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# Impact of the application of pressure on the fundamental understanding of glass transition

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## Abstract

Several remarkable dynamic properties of glass-forming materials have recently been discovered experimentally by the application of pressure. These properties have had a great impact on the research field of glass transition because they are general and fundamental, and not easy to explain. We review some of these experimental facts and show that they originate from the intermolecular interactions and many-body relaxation dynamics of the structural  $\alpha$ -relaxation. While these properties are either not explained or not explainable by conventional theories and models, they can be rationalized by the coupling model.

## 1. Introduction

The study of relaxation of glass-forming liquids by using elevated pressure has a long history. As early as 1926, Bridgman [1] measured viscosities at pressures of up to 1.2 GPa with a falling body viscometer. This was followed by more recent measurements of viscosity under applied pressure [2]. The earliest use of pressure to study the dynamics by dielectric spectroscopy measurements was probably the measurements by Gilchrist *et al* [3] on propanol and glycerol at pressures as high as 100 MPa. This was followed by others including the dielectric studies on polymers by Williams [4–6], and by Sasabe *et al* [7, 8]. Another example of early dielectric relaxation studies at elevated pressure is that of Johari and Whalley [9], and of Naoki and co-workers [10, 11]. Some examples of light scattering experiments up to about 200 MPa include the works by Fytas, Patkowski, and their co-workers [12–18]. Light scattering measurements in the gigahertz regime at 12 GPa using a diamond anvil cell have been reported [19]. A few neutron scattering experiments carried out at high pressure have been reported [20–23]. Calorimetric measurements in specially designed instruments had been carried out under pressures as high as 400 MPa [24–26].

The above cited papers are examples of investigations of properties of glass-formers under pressure, mostly in the past. These papers have shown the benefit of adding pressure as a thermodynamic variable in the study of glass transition.

However, the majority of these earlier studies are on the effect of pressure on transport coefficients and dynamics over limited spectral ranges. The emphasis is solely on the structural or primary  $\alpha$ -relaxation. Since the turn of the century, we have witnessed a significant increase of experimental investigations of the relaxation dynamics of glass-formers under elevated pressure. Often carried out by broadband dielectric relaxation spectroscopy, these more recent studies reveal the change of dynamics over wider ranges of frequency, temperature  $T$  and pressure  $P$ . The broad time/frequency range enables us to see with applied pressure the change of the primary  $\alpha$ -relaxation but also that of the fast relaxations, including the secondary relaxations. In the case of polymers, the slower normal modes of chain motion can be studied together with the  $\alpha$ -relaxation under pressure. The results of these studies are general and fundamental properties, which should have tremendous impact on our understanding of the dynamics and thermodynamics of glass-formers. In this paper, some outstanding examples are reviewed and discussed with the purpose of elucidating the cause. For instance, one property is the crossover of the  $T$ - or  $P$ -dependence of the  $\alpha$ -relaxation  $\tau_\alpha$  or viscosity  $\eta$  at the same value of  $\tau_\alpha$  or  $\eta$  independent of thermodynamic conditions, i.e. different possible combinations of  $T$ ,  $P$  and  $V$ . This remarkable and universal dynamic property has not been addressed before by any theory or model, and is the subject of a detailed treatment in this paper.

## 2. Examples of general properties of glass-formers discovered by applying pressure

### (i) Co-invariance of $\tau_\alpha$ and $n$ to changes in $P$ and $T$

Broadband dielectric relaxation measurements of glass-formers can be made at elevated pressures up to about 2 GPa, which is four orders of magnitude higher than ambient pressure of 0.1 MPa. Usually, all relaxation mechanisms of glass-formers slow down with increase in pressure. The slowing down at elevated pressure can be compensated by raising temperature. Thus different combinations of  $P$  and  $T$  can be found such that the most probable  $\alpha$ -relaxation time,  $\tau_\alpha$ , has the same value. In practice, this condition is achieved when the maxima of the dielectric loss peaks are located at the same frequency,  $\nu_\alpha$ . Concomitant with the large variations of  $P$  and  $T$  are large differences in the thermodynamic states (specific volume  $V$  and entropy  $S$ ) of the glass-formers even though they all have the same  $\tau_\alpha$ . The remarkable finding from the experimental data of many different molecular and polymeric glass-formers is that the frequency dispersion (i.e. the shape) of the  $\alpha$ -relaxation remains the same for various combinations of  $P$  and  $T$  having the same  $\tau_\alpha$ . Hydrogen bonded glass-formers are excluded because high temperature in combination with high pressure tends to break hydrogen bonds, and these glass-formers no longer have the same structure [11, 27]. Plenty of such experimental results can be found [28, 29]. In many glass-formers, the breadth of the  $\alpha$ -loss peak increases with  $\tau_\alpha$ , but the loss peaks obtained at different  $P$  and  $T$  combinations superpose well for any choice of  $\tau_\alpha$ . The frequency dispersion of the  $\alpha$ -relaxation is uniquely and well described by the one-sided Fourier transform of the Kohlrausch functions,

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

with the following caveat. When fitting the frequency dependence of the  $\alpha$ -loss peaks obtained by dielectric relaxation by the one-sided Fourier transform of the Kohlrausch function, emphasis of good agreement with the loss data is placed on the main peak especially on the low frequency side, if the conductivity contribution is not present there or the contribution has been removed if present. This fit has taken into account nearly all the dielectric or mechanical strength of the  $\alpha$ -relaxation and the viscosity if the glass-former is not polymeric. Deviations of the Kohlrausch fit to the data invariably occur at frequencies sufficiently high above the loss maximum. The deviations are considered natural in the coupling model (CM) interpretation of the evolution of dynamics with time [30–32]. They come from processes of smaller length-scales that transpire at shorter times before the dynamics evolve to the one with maximum length-scale and correlation function given by the Kohlrausch function. Thus, the experimental fact of constant dispersion at constant  $\tau_\alpha$  for different  $T$  and  $P$  can be restated as the invariance of the fractional exponent  $n$  (or the Kohlrausch exponent,  $\beta_{\text{KWW}} \equiv 1 - n$ ), which is a measure of the breadth of the dispersion. In other words,  $\tau_\alpha$  and  $n$  (or  $\beta_{\text{KWW}}$ ) are co-invariants of changing thermodynamic conditions ( $T$  and  $P$ ). This remarkable finding has immense impact on glass transition. This is because

theories or models of glass transition, in which the dispersion of the structural  $\alpha$ -relaxation is not one of the determining factors of the structural relaxation time, are unlikely to be consistent with this property by happenstance. An exception is the coupling model (CM) [30–34], whose defining equation,

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

links together  $\tau_\alpha$  and the dispersion parameter  $n$ . The crossover time  $t_c$  of the CM determined by the interaction potential is independent of  $T$  and  $P$ . Hence constant dispersion parameter  $n$  is a prerequisite to maintain a constant  $\tau_\alpha$ .

