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Guides to solving the glass transition problem

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Abstract

Relaxation in glass-forming substances is necessarily a many-body problem because of intermolecular interactions and constraints. Results from molecular dynamics simulations and experiments are used to reveal the critical elements and general effects originating from many-body relaxation, but not dealt with in conventional theories of the glass transition. Although many-body relaxation is still an unsolved problem in statistical mechanics, these critical elements and general effects will serve as guides to the construction of a satisfactory theory of the glass transition. This effort is aided by concepts drawn from the coupling model, whose predictions have been shown to be consistent with experimental facts.

1. Introduction

In any glass-former, the intermolecular interaction potential, $V(r)$, plays some role in determining the dynamic, thermodynamic, and vibrational properties at temperatures both below and above T_g. For fundamental understanding and predictions of the dynamic properties of glass-formers, and for ultimately solving the centuries old glass transition problem, it is necessary to establish a quantitative connection between the relaxation properties of a liquid and the intermolecular interactions among its constituent molecules. The equation of state of the equilibrium supercooled liquid (i.e. pressure P, specific volume υ, and temperature T relationship) is also determined by intermolecular forces and by steric constraints (excluded volume). In turn pressure, temperature, and volume have significant effects on the structural relaxation time, so that they are essential experimental variables in determining the relaxation properties. The glass transition is usually observed by lowering temperature or elevating pressure. Having direct connections to relaxation and vitrification, these thermodynamic variables had traditionally been considered as necessary and sufficient for construction of a theory of the glass transition phenomenon. Examples include the free volume theory [1] and the configurational entropy theory [2], both of which are still commonly used to rationalize experimental data.

However, intermolecular interaction does not only underlie thermodynamic variables but also complex many-body relaxation dynamics. The presence of the latter has only become evident from results of experimental investigations carried out in the last two or three decades, and thus the limitations of free volume and configurational entropy theories proposed five decades ago are understandable. The better known evidence of the many-body nature of the structural α-relaxation are [3, 4] (i) the nonexponential correlation functions often represented by the Kohlrausch stretched exponential function,

$$\phi(t) = \exp[-(t/\tau_\alpha)^{1-n}], \qquad 0 < n < 1, \tag{1}$$

(ii) the simultaneous presence of fast and slow relaxation molecules (i.e. dynamic heterogeneity), and (iii) the breakdown of the Stokes–Einstein and Debye–Stokes–Einstein relations. When intermolecular interactions between the molecules studied are absent, such as for Brownian motion or the Debye model of relaxation of molecules in dilute solution in solvents with much higher mobility, these characteristics of many-body relaxation disappear. This gives rise to a correlation function that is strictly an exponential function of time. Thus, the deviation from exponential given by n in equation (1) is a measure of the many-body dynamics. Although the many-body relaxation problem remains unsolved, its influence is apparent in the relations that n has with measurable relaxation properties. One clear evidence that many-body effects are operative is the observation that the dynamic properties of the α-relaxation and its relaxation time τ_α in bulk glass-formers are governed by or correlated with n [3, 4]. It is sufficient to cite here just the general result found in many glass-formers. For a given material at fixed τ_α, the time or frequency dependence of the

α-relaxation is constant, independent of thermodynamic conditions (different combinations of T and P). In other words, the shape of the structural α-relaxation function or the value of n of the Kohlrausch fit depends only on the relaxation time. Certainly, the thermodynamic theories of the glass transition do not address the properties of dynamics related to many-body relaxation, but this is not the only matter of concern. Most troublesome is the likely possibility that many-body relaxation also exerts a major influence on the α-relaxation time τ_α beyond the thermodynamic factors, T, S, P, and υ. This would render the principal prediction of the thermodynamic theories of the glass transition (i.e. the T and P dependences of τ_α and the glass transition temperature T_g) moot. Thus, neglect of the effects of many-body relaxation on τ_α in conjunction with the thermodynamic variables is a serious matter. Even when vestiges of many-body dynamics are observed, their effect is only rationalized *ad hoc* but no prediction is made concerning the direct connection of the many-body dynamics to τ_α.

An exception to this usual theoretical approach is the coupling model (CM) [5–8], whose defining prediction,

$$\tau_\alpha = [t_c^{-n}\tau_0]^{1/(1-n)}, \tag{2}$$

links τ_α and the dispersion parameter n, the latter an indicator of many-body dynamics. In equation (2), the onset time of many-body dynamics t_c is determined by the interaction potential, which is assumed independent of T and P. The parameter τ_0 is the one-body relaxation time often referred to as the primitive relaxation time of the CM. The primitive relaxation time of the CM in equation (2) brings out two other important points. First, although the α-relaxation is the focus of studies of the glass transition dynamics, a fundamental and thorough treatment of the problem requires consideration of the processes preceding it, and what relations exist between structural relaxation and its precursors. At sufficiently early times, molecules are caged, so that they can only vibrate and then relax within the cage. Anharmonicity of the potential leads to some loss that persists as long as the molecules are caged without a characteristic timescale, and hence the time dependence of caged relaxation is a power law or logarithmic decay of time. If a power law, the exponent has to be small because the mean square angular or translational displacement within the cage is always small. This 'fast' relaxation is the nearly constant loss (NCL) observed in supercooled liquids, glasses, and glassy and crystalline ionic conductors [9–13]. The local independent rotation or translation of the molecules out of the cage as governed by the primitive relaxation time τ_0 demarcates the end of the caged-molecule NCL regime. Starting from the primitive relaxation, the dynamics evolves with time to involve an increasing number of molecules with longer length-scales [14] until the terminal process with the maximum length-scale allowed by the intermolecular interaction is attained. This description is supported by motions of colloidal particles at different times measured by confocal microscopy [15], by molecular dynamics simulations of motion of Li ions in Li meta silicate glass [16], and the similarity of these data to those of binary Lennard-Jones particles found by molecular dynamics simulations [17]. This terminal many-body relaxation is identified with the structural α-relaxation, whose time correlation function is given by the Kohlrausch function in equation (1). Preceding the terminal Kohlrausch α-relaxation are the earlier time processes that include the NCL caged relaxation, the primitive relaxation, and the intermediate many-body relaxation processes. If these earlier time processes are independent of or bear no relation to the terminal Kohlrausch α-relaxation, then they are just interesting features but unimportant for consideration of the glass transition. In reality, there are experimental facts [3, 4, 9, 11, 18–24][3], molecular dynamics simulation results [25], and the CM (equation (2)), which all show that these earlier processes are related to or correlated with properties of the primary α-relaxation. Hence, no theory is complete unless these earlier processes are included and their connection to the α-relaxation addressed.

