating the physical aging process of glasses [149].

Besides, compared with polymers which usually have some side-functional groups, the picture of metallic glass formers looks simple since the whole system is usually described as the combination of clusters with short-range or medium-range order and free volume among clusters. It has been found that the characteristics of these clusters control the fragility strength involved in the  $\alpha$  relaxation [150]. The structures in clusters can be detected both experimentally and simulationally, which presents the possibility to go deep insight into the real role of clusters in the JG relaxation, i.e. whether there is some common correspondence in changes between clusters and relaxation mechanism. Chen and Inoue investigated the enthalpy relaxation spectra in series and found there were two different relaxation processes at  $T_g$  [151,152]. Studies show that the enthalpy relaxation manner of the bulk metallic glass system such as Zr-based and that of the non-metallic glass system are similar. However, for the marginal alloy such as Fe-based, its sub- $T_g$  peak and shoulder are more obvious [153,154]. It seems that the relaxation process at low temperature originates from the short-range or the medium-range rearrangement of the weak bond between the metallic atoms while the high temperature relaxation behavior corresponds with the cluster rearrangement of strong bond in a long range. All these findings provide valuable information for acquiring the characteristics and the rules of the JG relaxation in metallic glasses and also put forward questions for further work, such as whether the low-temperature relaxation process is the JG relaxation or not and how the JG relaxation in metallic glasses evolves with the temperature and so on.

## 4 Summary

From the literature survey made above, it can be stated that

the slow  $\beta$  relaxation induces the occurrence of glass transition prior to the  $\alpha$  relaxation; the slow  $\beta$  relaxation determines the characteristics of the cooperative  $\alpha$  relaxation. These conclusions result in the important role of the slow  $\beta$  relaxation in the field of glassy materials as a new insight. Although an understanding of the JG relaxation has been considerably enhanced in the past decade, however, a universal model describing the thermodynamic and dynamic characteristics of JG relaxations is still lack, as well as its structural explanation. The studies concerning metallic and tetrahedron-network glasses are also seldom reported in this field. We believe that in the next decade scientists have high potentialities to clarify the following key issues to uncover the nature of the slow  $\beta$  relaxation. Firstly, what is the structural origin of the JG relaxation? Secondly, considering the temperature and pressure dependences, how the slow  $\beta$  relaxation relates to the  $\alpha$  relaxation, to the excess wing and to the boson peak? Thirdly, how does the JG relaxation contribute to the glass transition thermodynamically? Fourthly, how does the JG relaxation influence the glass forming ability? Finally, can we incorporate different theories to find a universal model describing the JG relaxation for all glass formers? To answer these questions promises to perfect the traditional theoretical scheme of glasses.

*This work was supported by the National Natural Science Foundation of China (Grant No. 50801041), National Basic Research Program of China (Grant No. 2007CB613901) and Research Fund for the Doctoral Program of Higher Education of China (Grant No. 200804221041).*

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