Dielectric spectroscopy was used to monitor the component dynamics in the miscible blends of poly(vinyl methylether) (PVME) and polystyrene (PS) [35, 36], and PVME and poly(2-chlorostyrene) (P2CS) [37]. For the PVME component, the shape of the segmental relaxation loss peak depends only on the relaxation time and is otherwise independent of various combinations of  $P$  and  $T$ , i.e. different thermodynamic conditions. So are the binary mixtures of the small molecular glass-formers, including picoline or quinaldine with tri-styrene [38, 39]. This property found for component dynamics in several polymer blends and van der Waals liquid mixtures is in accord with the general behavior of neat materials, and can be explained by the CM for mixtures and blends [40–44]. Due to concentration fluctuations, there is a distribution of environments  $\{i\}$  of the  $A$  molecules in the mixture  $A_{1-x}B_x$ , which in turn engenders a distribution of coupling parameters  $\{n_{Ai}\}$  and relaxation times  $\{\tau_{Aoi}\}$  of the  $A$  molecules. The loss spectrum of  $A$  is made of the superposition of losses from the distribution. Like in neat glass-formers, for each  $i$ ,  $\tau_{Aoi}$  and  $n_{Ai}$  are co-invariants to  $P$  and  $T$  combinations. Hence the superposition of losses maintains the same frequency dependence for the overall loss for different combinations of  $P$  and  $T$  provided the most probable relaxation time  $\hat{\tau}_{A\alpha}$  of the distribution  $\{\tau_{Aoi}\}$  is kept constant as found experimentally.

Recently, the same was found in the electric loss modulus spectra of a room temperature ionic liquids [45]. This glass-former is made of molecular cations and anions, which are highly coupled together in both structural and conductivity relaxations.

### (ii) Classifying secondary relaxations by the pressure dependence of relaxation time

The loss spectra of glass-formers all have the primary  $\alpha$ -relaxation, but the features at higher frequencies can vary greatly. Some have one or more than one well resolved secondary relaxation. Some have an ‘excess wing’ on the high frequency flank of the  $\alpha$ -loss peak with either an additional or no other secondary relaxation. At ambient pressure, all these features shift to lower frequencies with decreasing temperature, and temperature alone cannot distinguish them in their properties. However, this is made possible by the application of pressure. Some secondary relaxations do not shift to lower frequencies on increasing pressure, and can be considered as local motion arising from intramolecular degree of freedom and having no significance for the glass

transition. On the other hand, the secondary relaxations that shift with pressure are sensitive to change in specific volume and entropy like the  $\alpha$ -relaxation, and must be considered in any fundamental explanation of glass transition. The excess wing of some glass-formers can be transformed to a shoulder or resolved peak by various means including physical aging [46, 47], application of pressure [48], and by mixing with another glass-former with a higher  $T_g$  [49–52]. The transformations show that the excess wing is an unresolved secondary relaxation. Invariably, the excess wing, if present, shifts along with the  $\alpha$ -relaxation to lower frequencies on elevating pressure [28, 29]. Hence the unresolved secondary relaxation associated with the excess wing is also of fundamental importance. An important example can be found in the very recent studies of monosaccharides [53] in which the excess wing seen near and above  $T_g$  is transformed to a resolved secondary relaxation loss peak, proving the excess wing is the hidden secondary relaxation. Application of pressure to the monosaccharides, fructose and ribose, shifts the excess wing to lower frequencies in the former and transforms the excess wing to a shoulder in the latter. Both changes are additional evidence that the excess wings in the two monosaccharides are unresolved secondary relaxations

Most interesting are totally rigid glass-formers, like chlorobenzene, which all exhibit a single secondary relaxation [54–56]. Since they have no intramolecular degrees of freedom, the secondary relaxation must involve the motion of the entire rigid molecule. It is naturally the precursor of the  $\alpha$ -relaxation as evidenced by properties including the change of relaxation strength when crossing  $T_g$  [52, 57] and the dependence of relaxation time on applied pressure [32]. This is an important discovery and to honor the two colleagues who made it, secondary relaxations that have properties mimicking the  $\alpha$ -relaxation are summarily called the Johari–Goldstein (JG)  $\beta$ -relaxations [32]. Since the excess wing discussed above mimics the  $\alpha$ -relaxation depending on pressure and other properties, it is a JG  $\beta$ -relaxation unresolved.

Some hydrogen bonded glass-formers like *m*-fluoroaniline [58] at ambient pressure show only one prominent secondary relaxation which originates from relaxation of the hydrogen bonded clusters, and is not the JG  $\beta$ -relaxation. This latter lies in between the secondary relaxation of the hydrogen bonded clusters and the  $\alpha$ -relaxation and is unresolved. At elevated pressures and compensated by raising temperature to maintain the same relaxation time, the hydrogen bonded clusters are removed as revealed by neutron scattering [59], and the non-JG secondary relaxation is suppressed. The change of structure is accompanied by a change in dynamics shown as broadening of the  $\alpha$ -loss peak and the emergence of a new secondary relaxation, which is the JG  $\beta$ -relaxation of the new structure [58] because its relaxation time is in approximate agreement with the primitive relaxation time of the CM [32].

(iii) *Invariance of the ratio  $\tau_{JG}/\tau_\alpha$  for different  $T$  and  $P$  when  $\tau_\alpha$  is kept constant*

An advance of the CM was made [28–32] in showing that a correspondence between the primitive relaxation time  $\tau_0$  and

the JG  $\beta$ -relaxation time  $\tau_{JG}$  should exist at any temperature  $T$  and pressure  $P$ , and is given by

$$\tau_{JG}(T, P) \approx \tau_0(T, P) = t_c^n [\tau_\alpha(T, P)]^{1-n}. \quad (3)$$

The last equality in equation (3), obtained from equation (2), enables  $\tau_0$  to be calculated entirely from the parameters,  $\tau_\alpha$  and  $n$ , of the Kohlrausch correlation function for the  $\alpha$ -relaxation for molecular and polymeric glass-formers because for them  $t_c$  is known to be about 2 ps. Remarkably, the relation,  $\tau_{JG}(T, P) \approx \tau_0(T, P)$ , between the experimental  $\tau_{JG}(T, P)$  and the calculated  $\tau_0(T, P)$  holds for many small molecular and polymeric glass-formers [28–32, 38, 39].