The second important point related to the primitive relaxation time is that the intermolecular interaction represented by its potential alone is not sufficient to solve the problem because input of some relaxation rate at some point in time is necessary to predict structural α-relaxation properties. The primitive relaxation rate given by $1/\tau_0$ is a natural choice because it is basic and has tractable properties. Involving either rotation or translation of molecules, the primitive relaxation rate is dependent on the physical and chemical structure of the glass-former, and this dependence is transferred to the structural α-relaxation through the theory. These connections cannot be established by considering only the intermolecular interaction potential. Another natural choice is the relaxation rate $1/\tau_\beta$ of the secondary relaxation that has properties mimicking those of the α-relaxation. Such secondary relaxations are called Johari–Goldstein (JG) β-relaxations [23]. It turns out there is no difference between the two choices because τ_0 calculated from the CM is approximately the same as τ_β of the observed JG β-relaxation in many glass-formers.

Thus, a fundamental and complete solution of the glass transition problem must originate from the intermolecular interaction potential and take into account both the earlier time processes, particularly the primitive relaxation, and the evolution of many-body dynamics terminating in the α-relaxation. The remainder of this paper is intended to justify these statements by presenting results from molecular dynamics simulations, experiments, and the coupling model. Although not rigorous, a solution of the glass transition problem is at hand.

2. Guides from molecular dynamics simulations

Molecular dynamics simulation (MDS) is a natural way to demonstrate that the intermolecular interaction potential $V(r)$, in some cases combined with steric constraints, determines the

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[3] The authors plot $\log\tau_\alpha$ versus the reduced mean square displacement $\langle u_g^2\rangle/\langle u^2\rangle$ for many glass-formers and show the data approximately fall on a master curve especially near and above T_g. We point out that this 'universal scaling' result can be viewed as the result of combining $\log\tau_\alpha$ versus T_g/T with $\langle u_g^2\rangle/\langle u^2\rangle$ versus T_g/T. Glass-formers having larger n have both $\log\tau_\alpha$ and $\langle u_g^2\rangle/\langle u^2\rangle$ decrease more rapidly with decreasing T_g/T. This correlation of the T_g-scaled T-dependence of $\log\tau_\alpha$ with n is well known (Böhmer *et al* [24]). The other correlation of the T_g-scaled T-dependence of $\langle u_g^2\rangle/\langle u^2\rangle$ with n can be found from experiments in [3] and discussed in [11].

dynamic properties and their dependence on thermodynamic variables. This is because MDS starts from $V(r)$ and all dynamic and thermodynamic properties are obtained from $V(r)$ by calculation. Changes of properties due to changes of $V(r)$ in the simulation can elucidate which aspects of $V(r)$ are responsible for the observed properties of the many-body α-relaxation dynamics.

2.1. Dynamic properties

The simplest system is the glass-forming binary mixture of type A and type B uncharged particles of the same mass interacting with the standard Lennard-Jones (LJ) potential [26–28], which is a special case of the generalized LJ potential

$$V(r) = [E_0/(q-p)][p(r_0/r)^q - q(r_0/r)^p] \tag{3}$$

with $q = 12$ and $p = 6$. The parameters r_0 and E_0 represent the position of the minimum of the well and its depth, respectively, and are different for A–A, A–B, and B–B interactions. For the purpose of investigating the change of dynamics of the A particles with controlled change of $V(r)$, Bordat *et al* [25] developed two other models by changing only the exponents, q and p, of the LJ potential for the A–A interactions. They are ($q = 8$, $p = 5$) and ($q = 12$, $p = 11$) in addition to the standard ($q = 12$, $p = 6$). The well depth and the position of the minimum of $V(r)$ are unchanged. The standard ($q = 12$, $p = 6$) LJ potentials for the A–B and B–B interactions are kept in order to retain the glass-forming ability of the mixture. The (12, 11) LJ potential is more harmonic than the classical (12, 6) LJ potential, while the (8, 5) LJ potential is a flat well and exceedingly anharmonic. The (12, 11), (12, 6), and (8, 5) potentials have been referred to as models I, II, and III, respectively, in order of increasing degree of anharmonicity, which can be quantified by the dimensionless parameter ξ, defined as the ratio between the third and the second derivatives of $V(r)$ at the minimum position r_0, and given by $\xi = V'''(r_0)/V''(r_0) = (p+q+3)^2/pq$. The anharmonicity parameters ξ for the three models I, II, and III are 5.12, 6.13, and 6.4 respectively. The steepness of the repulsive part of the A–A potential in model III, with $q = 8$, is lower than the other two models. All quantities are given in LJ units.

Dynamics have been investigated by computing the self-intermediate scattering function, $F_S(Q;t)$ of particles A at $Q_0 = 2\pi/r_0$, close to the maximum of the collective static structure factor $S(Q)$, for the three models. At high temperatures, $F_S(Q_0;t)$ decays exponentially to zero, a result found before by others by MD simulations in LJ mixtures [26] and in real glass-formers [29–31], and is a key feature of the CM. The latter stipulates that many-body relaxation has an onset time t_c determined by $V(r)$. If the relaxation time of $F_S(Q_0;t)$ becomes shorter than t_c, many-body relaxation is absent, and the relaxation proceeds exponentially with time. When temperature is lowered, the dynamics slows down and a two-step process appears composed of a first part where $F_S(Q_0;t)$ decreases toward a plateau, $f_S(Q_0;T)$, and a second part where $F_S(Q_0;t)$ decreases with a different time dependence toward zero. This behavior is well described by the mode coupling theory (MCT), where the height of the plateau $f_S(Q_0;T)$ is usually called the nonergodicity parameter [32]. However, there is an alternative interpretation of $f_S(Q_0;T)$ as coming from relaxation within the anharmonic cage with small mean square displacement $\langle u^2(T)\rangle$ limited by the size of the cage. The more anharmonic the potential, the larger is the $\langle u^2(T)\rangle$ within the cage and the lower is the plateau level $f_S(Q_0;T)$.