The study of the  $\alpha$ - and JG  $\beta$ -relaxations at ambient and elevated pressures confers a bonus in achieving a complete understanding of the origin of the co-invariance of  $\tau_\alpha$  and  $n$  (or  $\beta_{KWW} \equiv 1 - n$ ) to changes in thermodynamic state of the glass-former when subjected to different combinations of  $T$  and  $P$ . The CM explanation from equation (2) discussed in (i) can be fully consistent with the observed co-invariance of  $\tau_\alpha$  and  $n$  only if the primitive relaxation time  $\tau_0$  is simultaneously invariant to different  $T$  and  $P$ . To test this, we make use of the relation  $\tau_0 \approx \tau_{JG}$  and equation (3). This relation has been shown to hold for many glass-formers by data taken at ambient pressure, whereby  $\tau_0$  calculated from the experimental quantities  $\tau_\alpha$  and  $n$  of the  $\alpha$ -relaxation by this equation is indeed approximately the same as the JG relaxation time  $\tau_{JG}$ . Thus, a critical test of the CM's explanation of the co-invariance of  $\tau_\alpha$  and  $n$ , is the concomitant invariance of  $\tau_{JG}$  to different  $T$  and  $P$ . Glass-formers having smaller  $n$  have smaller separation between  $\log \tau_\alpha$  and  $\log \tau_0$  (or  $\log \tau_{JG}$ ) according to equation (2). As a result, the JG relaxation is not resolved and appears as an excess wing on the high frequency flank of the  $\alpha$ -loss peak. Dielectric relaxation experiments carried out at elevated pressures up to 2 GPa and high temperatures to compare with data taken at ambient pressure of 0.1 MPa have shown that the shape of the entire dispersion, including the  $\alpha$ -loss peak and the excess wing, remains unchanged at constant  $\tau_\alpha$  [28, 29, 59]. Of course, the intensities or strengths of the two processes may have different  $T$ - and  $P$ -dependences and are responsible for slight deviations from perfect superposition of the data at high frequencies. These experimental data already provide experimental support of the co-invariance of  $\tau_\alpha$ ,  $n$ , and  $\tau_{JG}$ , or equivalently the co-invariance of  $\tau_\alpha$ ,  $n$ , and  $\tau_0$  as predicted by the CM. Nevertheless, it would be more complete and convincing if one could observe the co-invariance of  $\tau_\alpha$ ,  $n$ , and  $\tau_{JG}$  in glass-formers that have a resolved JG secondary relaxation. Such new data in which the JG relaxation has been resolved in the liquid state and below  $T_g$  were reported by Capaccioli and co-workers [51] in the neat glass-former benzoin-butyl-ether (BIBE) and picoline and quinaldine in mixtures with tri-styrene [38, 39, 60], and by Prevosto *et al* and Capaccioli *et al* [61] in polyphenylglycidylether (PPGE), diglycidyl ether of bisphenol-A (DGEBA), and dipropylene glycol dibenzoate (DPGDB). Co-invariance of  $\tau_\alpha$ ,  $n$ , and  $\tau_{JG}$  for different  $T$  and  $P$  were found in all these neat glass-formers and the component picoline or quinaldine in mixtures with tristirene [38, 39]. This is a remarkable experimental fact that

challenges explanation by any theory, but is fully consistent with the CM. In addition, the calculated  $\tau_0$  is in agreement with the observed  $\tau_{JG}$  within experimental uncertainty in all cases. The above-mentioned new results, again made possible by applying pressure, verify the CM explanation (equations (2)) of the invariance of the  $\alpha$ -dispersion at constant  $\tau_\alpha$  for different  $T$  and  $P$ . An implication of the results is that the volume and entropy dependences of  $\tau_\alpha$  are ultimately originating from those of  $\tau_0$  or  $\tau_{JG}$ , which has been used as the basis for constructing a theory of glass transition [31].

Consider the special case when  $\tau_\alpha$  is a sufficiently long time say  $10^3$  s which can be reached at the glass transition temperature  $T_g$  at any constant  $P$ . Although  $T_g$  is a function of  $P$ , it follows from the general property discussed in this subsection that  $\tau_{JG}(T_g)$  is the same for all  $P$ . By now it is well known that the JG relaxation time  $\tau_{JG}$  as well as its dielectric relaxation strength  $\Delta\epsilon_{JG}$  changes their temperature dependences when crossing  $T_g(P)$ . The  $\alpha$ -relaxation time  $\tau_\alpha$  usually has the Vogel–Fulcher  $T$ -dependence for  $T > T_g(P)$ , and the Arrhenius  $T$ -dependence when  $T$  is sufficiently below  $T_g(P)$ . The property of changing  $T$ -dependence when crossing  $T_g(P)$  of  $\tau_\alpha$  is mimicked by  $\tau_{JG}$  for neat glass-formers [32] as well as a component in binary mixtures [38, 39, 60]. This property is an immediate consequence of equation (3) from which one can see that the crossover of  $T$ -dependence of  $\tau_\alpha$  from Vogel–Fulcher dependence above  $T_g$  to Arrhenius dependence below  $T_g$  is transferred from  $\tau_\alpha$  to  $\tau_{JG}$  (or vice versa) in a qualitative manner. This crossover property of  $\tau_{JG}$  and the value of  $\tau_{JG}$  at  $T_g(P)$  are preserved on varying  $P$ .

(iv) *Indication of ‘fragility’ is not a basic concept or parameter*

In most if not all studies of glass transition, the time/frequency dependence of the structural  $\alpha$ -relaxation (or  $n$ ) is not considered as a basic quantity that governs the dynamics and bears a relation to the relaxation time  $\tau_\alpha$ . Instead, ‘fragility’ [62] as quantified by the steepness index [63]

$$m = d \log \tau_\alpha / d \log (T_{\text{ref}}/T) |_{T=T_{\text{ref}}} \quad (4)$$

has occupied the attention of many researchers. Here  $T_{\text{ref}}$  is the temperature at which  $\tau_\alpha$  attained an arbitrarily chosen long time. The emphasis on  $m$  is evident from the numerous attempts to correlate  $m$  with other observed dynamics, thermodynamic, vibrational, and mechanical properties [64]. The first attempt is the correlation of  $m$  with the jump in heat capacity, which has been recently withdrawn [65] in favor of correlation of  $m$  with thermodynamic fragility [66]. The thermodynamic fragility of glycerol ( $m = 53$ ) was shown to be smaller than that of cis-decalin ( $m = 147$ ), confirming the correlation. However, the thermodynamic fragility of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  is still larger than that of cis-decalin, the  $m$  value of the former was not given. The correlation would still break down unless  $m$  of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  is larger than 147 of cis-decalin. Breakdown of the correlation when considering other glass-formers was demonstrated before [67], and difficulty in obtaining the exact excess entropy for calculating thermodynamic fragility was pointed out [68].