From the $F_S(Q_0;t)$ at each temperature, we determine $f_S(Q_0;T)$. By fitting the second step decay of $F_S(Q_0;t)$ by $f_S(Q_0;T)\exp[-(t/\tau_A)^{1-n}]$, the relaxation time τ_A and the stretch exponent, $(1-n)$ are determined. For the same τ_A, the nonexponentiality parameter n increases in the order of models I, II, and III, that is with increasing anharmonicity of $V(r)$. An arbitrarily long $\tau_A = 4.64 \times 10^4$ was chosen to compare the T_{ref}-scaled T-dependence of τ_A of the three models. Here T_{ref} is the temperature at which $\tau_A(T_{\mathrm{ref}}) = 4.64 \times 10^4$, and the values are 0.688, 0.431, and 0.263 for models I, II, and III respectively. The T_{ref}-scaled T-dependence of τ_A of the three models as well as the 'fragility' index at constant volume m_V, calculated from $\mathrm{d}\log\tau_\alpha/\mathrm{d}(T_{\mathrm{ref}}/T)$ at $T_{\mathrm{ref}}/T = 1$, increase with the anharmonicity of $V(r)$. The dependence of $1/f_S(Q_0;T)$ on T/T_{ref} is approximately linear for all three models, and well described by the equation $1/f_S(Q_0;T) = 1 + \lambda(T/T_{\mathrm{ref}})$. A similar expression represents the dependence of $f(Q;T)$ on T/T_g of real glass-formers obtained by inelastic x-ray scattering [21]. The parameter λ increases in the order of models I, II, and III or with anharmonicity. This tells us that $1/f_S(Q_0;T)$ and also the corresponding $\langle u^2(T)\rangle$ within the cage (since these two quantities are proportional to each other) increase and their (T/T_{ref})-dependences become stronger with the degree of anharmonicity. Experiments found a similar correlation between λ and the 'fragility' index [21].

Summarizing the results above, the dynamics is controlled by the potential $V(r)$ in a systematic manner. On increasing anharmonicity of $V(r)$, the α-relaxation becomes more nonexponential, the T_{ref}-scaled T-dependence of τ_A becomes stronger, the $\langle u^2(T)\rangle$ within the cage and $1/f_S(Q_0;T)$ become larger, and their T_{ref}-scaled T-dependences become stronger. Since the number of particles and density are the same, these changes are predominantly due to the change in anharmonicity and the capacity of intermolecular coupling of $V(r)$. The parameters, n, m_V, λ and the caged $\langle u^2(T/T_{\mathrm{ref}})\rangle$, which quantify the dynamic properties, all increase with anharmonicity of $V(r)$, and consequently these quantities are correlated with each other, as also found in real glass-formers by various experimental investigations [3, 4, 11]. An example is the correlation between the caged $\langle u^2(T/T_g)\rangle$ obtained by quasielastic neutron scattering and n [3, 11]. A glass-former with larger n has a larger $\langle u^2(T/T_g)\rangle$ at the same value of T/T_g and rises more rapidly as a function of T/T_g, below T_g as well as above T_g. The correlation is particularly strong when the glass-formers are restricted to the same family.

Another molecular dynamic simulation was carried out on a binary mixture of soft particles with interaction potential that includes only the interparticle repulsive potential in equation (3) and the attractive part of the potential is dropped [33]. For different powers q of the interparticle repulsive potential, the results show that the diffusion coefficients as a function of T for various values of the exponent of the repulsive potential collapse onto a single curve, thus showing that fragility is independent of the exponent q characterizing the short range repulsion. This result shows that the steepness of the potential alone does not determine the dynamics. Comparing this with the opposite finding of Bordat *et al* discussed above that fragility depends on $V(r)$, we are led to conclude that the attractive part of the potential and the anharmonicity in $V(r)$ that it produces with the repulsive part is important in the determination of dynamic properties.

Chakrabarti and Bagchi (CB) [31] performed a molecular dynamics simulation of an equimolar mixture of Gay–Berne ellipsoids of revolution and LJ spheres along an isochore at a series of temperatures down to the deeply supercooled state. For this system with orientational degrees of freedom, CB obtain for the ellipsoids of revolution the self-intermediate scattering function $F_s(k_{\max}, t)$, and the first-and second-rank single particle orientational time correlation functions, $C_1(t)$ and $C_2(t)$, involving respectively the first-order and the second-order Legendre polynomials. All three functions have time dependences well described by the Kohlrausch form at all temperatures. The Kohlrausch correlation time and exponent are designated by $\tau_D(T)$ and $\beta_D(T) \equiv (1 - n_D(T))$ respectively for $F_s(k_{\max}, t)$ where the subscript is used to indicate self-diffusion; $\tau_1(T)$ and $\beta_1(T) \equiv (1 - n_1(T))$ respectively for $C_1(t)$; and $\tau_2(T)$ and $\beta_2(T) \equiv (1 - n_2(T))$ respectively for $C_2(t)$. The values of $n_D(T)$, $n_1(T)$, and $n_2(T)$ are reproduced in figure 2 of [31]. It can be seen from the figure that all of them are very close to zero at high temperatures and increase as temperature falls. At high temperatures, $n_D(T)$, $n_1(T)$ and $n_2(T)$ are nearly zero and all correlations are exponential functions of time, and the products $D(T)\tau_2(T)$ and $D(T)\tau_2(T)$ are nearly independent of temperature, as predicted by the Debye–Stokes–Einstein (DSE) relation. However, as temperature falls, $n_D(T)$ becomes increasingly less than $n_2(T)$ but larger than $n_1(T)$. These MD simulation results show that different dynamic variables weight the effects of many-body relaxations differently. Furthermore, the product $D(T)\tau_1(T)$ shows almost no temperature dependence. This observed behavior of $D(T)\tau_1(T)$ with temperature poses difficulty to the explanation for the decoupling between rotational and translational diffusion in terms of dynamical heterogeneity [34] because this explanation necessarily predicts enhancement of translation diffusion over local rotation. A lesson learned from the MD simulations is that heterogeneous dynamics is only one of the many consequences of many-body relaxation but it cannot replace the latter.

The MD simulations of binary LJ mixtures have not produced evidence of the secondary relaxation. This may be due to the particles having no rotational degree of freedom, unlike most real glass-formers, and also the secondary relaxation may not be sufficiently well separated from the dominant α-relaxation. In fact, the primitive relaxation time τ_0 calculated by equation (2) from the parameters of $F_S(Q;t)$ of model III shown in figure 2 of [25], $\tau_A(T_{\text{ref}}) = 4.6 \times 10^4$ and $n(T_{\text{ref}}) = 0.4$, and $t_c \approx 4$, gives $\tau_0(T_{\text{ref}}) = 10^3$, and $\tau_0(T_{\text{ref}})/\tau_A(T_{\text{ref}}) = 2 \times 10^{-2}$. Assuming, $\tau_0(T_{\text{ref}}) \approx \tau_\beta(T_{\text{ref}})$, it can be seen from the same figure that the JG β-relaxation, if present, is located where $F_S(Q;t)$ is already decreasing with time. Thus, it cannot be resolved and has been considered as part of the Kohlrausch α-relaxation. The values of $n(T_{\text{ref}})$ of models II and I are approximately 0.35 and 0.30 and smaller than $n(T_{\text{ref}}) = 0.4$ of model III. For this reason, the values of $\tau_0(T_{\text{ref}}) \approx \tau_\beta(T_{\text{ref}})$ of models II and I are longer and the β-relaxation is even more difficult to resolve than that in model III. For example, $\tau_0(T_{\text{ref}})$ of model I is 3.2×10^3, and $\tau_0(T_{\text{ref}})/\tau_A(T_{\text{ref}}) = 7 \times 10^{-2}$. This comparison of $\tau_0(T_{\text{ref}}) \approx \tau_\beta(T_{\text{ref}})$ for the three models can explain the longer and more pronounced caged regime shown by the time dependence of $f_S(Q_0;T)$ in model I than in model III (see figure 2 of [25]). This is because the primitive or the JG β-relaxation is naturally the process that terminates the caged regime and a longer $\tau_0(T_{\text{ref}}) \approx \tau_\beta(T_{\text{ref}})$ means that the termination occurs at longer times.

To observe the JG β-relaxation by MD simulations it is necessary to study glass-formers that have rotational degrees of freedom. An example is the MD simulations of model miscible polymer blends consisting of chemically realistic 1,4-polybutadiene (CR-PBD) as the slow component (higher T_g) and PBD chains with reduced dihedral barriers (LB-PBD) as the fast component (lower T_g) [35–37]. The principal objective of the simulation is to study the change of dynamics of the fast LB-PBD component with increasing concentration of the slow component in the mixture. Intramolecular and intermolecular potentials are maintained constant, but the constraints imposed by the relatively immobile CR-PBD on the dynamics of LB-PBD increase with increasing concentration of CR-PBD, with the effects elucidated by the simulations. Both the α- and the JG β-relaxations of LB-PBD were found in the mixtures. An increasing presence of the slow CR-PBD component leads to a strong increase of the α-relaxation time τ_α, accompanied by an increase of breadth of the α-dispersion or decrease of the stretch exponent of the Kohlrausch function (equation (1)) used to fit the correlation function. Part of the broadening is due to concentration fluctuations in some of the mixture, but beyond it the increase of intermolecular constraints contributes to the broadening by increasing the coupling parameter n in the context of the CM [36, 38]. On the other hand, there is negligible change of the relaxation time, τ_β, of the β-relaxation, which is understandable because it is a local and independent relaxation process and the chemical structure of the two components is very similar. In fact, in this case, the energy barrier to be overcome for the rotational motion is dominant over the intermolecular potential. The resulting monotonic increase in the separation between the α- and the JG β-relaxations of LB-PBD is correlated with the monotonic increase of n. Also, one can show from the T-dependences of τ_α of LB-PBD with 90% and 50% of CR-PBD in figures 10(b) and (c) of [36] that the dependence of τ_α on the scaled temperature T_{ref}/T (i.e. 'fragility') is stronger in the mixture with more CR-PBD or intermolecular constraints. Here T_{ref} is defined by $\tau_\alpha(T_{\text{ref}}) = 10^5$ ps for the two mixtures. The fact that intermolecular constraints rule the dynamics is supported by results of systematic changes of dynamics with increase of intermolecular constraints and hence the presence of correlations between n, m, and the ratio τ_α/τ_β. These results from MD simulations are fully compatible with the experimental data of mixtures of small molecule glass-formers [38–41], and polymer blends [42–44], which have been explained by the CM [37, 38, 43–45][4].

2.2. Dependence on thermodynamic variable, T, P, υ and S

It is obvious that T, P, υ, and S influence the relaxation time τ_α or transport coefficients such as diffusion constant D and viscosity η. Instead of using free volume and configurational entropy, another approach is to express them as a function F of the product of the specific volume υ and T, with the former raised to a material specific constant γ, e.g. $\log \tau_\alpha = F(T\upsilon^\gamma)$ [46–51]. The scaling exponent γ is a measure of the effect of specific volume (or density) in its effect on the relaxation rate, relative to that due to temperature. MD simulations of the binary LJ mixtures have been performed with potentials given by equation (3) with $p = 6$ but different values of q over the range $8 \leqslant q \leqslant 36$ [52]. The results show that D is a function of $T\upsilon^\gamma$, and γ increases with q, being related to the steepness of the repulsive part of $V(r)$, evaluated around the distance of closest approach between particles. Therefore, the MD simulations demonstrate that the potential $V(r)$ also determines the dependence of the dynamics on thermodynamic variables expressed in terms of the product $T\upsilon^\gamma$. Evidently, with p fixed, a steeper repulsive potential (larger q) has a more harmonic $V(r)$. These results from simulations of the LJ mixtures can be summarized as larger γ is associated with more harmonic $V(r)$. A steeper repulsive potential and deeper potential well makes τ_α more sensitive to density than temperature, and thus gives larger γ. Larger γ means the glass-former is more sensitive to density change, and this implies reduced T_g-scaled temperature dependence of τ_α if density is kept constant and hence smaller m_V. Thus it is easy to understand why γ correlates with $1/m_\mathrm{V}$ as found for real glass-formers [53].