All other correlations of  $m$  with other quantities suffer from breakdown. A recent example is that between the Poisson ratio and  $m$ , as shown by Yannopoulos and Johari [69]. Here we present results from the application of pressure to elucidate that ‘fragility’ and its index  $m$  or other indices are dependent on several factors including, volume, entropy and effects from the many-body nature of the  $\alpha$ -relaxation. All these factors influence the temperature dependence of  $\tau_\alpha$  and hence ‘fragility’ or  $m$ . It is likely that the influence of any of these factors on  $\tau_\alpha$  and  $m$  varies a great deal when considering glass-formers with widely different chemical structures and interaction potentials. Consequently, correlation of  $m$  with any other quantity can easily breakdown.

In conventional measurements of relaxation under ambient pressure, the only experimental variable is temperature, and hence thermal energy and volume effects are convoluted. With the addition of pressure to temperature as variables and PVT measurements, one can obtain  $\tau_\alpha$  of the same glass-former at constant  $T$  and varying  $V$  or density as well as a function of  $T$  at constant pressure [70], and thus the isobaric fragility index  $m_P$  at constant  $P$ , and the isochoric fragility index  $m_V$  at constant volume  $V$  from equation (4). The experimental data of many glass-formers show that neither  $T$  nor density uniquely determine  $\tau_\alpha$  since the empirical linear relation,  $m_P = 37 + 0.84m_V$ , is also found, with generally  $m_V$  less than  $m_P$ . This result may be expected since for  $m_V$  only temperature changes  $\tau_\alpha$ , while for  $m_P$  both volume and temperature contribute to change of  $\tau_\alpha$ . The values of  $m_P$  usually decrease with increasing  $P$  and densification. The only exceptions to this appear to be the hydrogen bonded materials due to a change in the chemical structures of the materials by the increase in temperature accompanying elevated pressure. The widely different values of  $m_V$  and  $m_P$  obtainable for one and the same glass-former are sufficient evidence to show that ‘fragility’ is not as fundamental as the time/frequency dispersion (or  $n$ ) of the  $\alpha$ -relaxation. From the values of  $m_V$  obtained for molecular liquids and polymers [64, 70] one can observe that there is no correlation between  $m_V$  and the nonexponentiality parameter  $n$  even when restricted to the same chemical class of glass-formers. On the other hand, on combining (i) and (iii), the result is co-invariance of  $\tau_\alpha$ ,  $n$ , and  $\tau_0$  or  $\tau_{JG}$ , independent of whether the data are obtained isobarically at any constant pressure  $P$  or isochorically at any constant volume  $V$  [70]. Merely the fact that, at constant  $\tau_\alpha$ , the time/frequency dependence (or  $n$ ) of the  $\alpha$ -relaxation remains unchanged when the glass-former is subjected to different thermodynamic conditions is remarkable. This property indicates that the time/frequency dependence of the  $\alpha$ -relaxation (or  $n$ ) is a more basic quantity than ‘fragility’.

The application of pressure also has led to the result that  $\tau_\alpha$  is a function of  $TV^\gamma$ , where  $\gamma$  is positive and varies over a wide range from zero to about 9 depending on the glass-former [70]. The size of  $\gamma$  indicates the relative contribution of  $T$  and density to  $\tau_\alpha$ . Small or zero  $\gamma$  means thermally activated relaxation and large  $\gamma$  for density dominated dynamics. By examining the values of  $\gamma$  in table 2 and  $m_P$  or  $m_V$  in table 3 in [70] of many glass-formers, it is clear that there is no correlation between  $\gamma$  and  $m_P$  or  $m_V$ , even when restricted

to the same class of glass-formers. However, by excluding hydrogen bonded glass-formers, a correlation between  $\gamma$  and  $1/m_V$  was found [71]. This correlation is understandable simply from the fact that large  $\gamma$  implies a strong dependence of  $\tau_\alpha$  on volume or density. Thus, a larger  $\gamma$  means a smaller  $m_V$  because the latter is determined from the  $T$ -dependence of  $\tau_\alpha$  by keeping  $V$  constant. The parameter  $\gamma$  has been linked to the short range repulsive part of the intermolecular potential [70, 71]. A steeper repulsive potential and deeper potential well naturally make  $\tau_\alpha$  more sensitive to density than temperature, and thus larger  $\gamma$  and smaller  $m_V$  as well as smaller  $m_P$  (or lower fragility). The last follows from the empirical linear relation between  $m_V$  and  $m_P$ . Actually these conclusions from [71] can be deduced from molecular dynamic simulations of binary Lennard-Jones liquids with three different potentials (see figure 1 in [71]) performed under constant volume [72]. The dynamics obtained from potentials with steeper repulsive potential and narrower potential well has smaller  $m_V$  and larger stretch exponent  $(1 - n)$  in the Kohlrausch function (equation (1)). The last result, not considered in [71], is particularly interesting because it means that smaller  $m_V$  or larger  $\gamma$  is linked to smaller  $n$  or a lesser degree of many-body relaxation dynamics as expected from the coupling model for the closely related Lennard-Jones systems. This link between  $1/m_V$  or  $\gamma$  with  $(1 - n)$  probably will not work when real glass-formers of different chemical structures are considered, because ‘fragility’ depends not only on temperature and density but also on the effect of many-body relaxation. This can be deduced from figure 3 of [72] where the order of increasing  $m_V$  or  $\gamma$  for 26 glass-formers is given. On comparing them with their corresponding known values of  $n$ , one can find no correlation between  $1/m_V$  or  $\gamma$  with  $(1 - n)$ .