3. Guides from experiments

The Kohlrausch stretched exponential function (equation (1)), usually considered as the indicator of many-body relaxation, gives way to the linear exponential function at high temperatures where the relaxation time becomes comparable to or shorter than some time t_c. At lower temperatures, the Kohlrausch form of the observed relaxation or correlation function is seen but only at times longer than t_c. At times before t_c, the relaxation function has the exponential form. This property was seen by MD simulations and mentioned in the previous section. Quasielastic neutron scattering experiments have found the same property in real glass-formers [54, 55], and provided 2 ps as the approximate value of t_c for molecular glass-formers. This crossover property is found also in other many-body relaxation systems besides glass-formers [7, 56–62], and hence it is a general property. The magnitude of t_c depends on the intermolecular potential $V(r)$. A weaker $V(r)$ has longer t_c, as evidenced by several examples that are summarily discussed in [7]. This is one of several indications from experiments that $V(r)$ determines the dynamics of many-body relaxation.

Carbon based glass-formers that have rigid phenyl or benzene rings have stronger intermolecular constraints than glass-formers comprised of flexible linear carbon bonds. For polymers, we can compare polystyrene with polyisobutylene, and for small molecular glass-formers 1,2 diphenylbenzene (OTP) with glycerol [3]. Stronger intermolecular constraints yield larger n and larger isobaric steepness index m_P. However, the correlation between n and m_P can break down if the glass-formers have widely different chemical structures. This is because while n is solely determined by many-body relaxation dynamics, m_P depends also on thermodynamic variables, which can vary greatly with chemical structure.

If we consider the Kohlrausch nonexponentiality parameter n as an indicator of the many-body α-relaxation, then, the experimental fact of the invariance of the dispersion of the α-relaxation to changes in the combinations of pressure and temperature at constant τ_α is strong evidence for the α-relaxation being controlled by $V(r)$ and intermolecular constraints [63, 64]. This is just one of the recent experimental facts showing that n governs the properties of the α-relaxation of glass-formers in bulk, as well as in nano-confinement [3, 64].

Experiments also show the fundamental importance of the primitive relaxation or the JG β-relaxation, their relation to the α-relaxation, and their dependence on the intermolecular potential $V(r)$ and intermolecular constraints. The strong empirical correlation found between n and the ratio τ_α/τ_β or τ_α/τ_0 at a predetermined value of τ_α is the first indication of their fundamental importance [9, 18, 23, 65]. Glass-formers with larger n have a larger ratio of τ_α/τ_β for the same τ_α. This correlation is predicted by the CM equation (2) and $\tau_0 \approx \tau_\beta$, as verified for many glass-formers [3, 9, 18, 23]. Together they yield $\tau_\alpha/\tau_\beta = (\tau_\alpha/t_\mathrm{c})^n$, which increases monotonically with n since usually $(\tau_\alpha/t_\mathrm{c}) \gg 1$. This result can be restated as longer τ_β for glass-formers having smaller n for the same τ_α. The temperature dependence of τ_β is Arrhenius in the glassy state where $T < T_\mathrm{g}$. However, this Arrhenius temperature dependence changes to a stronger dependence at temperatures above T_g, as proven by several experiments where τ_β was directly determined from clearly resolved dielectric JG β-loss peaks without using any fitting procedure [39–41, 66, 67]. Some have used the so-called 'Williams ansatz' to fit the dielectric spectrum of unresolved JG β-relaxation and concluded that τ_β has the same Arrhenius T-dependence above and below T_g. This conclusion is dubious because the Williams ansatz assumes that the JG β-relaxation and the α-relaxation are independent processes, but NMR experiments [19] have proven otherwise. Moreover, for

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[4] In this paper, we pointed out that τ_β from simulation (and hence also τ_0) is only a little more than a decade longer than $t_\mathrm{c} = 2$ ps. In this case, the relation, $\tau_\alpha = [(1-n)t_\mathrm{c}^{-n}\tau_0]^{1/(1-n)} \approx [(1-n)t_\mathrm{c}^{-n}\tau_\beta]^{1/(1-n)}$, obtained by using the continuity of relaxation rate across t_c, is more appropriate. Thus, these equations of the CM should be used to test the simulation data against the CM, and result is good agreement with the MD simulation data.

some systems, the deviation of T-dependence of τ_β from the Arrhenius behavior of the glassy state was found also by using a fitting procedure following the Williams ansatz [40]. In general, the change of T-dependence of τ_β mimics that of τ_α as observed when crossing T_g.

The JG β-relaxation or the primitive relaxation (relaxation time) of the CM is naturally the process (time) that terminates the caged relaxation dynamics. The latter is manifested either as a plateau in the correlation function $F_S(Q_0;t)$, a nearly constant loss (NCL) in the imaginary part of the susceptibility $\chi''(\omega)$, or a small $\langle u^2(t)\rangle$ as limited by the cage size. It has also been seen in several glass-formers including OTP and salol by the optical heterodyne detected optical Kerr effect as a power law decay with temperature independent exponents close to -1 of the time derivative of the orientational correlation function [12]. At any fixed value of (T/T_g), glass-formers with smaller n have longer $\tau_\alpha(T/T_g)$ if the correlation of n with the steepness index m of the T_g-scaled T-dependence of τ_α holds. This means that a larger T/T_g is needed to have the same τ_α for glass-formers with smaller n. In concert with the aforementioned property of longer $\tau_\beta(T/T_g)$ for the same $\tau_\alpha(T/T_g)$ in glasses with smaller n, this means that a much larger T/T_g is required to have the same τ_β and the same length of the caged dynamics. This explains why the NCL was seen in polyisobutylene (a polymer with small $n = 0.45$ near $T_g = 200$ K) up to 290 K corresponding to $T/T_g = 1.45$ [10, 11]. The NCL is also preeminent in non-fragile glass-formers having small n such as B_2O_3 [68] and $ZnCl_2$ [69, 70] and this is also the reason why the MCT cannot explain the caged relaxation in these cases.

The NMR experiment showing that suppressing part of the JG β-relaxation has a consequence on the α-relaxation is direct evidence of an intimate relation between the two processes. Other indications include the T-dependence of the relaxation strength of the JG β-relaxation having an elbow shape when crossing T_g mimicking that of volume, enthalpy, and entropy [22, 67], and the increase of the JG β-relaxation time τ_β with applied pressure P [23, 63, 64]. These properties reveal that, like the α-relaxation, the JG β-relaxation is sensitive to changes in thermodynamic variables including pressure, volume, and entropy, and not just temperature as commonly believed.

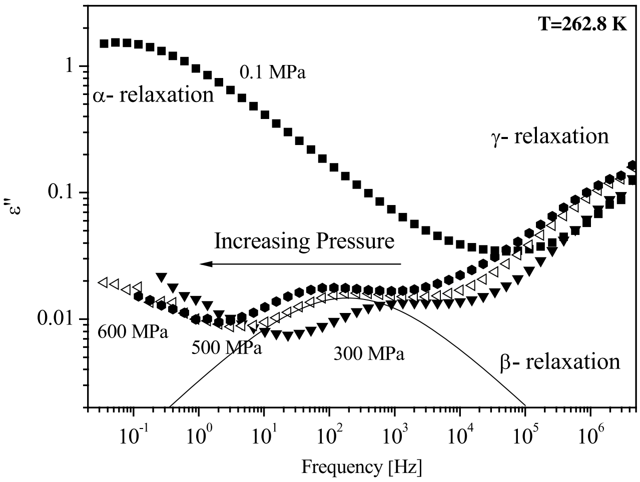

Figure 1. Dielectric loss spectra (symbols) of PPGE measured under isothermal conditions (263 K) at different values of applied pressure as indicated in the figure. The continuous line highlights the contribution of the JG β-process at 500 MPa.

To illustrate this, we present some recently acquired experimental data that show the fundamental nature of the JG β-relaxation and its inseparable relation to the α-relaxation. The data are from dielectric relaxation measurements of the glass-forming epoxy resin, poly(phenyl glycidyl ether) (PPGE), on varying both temperature and pressure P. PPGE has two secondary relaxations. Shown in figure 1 are the dielectric loss data at $T = 262.8$ K and four different pressures, 0.1, 300, 500, and 600 MPa. The slower β-relaxation resolved at elevated pressures is the JG relaxation because it shifts to lower frequencies with increasing P even in the glassy state. However, the faster γ-relaxation is invariant to P above and below T_g [23]. Figure 2 presents the τ_α and τ_β as a function of P at constant T or as a function of T at constant P. The fit by the Vogel–Fulcher–Tammann–Hesse (VFTH) equation to the measured $\tau_\alpha(T)$ at constant P is extrapolated to 10 s to obtain a reference temperature $T_{\text{ref}}(P)$ operationally defined as $\tau_\alpha(T_{\text{ref}}(P)) = 10$ s. The analog of the VFTH temperature dependence for the pressure dependence is used to extrapolate the data of $\tau_\alpha(P)$ at constant T to the reference pressure $P_{\text{ref}}(T)$ defined similarly by $\tau_\alpha(P_{\text{ref}}(T)) = 10$ s. The Arrhenius dependence on T and the linear dependence on P of $\log\tau_\beta$ are used to determine its values at $T_{\text{ref}}(P)$ and $P_{\text{ref}}(T)$ respectively. These values of τ_β are approximate because the T- and P-dependences of τ_β are known to be stronger in the equilibrium liquid state [23, 64]. Nevertheless, they all lie within the range of relaxation times indicated by the black rectangle drawn near the left y-axis. They differ from each other by no more than a factor of 3, which can be considered equivalent within the errors of the extrapolations. The result shows that at $\tau_\alpha = 10$ s, τ_β is located at about 5×10^{-6} s, independent of the combinations of P and T. This demonstrates the intimate relation between the JG relaxation and the α-relaxation, which is unchanged by variation of density or temperature. The shape of the α- loss peak is also the same for different combinations of P and T, a special case of the general behavior [63, 64]. The fit by the Kohlrausch function gives $n = 0.54$ [71] when $\tau_\alpha = 10$ s. The primitive relaxation time τ_0 as calculated by equation (2), from $\tau_\alpha = 10$ s, $n = 0.54$, and $t_c = 2$ ps, is 1.4×10^{-6} s, which is comparable to the experimental values of τ_β. Vitrification of PPGE from the liquid state to the glassy state starting with the same P_l and T_l and ending with the same P_g and T_g show that the JG relaxation spectrum and relaxation time depend on the path taken [72]. Also, near T_g, τ_β increases with aging time. These behaviors of the JG β-relaxation of PPGE indicate that it is similar and thus related to the α-relaxation, although the magnitudes of these effects is smaller. Finally for PPGE, using the $P\upsilon T$ equation of state [73], the data of τ_α measured for different P and T can be scaled to show their dependence on the product variable, $T\upsilon^\gamma$, with $\gamma = 3.45$ (figure 3).