(v) *Dependences of the global and segmental dynamics in polymers on  $TV^\gamma$ : same  $\gamma$  but different functional forms*

It is by now well known that the temperature dependence of the local segmental motion is stronger than the global chain motions [73–78]. This breakdown of thermorheological simplicity in polymers is at odds with most rheological models [79, 80], where global motions are governed by the same local friction coefficient associated with local segmental motion. Observed by dielectric relaxation, the dielectric loss peaks from global chain motions are commonly referred to as the normal modes. Recent dielectric studies at elevated pressure show that both the pressure and volume dependences of the normal mode of polypropylene glycol, 1,4-polyisoprene and poly(oxybutylene) are also weaker than those for the segmental mode [80–83]. Both the local segmental  $\alpha$ -relaxation time  $\tau_\alpha$  and the normal mode relaxation time  $\tau_n$  were shown to yield master curves when plotted versus the parameter  $TV^\gamma$ . Remarkably, the value of the exponent  $\gamma$  yielding superposition is the same for the two relaxation modes. However, notwithstanding the same  $\gamma$ , the dependence of  $\tau_\alpha$  on  $TV^\gamma$  is stronger than that of  $\tau_n$ . Such behavior is inconsistent with most models of polymer rheology, including the Rouse and tube models. However, the results had been quantitatively accounted for by the CM for the different  $TV^\gamma$ -dependences [84] following the same line as the previously

given explanation for the different  $T$ -dependence [85]. The framework of the solution of the problem supports the proposal that the temperature and volume dependences of molecular mobility, which trigger the glass transition, do not originate from the primary  $\alpha$ -relaxation. Instead, they have their origin in the primitive relaxation of the coupling model [84].

(vi) *Pressure dependence of fast relaxation from neutron and light scattering*

Study of 1,4-polybutadiene by neutron scattering was able to find different  $(T, P)$  combinations such that the static structure factor  $S(Q)$  is the same while the density constant remains constant [20]. However, the  $\alpha$ -relaxation and the fast relaxation (showing up as a susceptibility minimum) were observed to change. This result has an impact on the mode coupling theory (MCT) of glass transition [86]. In MCT, both temperature and pressure control the dynamics through the static structure factor. Hence, for the same static structure factor, the same fast relaxation and  $\alpha$ -relaxation should be observed. This basic prediction of the MCT is contradicted by the experimental findings that both the fast relaxation and  $\alpha$ -relaxation changes [20]. The contradiction suggests the fast relaxation observed in polybutadiene may not be the kind predicted by the MCT. This is not the only problem that MCT had encountered with neutron scattering data of 1,4-polybutadiene. Deviations from the MCT relation between the critical exponents  $a$  and  $b$  were found before [87].

Measurements of the high frequency depolarized light scattering susceptibility of ortho-terphenyl (OTP) were made by Patkowski *et al* over broad temperature and pressure ranges [88]. They found that the time–temperature–pressure superposition does not work for OTP in the frequency range of the susceptibility minimum, and both the  $a$  and  $b$  exponents of the MCT [86] are temperature and pressure dependent. Universal scaling of the entire susceptibility including both the  $\alpha$ -peak and the MCT susceptibility minimum is not possible, in contradiction to the analysis of incoherent neutron scattering data of OTP and the conclusion that the pressure dependences are fully compatible with MCT [89].

Let us further examine the neutron scattering data of 1,4-polybutadiene obtained by Frick *et al* [20] at different  $(T, P)$  combinations while keeping the static structure factor  $S(Q)$  and the density the same. They found for two  $(T, P)$  combinations, the one with a higher  $T$  has shorter  $\alpha$ -relaxation time  $\tau_\alpha$  and higher intensity of the fast relaxation. The fast relaxation shows up like a susceptibility minimum, but the minimum is so flat (particularly for the  $(T, P)$  combination having a higher temperature), that it resembles the high frequency ( $>1$  GHz) light scattering susceptibility data of PIB at 260 K [90]. As temperature was lowered down to  $T_g$ , the PIB data become increasingly flatter to the point that no minimum can be discerned. The fast relaxation observed is better described as the nearly constant loss (NCL). This NCL description of the fast relaxation is consistent with the data obtained by the optical Kerr effect (OKE) on benzophenone (BZP) and other glass-formers [91]. Interpreting the fast relaxation of 1,4-polybutadiene observed by neutron scattering

as NCL, an explanation was proposed [92] that showed via the CM that a shorter  $\tau_\alpha$  engenders shorter primitive relaxation time  $\tau_0$  and hence larger NCL. The  $(T, P)$  combination that has a shorter  $\alpha$ -relaxation time has a higher NCL intensity and hence a shallower susceptibility minimum. This prediction is in accord with the findings of Frick *et al* [20].

The asymptotic power laws of basic MCT [86] could not describe the NCL observed by light scattering data in PIB and by OKE in benzophenone (BZP) even at  $T$  higher than the MCT critical temperature  $T_c$ . However, by accounting for rotation–translational coupling in a schematic model, Götze and Sperl demonstrated that these data indeed are consistent with this version of MCT [93, 94]. They further showed that the fast relaxation of this schematic MCT can lead to a loss peak that is approximately described by the Cole–Cole frequency dependence, resembling that of secondary relaxation. However, Pardo *et al* [95] showed that this new spectral feature predicted by the new version of MCT is unrelated to the secondary relaxation of BZP observed by dielectric relaxation. Therefore, it is not clear whether the loss peak of this version of MCT corresponds to reality or not.

### 3. Crossover of $T$ or $P$ -dependence of $\tau_\alpha$ or $\eta$ at the same $\tau_\alpha$ or $\eta$ independent of $T, P,$ and $V$ at the crossover

This is actually the last example we give in this paper on the impact of application of pressure on glass transition. It is also the subject of detailed treatment and discussion in this paper because a theoretical explanation has not been provided before.