The above discussed the similarity of properties of the JG β- and α-relaxations and their relation as found in other

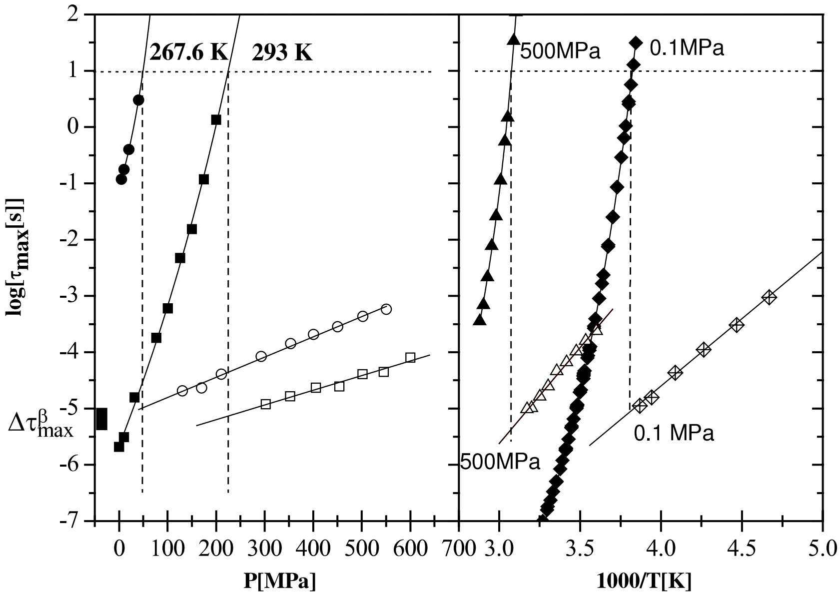

Figure 2. Plot of the structural α- (closed symbols) and JG β- (open symbols) relaxation times of PPGE against pressure at constant temperature (left panel), and against reciprocal temperature at constant pressure (right panel). The thick short line located near the extreme left y-axis indicates the range of variation of τ_β obtained at P_{ref} and at T_{ref} by extrapolation of T- and P-dependences established by data of τ_β in the glassy states respectively.

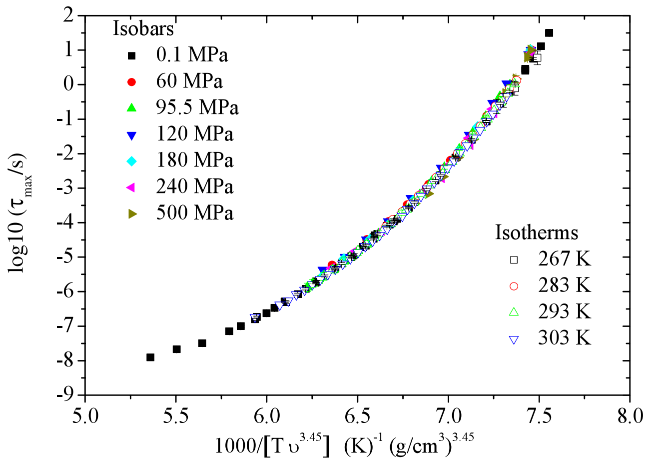

Figure 3. Dielectric α-relaxation times for PPGE obtained at different isobaric and isothermal conditions (as indicated) plotted versus the reciprocal of the product of specific volume, raised to the power of 3.45, and temperature.

(This figure is in colour only in the electronic version)

glass-formers. In passing, we mention the two simultaneous properties observed on varying the combinations of P and T while keeping τ_α constant: (1) the ratio τ_α/τ_β and (2) the dispersion of the α-relaxation are both invariant. In PPGE these two properties were observed at $\tau_\alpha = 10$ s after extrapolation. In other glass-formers such as picoline [74] and quinaldine [75] dissolved in tristyrene, these two properties have been observed at several τ_α above T_g. Thus, these extraordinary properties are general. From the invariance of the ratio τ_α/τ_β at constant τ_α and the $T\upsilon^\gamma$-dependence of τ_α, it follows that τ_β also is a function of $T\upsilon^\gamma$ albeit its functional form, $f_\beta(T\upsilon^\gamma)$, is different from $f_\alpha(T\upsilon^\gamma)$ of τ_α. Moreover, $f_\beta(T\upsilon^\gamma)$ is a weaker function of $T\upsilon^\gamma$ than $f_\alpha(T\upsilon^\gamma)$, which can be inferred from the well known fact that the ratio τ_α/τ_β increases with increasing τ_α. The importance of this result is that the $T\upsilon^\gamma$-dependence of the relaxation rate is inherent to the JG β-relaxation, which has transpired long before the α-relaxation commences. From this, the origin of the $T\upsilon^\gamma$-dependence of molecular mobility may be attributed to the JG β-relaxation. The stronger $T\upsilon^\gamma$-dependence of τ_α than τ_β is due to its many-body nature, which magnifies all effects [14].

Additional support for this statement comes from dielectric relaxation measurements obtained for various T and P on polypropylene glycol, 1,4-polyisoprene and poly(oxybutylene) [76, 77]. Both the primary α-relaxation time τ_α and the normal mode relaxation time τ_n were shown to be functions of $T\upsilon^\gamma$ with the same γ, but $f_n(T\upsilon^\gamma)$ of τ_n is weaker than $f_\alpha(T\upsilon^\gamma)$. Such a result is consistent with the CM when applied to polymer viscoelasticity [78]. In this theory, the friction factor for the normal modes of unentangled polymers is given by the friction factor of the primitive relaxation. Since the primitive relaxation has been linked to the JG β-relaxation, it follows that $f_n(T\upsilon^\gamma)$ of τ_n of unentangled polymers is the same as $f_\beta(T\upsilon^\gamma)$. The polymers studied in [76, 77] are not ideally unentangled and there is residual coupling between the normal modes. Nevertheless, the weaker dependence of τ_n on $T\upsilon^\gamma$ than τ_α has been explained by a primitive friction factor that is also a function of $T\upsilon^\gamma$ and is weaker than that of τ_α. For details, see [79].