#### 3.1. Experimental facts

Marked changes of the temperature dependence of  $\tau_\alpha$  and viscosity  $\eta$  were found at temperatures above  $T_g$  in many glass-formers. This general phenomenon was first observed by Plazek and Magill [96, 97] in  $\eta$  of 1,3-bis(1-naphthyl)-5-(2-naphthyl)benzene (TNB). High above  $T_g$ , the viscosity of TNB is Arrhenius. On cooling TNB, the Arrhenius temperature dependence changes to Vogel–Fulcher–Tammann–Hesse (VFTH) at some temperature  $T_A$ , but this VFTH dependence does not persist all the way down to  $T_g$ . At some temperature  $T_B$  in between  $T_A$  and  $T_g$ , there is a marked change to another VFTH temperature dependence. The observation of this interesting phenomenon in many other glass-formers was made easy by using the model-independent derivative function,  $\phi_T \equiv [d \log x / d(1/T)]^{-1/2}$ , introduced by Stickel *et al* [98, 99], where  $x$  is either  $\tau_\alpha$  or  $\eta$ . Any VFTH temperature dependence of  $\tau$  or  $\eta$ ,  $A \exp[D/(T - T_0)]$ , has a corresponding  $\phi_T = (D/2.303)^{-1/2} [1 - (T_0/T)]$ . Hence, the crossover at fixed pressure,  $P_{\text{fix}}$ , can be easily seen in a plot of  $\phi_T$  against reciprocal temperature. The temperature,  $T_B$ , at which the crossover occurs and the corresponding crossover  $\alpha$ -relaxation time or viscosity,  $\tau_\alpha(T_B)$  or  $\eta(T_B)$ , were determined. Isobaric data with pressure  $P_{\text{fix}}$  the same as ambient pressure  $P_{\text{amb}}$  are more common [98–104]. Data with  $P_{\text{fix}}$  at elevated levels also show the crossover [105, 106], but  $T_B$  depends on  $P_{\text{fix}}$  and increases significantly with  $P_{\text{fix}}$ . Thus,

it is more exact to rewrite  $\tau_\alpha(T_B)$  as  $\tau_\alpha(T_B(P_{\text{fix}}))$ . In spite of the large variations of  $T_B$  and  $P_{\text{fix}}$ ,  $\tau_\alpha(T_B(P_{\text{fix}}))$  was found to be the same for all  $P_{\text{fix}}$ .

The dynamic crossover is also evident in measurements taken as a function of pressure at fixed temperature,  $T_{\text{fix}}$  [107–109]. The pressure dependence of  $\tau_\alpha$  and  $\eta$  can be well described [9, 110] by the VFTH-like pressure dependence,  $x(P) = x_0 \exp[D_P P / (P_0 - P)]$ . In this case, the derivative function is  $\phi_P = [d \log(x) / dP]^{-1/2}$ , which transforms the VFTH-like pressure dependence of  $x(P)$  to  $\phi_P = a - bP$ . The crossover from one VFTH-like pressure dependence to another at  $P_B$  can be clearly seen in a plot of  $\phi_P$  against  $P$ , and the  $\alpha$ -relaxation time at the crossover,  $\tau_\alpha(P_B)$  or  $\eta(P_B)$ , determined. The crossover occurs for different choices of  $T_{\text{fix}}$ .  $P_B$  depends on  $T_{\text{fix}}$ , increasing significantly with  $T_{\text{fix}}$ . Thus, we may write  $\tau_\alpha(P_B)$  or  $\eta(P_B)$  as  $\tau_\alpha(P_B(T_{\text{fix}}))$  or  $\eta(P_B(T_{\text{fix}}))$ .

The remarkable finding by experiments on several different glass-formers is that  $\tau_\alpha(P_B(T_{\text{fix}}))$  or  $\eta(P_B(T_{\text{fix}}))$  does not depend on  $P_B$  and  $T_{\text{fix}}$ . Moreover, the constant value  $\tau_\alpha(P_B(T_{\text{fix}}))$  or  $\eta(P_B(T_{\text{fix}}))$  obtained from crossover at  $P_B$  at fixed  $T_{\text{fix}}$  is the same as  $\tau_\alpha(T_B(P_{\text{fix}}))$  or  $\eta(T_B(P_{\text{fix}}))$  from crossover at  $T_B$  at fixed pressure  $P_{\text{fix}}$ . The crossover is seen under widely different thermodynamic conditions (pressure, temperature, and volume), but  $\tau_\alpha$  and  $\eta$  at the crossovers is a constant for a given glass-former.

The crossover from one VFTH dependence to another was also found generally under constant volume (isochoric) conditions for phenylphthalein-dimethylether (PDE), 62% chlorinated biphenyl (PCB62), cresolphthalein-dimethylether (KDE), propylene carbonate (PC), 1,1'-di(4-methoxy-5-methylphenyl)-cyclohexane (BMMPC), and salol. The isochoric curve,  $[d \log \tau_\alpha / d(1/T)]^{-1/2}$  was calculated at some constant specific volume  $V_{\text{fix}}$  [70, 105]. From the crossover, the crossover temperatures  $T_B(V_{\text{fix}})$  and relaxation times  $\tau_\alpha(T_B(V_{\text{fix}}))$  at constant  $V$  were obtained. Remarkably,  $\tau_\alpha(T_B(V_{\text{fix}}))$  under isochoric conditions is the same as  $\tau_\alpha(T_B(P_{\text{fix}}))$  under isobaric conditions for all five glass-formers studied.

Although  $\tau_\alpha(T_B(P_{\text{fix}})) \approx \tau_\alpha(P_B(T_{\text{fix}})) \approx \tau_\alpha(T_B(V_{\text{fix}}))$  holds for many glass-formers, their common value differs greatly when all the glass-formers studied are considered. The values are not confined within the narrow range of  $10^{-6.5}$ – $10^{-7.5}$  s, as surmised by Novikov and Sokolov [104]. For example, PDE has the longest relaxation times with  $\tau_\alpha(T_B) = 10^{-3.6}$  s; PCB62 has  $\tau_\alpha(T_B) = 10^{-5.9}$  s; BMMPC has  $\tau_\alpha(T_B) = 10^{-6.1}$  s; KDE and salol has  $\tau_\alpha(T_B) = 10^{-6.3}$  s; and PC has  $\tau_\alpha(T_B) = 10^{-7.0}$  s [98, 99, 108]. The epoxy, diglycidyl ether of bisphenol-A (DGEBA), has  $T_B = 275$  K and  $\tau_\alpha(T_B) = 10^{-4.3}$  s [111]. From these results alone, it is sufficient to conclude that  $\tau_\alpha(T_B)$  varies over a wide range (nearly four orders of magnitude from  $10^{-3.6}$  to  $10^{-7.5}$  s) when the above-mentioned glass-formers are considered. Hence, the results invalidate the claim by Novikov and Sokolov that  $\tau_\alpha(T_B)$  has the ‘magic’ values lying within the narrow range of  $10^{-7.0 \pm 0.5}$  s [104]. Connection of the crossover temperature  $T_B$  to the critical temperature  $T_c$  of mode coupling theory was also made by them. This proposal is questionable because of the fact that PDE has  $\tau_\alpha(T_B) = 10^{-3.6}$  s. It is inconceivable that

such a long or macroscopic relaxation time can be consistent with the much shorter relaxation time at  $T_c$  of mode coupling theory.