4. Guides from concept and prediction of the coupling model

In the previous two sections, we laid out the evidence from MD simulations and experiments on real glass-formers that the intermolecular potential $V(r)$ and intermolecular constraints are the origin of the dynamics, as well as the thermodynamic properties of glass-formers. The dynamics includes caged relaxation at short times, the JG β-relaxation at intermediate times, and the many-body relaxation that builds up with increasing time, terminating at the structural α-relaxation with a correlation function described by the Kohlrausch function. Many-body relaxation is an inescapable consequence of intermolecular interaction and constraints between molecules dictated by $V(r)$. Since all dynamic and thermodynamic properties come from the same origin, it is unsurprising that the parameters characterizing them are found to be correlated, particularly when glass-formers belonging to the same chemical class are considered. Among the parameters, the nonexponentiality parameter n appearing in the exponent of the Kohlrausch correlation function (equation (1)) for the α-relaxation is a direct measure of the degree of many-body relaxation dynamics. This is supported by the findings discussed in the previous sections that the value of n (1) either governs or correlates with various properties of τ_α, (2) is invariant to changes in the combinations of pressure and temperature while maintaining τ_α constant, and (3) determines the relaxation time τ_β of the JG β-relaxation relative to τ_α. Despite these well documented empirical facts showing the relevance of the time/frequency dispersion of the α-relaxation or n to the dynamics of glass transition, most theories of glass transition do not take it into consideration.

The fundamental importance of the JG β-relaxation is indicated by (4) its 'universal' presence in all glass-formers whether or not it can be resolved, (5) the invariance of the ratio τ_α/τ_β to changes in combinations of P and T while maintaining either τ_α or τ_β constant, (6) the change of T-dependence of τ_β on crossing T_g, mimicking the behavior of τ_α, (7) its shift to longer times on physical aging below T_g, (8) the change in T-dependence of its relaxation strength on crossing T_g, mimicking that of enthalpy, volume, and entropy, (9) the interdependency of it and the α-relaxation as shown by NMR, and (10) τ_β sets the upper bound of the time regime of the caged relaxation. Again, in spite of these indications, most theories of glass transition do not consider the JG β-relaxation to play any important role in glass transition.

The coupling model (CM) is different from most if not all other theories of glass transition in the following ways. First of all, as a disclaimer, the CM cannot directly predict τ_α and its T-dependence for a given material from quantities such as free volume as in the free volume theory or the configurational entropy as in the Adam–Gibbs theory. Nevertheless, conceptually it starts with the intermolecular interaction potential $V(r)$ in either the original semiclassical approach of 1979 [5] or the subsequent phase-coupled oscillator model [6]. The latter emphasizes nonlinear Hamiltonian dynamics (chaos) originating from an anharmonic potential. These are certainly not solutions of the many-body relaxation problem, but they have emphasized the effect of many-body dynamics in slowing down the relaxation rate in addition to that due to lowering temperature. The starting point is the local and independent relaxation called the primitive relaxation and the consideration of how intermolecular interactions slow down the primitive relaxation rate $1/\tau_0$ by many-body processes. It was shown exclusively for the terminal α-relaxation that it has the Kohlrausch stretched exponential time dependence (equation (1)), n increases with stronger intermolecular interaction, and its relaxation time τ_α is related to τ_0 by equation (2). The time t_c appearing in equation (2) is the time before which the Kohlrausch function no longer holds because the effects of intermolecular interactions become operative only after t_c, the magnitude of which depends on $V(r)$ [7]. From equation (2) we can see immediately that the properties of τ_α are governed by n. The dependence of τ_α on any parameter Q is derived from that of $\tau_0(Q)$ according to $\tau_\alpha(Q) \propto \tau_0(Q)^{1/(1-n)}$. From this relation, not only can one explain the often anomalous Q-dependence of τ_α from the transparent Q-dependence of τ_0, but also that various dependences of τ_α are correlated with n and with each other.

The primitive relaxation is identifiable with a local secondary relaxation of the JG kind because it involves the entire molecule and is intimately related to the α-relaxation [23], and therefore the approximate relation, $\tau_0 \approx \tau_\beta$ is expected as verified repeatedly by experiment in many glass-formers. Replacing τ_0 by τ_β in equation (2), the resulting approximate relation

$$\tau_\alpha(T, P) \approx [t_c^{-n}\tau_\beta(T, P)]^{1/(1-n)} \tag{4}$$

explains the properties (2)–(7) given in the above.

The concepts and predictions of the CM contain the essential elements needed to build a viable theory of the glass transition that can explain all the general and important properties. As remarked before, the CM is not a full solution but it can be used as a guide to solve the problem completely and rigorously. Supported by experimental facts, it tells us that the dependence of molecular mobility on T and P, $T\upsilon^\gamma$, or any preferred thermodynamic variables first enters into τ_0 or τ_β of the primitive or the JG β-relaxation that occurs long before the α-relaxation is formed out of the involvement of many more molecules. It is through the many-body relaxation that the dependence of τ_0 or τ_β, say $T\upsilon^\gamma$, is transferred to τ_α, and is magnified by many-body effects according to equations (2) or (4). The key in these equations is the coupling parameter n. The intermolecular potential and the density of the glass-former determine not only the extent of the many-body relaxation or n, but also the density dependence of dynamics (γ parameter), the anharmonicity of vibrations, and the isochoric and isobaric 'fragility' indices.

5. Conclusion

The structural α-relaxation of glass-forming substances is naturally a many-body process because of intermolecular interaction and constraints. Therefore properties of the α-relaxation originate from many-body dynamics or are directly related to the intermolecular potential and are unsurprisingly correlated with each other. Results from molecular dynamics simulations and experiments show close relations between the Johari-Goldstein (JG) β-relaxation and the structural α-relaxation in their relaxation times τ_α and τ_β, and in various properties, indicating that they are not independent of each other. JG β-relaxation time τ_β is dependent on pressure P (volume υ) and temperature T (entropy S). The experimental results as well as the coupling model suggest that the dependence of τ_α on P, υ, and T stems from that of τ_β, and is stronger because of the many-body nature of the α-relaxation. No glass transition theory is complete without taking the fundamental JG β-relaxation and its relation to the α-relaxation into account. Many-body relaxation is still an unsolved problem in statistical mechanics. Nevertheless, basic and general features of the dynamics are found by experiments. These features can serve as guides for the construction of a satisfactory theory of glass transition. The coupling model can help in this effort because it has these features built into it, and its predictions are consistent with experimental observations.

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