### 3.2. Coupling model explanation

As reviewed by Roland *et al* [70], various theoretical models either anticipate or interpret this dynamic crossover seen in many glass-formers at  $T_B$ , but the explanations offered are widely different. Most of the explanations either cannot or have not explained the general and remarkable property of the crossover, namely  $\tau_\alpha(T_B(P_{\text{fix}})) \approx \tau_\alpha(P_B(T_{\text{fix}})) \approx \tau_\alpha(T_B(V_{\text{fix}}))$ , not to say the other properties (i) and (iii) in section 2. We now show that this property is a natural consequence of the CM description of glass transition. First, we give an explanation for the origin of the dynamic crossover. Next, we show that at the dynamic crossover,  $\tau_\alpha$  is independent of the thermodynamic conditions of the glass-former.

In his thesis on dielectric relaxation of glass-formers at ambient pressure  $P_{\text{amb}}$ , Stickel [98] plotted the full-width at half maximum of the dielectric loss peak normalized to that of an ideal Debye loss peak,  $w(T)$ , as a function of temperature. From these results, the corresponding Kohlrausch nonexponentiality parameters  $n(T, P_{\text{amb}})$  were readily calculated by the relation of Dixon [112],  $[1 - n(T, P_{\text{amb}})] \equiv \beta_{\text{KWW}}(T, P_{\text{amb}}) = 1 - 1.047[1 - w(T, P_{\text{amb}})^{-1}]$ , for the glass-formers Stickel studied. For other glass-formers not reported in Stickel's thesis,  $n(T, P_{\text{amb}})$  were obtained by fitting the dielectric loss spectra by the one-sided Fourier transform of the Kohlrausch function. Examples of the temperature dependences of  $n(T, P_{\text{amb}})$  so obtained can be found in [47, 113–115], which exhibit the following general property. For molecular glass-formers, when  $T > T_B(P_{\text{amb}})$ , the values of  $n(T, P_{\text{amb}})$  are smaller and slowly varying with decreasing temperature. But, when past  $T \sim T_B(P_{\text{amb}})$ , more rapid increase of  $n(T, P_{\text{amb}})$  towards significantly larger value at  $T_g(P_{\text{amb}})$  is evident in the regime of  $T < T_B(P_{\text{amb}})$ . In addition, the absolute value of  $dn(T, P_{\text{amb}})/dT$  suffers a change when crossing a temperature near  $T_B$ . The increase of  $n(T, P_{\text{amb}})$  from  $T_B(P_{\text{amb}})$  down to  $T_g(P_{\text{amb}})$ , measured by  $[n(T_g, P_{\text{amb}}) - n(T_B, P_{\text{amb}})]$ , was found to correlate with the extent of the difference between the high and low temperature VFTH functions when both are evaluated at  $T_g(P_{\text{amb}})$ . This can be seen in figure 2 in [116] in comparing OTP ( $n(T_g, P_{\text{amb}}) \approx 0.5$ ,  $T_g(P_{\text{amb}}) = 244$  K,  $T_B(P_{\text{amb}}) = 290$  K) with propylene glycol ( $n(T_g, P_{\text{amb}}) \approx 0.25$ ,  $T_g(P_{\text{amb}}) = 167$  K,  $T_B(P_{\text{amb}}) = 280$  K). OTP having larger  $[n(T_g, P_{\text{amb}}) - n(T_B, P_{\text{amb}})]$  exhibits a larger difference between the two VFTH at  $T_g(P_{\text{amb}})$  than propylene glycol.

The change of the temperature dependence of the dynamics causing the crossover of the  $T$ -dependence of  $\tau_\alpha$  at  $T_B$  is expected to have an effect on the relaxation strength. This is because both the relaxation strength and the relaxation time  $\tau_\alpha$  are characteristics of the dynamics, and this has led Schönhals [117] to look for correlated changes of behavior of  $\tau_\alpha$  and the dielectric relaxation strength  $\Delta\varepsilon$  at  $T_B$  by broadband dielectric measurements. The correlated changes indeed exist when  $\Delta\varepsilon$  is plotted against  $\log f_p$  for dibutyl phthalate, salol,

propylene carbonate, propylene glycol, dipropylene glycol, and poly(propylene glycol) [117, 118]. Here  $f_p$  is the dielectric  $\alpha$ -loss peak frequency and is approximately equal to  $1/(2\pi\tau_\alpha)$ . These plots indicate two different frequency regions of dynamics separated by  $f_B$ . The two relations when extrapolated intersect at a crossover frequency  $f_B$ . It turns out that for all the glass-formers  $f_B$  is nearly the same as  $1/[2\pi\tau_\alpha(T_B)]$ . Similar results were found also for the polymer, poly(vinyl acetate) [115, 119]. Therefore, the change of the dependence of  $\Delta\varepsilon$  on  $\log f_p$  also occurs at the temperature  $T_B$ . This phenomenon can also be explained by the more rapid increase of  $n$  with decreasing temperature (frequency) after crossing  $T_B$  ( $f_B$ ), because  $n$  reflects the extent or length-scale of the many-body relaxation and in turn the magnitude of  $\Delta\varepsilon$ . The temperature dependence of  $\Delta\varepsilon$  is roughly proportional to  $1/T$  at temperatures much higher than  $T_B$ , consistent with the Kirkwood–Fröhlich theory based on the assumption of non-interacting isolated dipoles as well as the smaller coupling parameter. However, this dependence does not continue when temperature is lowered to approach  $T_B$  and below  $T_B$ . Thus, the observed change of  $T$ -dependence of  $\Delta\varepsilon$  is another indication of the increase of coupling and cooperativity (or  $n$ ) of the  $\alpha$ -relaxation with falling temperature after crossing  $T_B$ .

In the framework of the CM,  $n(T, P_{\text{amb}})$  is a measure of the strength of the intermolecular coupling or cooperativity. Thus the behavior of  $n(T, P_{\text{amb}})$  can be reinterpreted as a change from a slow increase of intermolecular coupling from small starting value with decreasing temperature above  $T_B(P_{\text{amb}})$  to a more rapid increase to larger values after crossing  $T_B(P_{\text{amb}})$ . This opened up the possibility of explaining the crossover of the temperature dependence of  $\tau_\alpha(T, P_{\text{amb}})$  at  $T_B(P_{\text{amb}})$  by the CM because in this model the  $\tau_\alpha(T, P_{\text{amb}})$  and its  $T$ -dependence are controlled by  $n(T, P_{\text{amb}})$  via equation (2). If this change in dynamics is a consequence of the more rapid development of stronger intermolecular coupling after crossing  $T_B$  from above, then removal of the effects of intermolecular coupling should likewise remove the crossover. The primitive relaxation is devoid of intermolecular coupling. Hence its relaxation time,  $\tau_0(T, P_{\text{amb}})$ , should not show any change in temperature dependence across  $T_B(P_{\text{amb}})$ . This prediction was assessed by using equation (3) to calculate  $\tau_0(T, P_{\text{amb}})$  from the experimentally determined values of  $\tau_\alpha(T, P_{\text{amb}})$  and  $n(T, P_{\text{amb}})$ . The temperature dependence of  $\tau_0(T, P_{\text{amb}})$  is expected to vary smoothly across  $T_B(P_{\text{amb}})$ , in accord with a single VFTH dependence due only to changes of configurational entropy and/or specific volume with temperature [120]. This procedure was carried out for PDE, salol, PC, OTP, and 54% chlorinated biphenyl (PCB54) using their ambient pressure dielectric data. While the derivative function  $\phi_T \equiv [d \log \tau_\alpha / d(1/T)]^{-1/2}$  exhibits a break at  $T_B(P_{\text{amb}})$  indicating the change in dynamics of  $\tau_\alpha(T, P_{\text{amb}})$ , it is absent in the plot of the corresponding  $\phi_T$  for  $\tau_0(T, P_{\text{amb}})$ . A single VFT equation describes well  $\tau_0(T, P_{\text{amb}})$  over the entire temperature range [120].

The next task is to explain why the same crossover is observed not only as a function of temperature at ambient pressure  $P_{\text{amb}}$  but also at any fixed elevated pressures  $P_{\text{fix}}$  or at any constant volume  $V_{\text{fix}}$ , and also as a function



of pressure at any fixed temperatures  $T_{\text{fix}}$ . Moreover, the same crossover time for all conditions, i.e.  $\tau_\alpha(T_B(P_{\text{fix}})) \approx \tau_\alpha(P_B(T_{\text{fix}})) \approx \tau_\alpha(T_B(V_{\text{fix}}))$ , also has to be explained. These general properties either have not been explained or are not explainable by conventional theories and models. In the framework of the CM, the explanation goes as follows. First, let us recall the co-invariance of  $\tau_\alpha(P, V, T)$  and  $n(P, V, T)$  to all thermodynamic conditions discussed in (i) and (iii) of section 2, a property consistent with the CM predictions. It follows from the co-invariance, irrespective of the choice of the elevated pressure,  $P_{\text{fix}}$ , if  $\tau_\alpha(T', P_{\text{fix}})$  is the same as  $\tau_\alpha(T, P_{\text{amb}})$  then necessarily we have  $n(T', P_{\text{fix}})$  the same as  $n(T, P_{\text{amb}})$ , and the following as special cases. First, for some  $T'_B(P_{\text{fix}})$  such that  $\tau_\alpha(T'_B, P_{\text{fix}}) = \tau_\alpha(T_B, P_{\text{amb}})$ , also  $n(T'_B, P_{\text{fix}})$  is equal to  $n(T_B, P_{\text{amb}})$ . Second, exactly as in the case of ambient pressure,  $n(T', P_{\text{fix}})$  is small if  $T' > T'_B(P_{\text{fix}})$ , but as  $T'$  falls below  $T'_B(P_{\text{fix}})$ , it increases towards the significantly larger value of  $n(T'_g, P_{\text{fix}})$  at  $T'_g(P_{\text{fix}})$ . Hence, the explanation of the crossover of  $\tau_\alpha(T, P_{\text{amb}})$  at  $T_B$ , as a consequence of the development of stronger coupling or cooperativity when  $T$  falls below  $T_B(P_{\text{amb}})$  applies to the crossover of  $\tau_\alpha(T', P_{\text{fix}})$  at  $T'_B$ . Similar reasoning as given above leads to the same conclusion for the crossover of  $\tau_\alpha(P, T_{\text{fix}})$  at  $P_B$  and the crossover of  $\tau_\alpha(T'', V_{\text{fix}})$  at  $T''_B$ . The calculated primitive relaxation times  $\tau_0(P, T_{\text{fix}})$  by equation(3) from  $\tau_\alpha(P, T_{\text{fix}})$  and  $n(P, T_{\text{fix}})$  no longer exhibit a crossover. The same conclusion is obtained when a similar argument is applied to  $\tau_0(T'', V_{\text{fix}})$  calculated from  $\tau_\alpha(T'', V_{\text{fix}})$  and  $n(T'', V_{\text{fix}})$ .

### 3.3. Other related dynamic properties

The dynamic crossover of the temperature dependence of  $\tau_\alpha$  is manifested in other properties at temperatures near  $T_B$ . Decoupling of translational and rotational motions (i.e. breakdown of Stokes–Einstein and Debye–Stokes–Einstein relations) occurs below a temperature which is near  $T_B$  [121–125]. A popular explanation offered is based upon the spatially heterogeneous dynamics in supercooled liquids [124, 126]. It assumes that regions of differing dynamics give rise to the Kohlrausch relaxation function in ensemble averaging measurements. The decoupling between self-diffusion and rotation was argued to occur because  $D$  and the rotational correlation time  $\tau_c$  are averages over different moments of the distribution of relaxation times, with  $D \propto \langle 1/\tau \rangle$  emphasizing fast dynamics, while  $\tau_c \propto \langle \tau \rangle$  is determined predominantly by the slowest molecules. In order for this explanation to be consistent with the observed monotonic increases of the products  $D\eta$  and  $D\tau_c$  as the temperature is lowered toward  $T_g$ , the breadth of the rotational  $\alpha$ -relaxation time distribution (or the nonexponentiality parameter  $n_\alpha$ ) has to increase correspondingly. However, Richert and co-workers [127–129] reported that the dielectric spectra of trisnaphthylbenzene (TNB), ortho-terphenyl and sucrose benzoate are all characterized by a temperature independent width from  $T_B$  down to  $T_g$ , as well as photon correlation spectroscopic and NMR measurements for TNB [130]. Thus, the explanation based on spatial heterogeneities is contradicted by the data of TNB, ortho-terphenyl and sucrose benzoate. It is also contradicted by

the results of molecular dynamics simulation of an equimolar mixture of Gay–Berne ellipsoids of revolution and Lennard–Jones spheres along an isochore at a series of temperatures down to the deeply supercooled state [131, 132]. There is an alternative explanation of the breakdown of Stokes–Einstein and the Debye–Stokes–Einstein relations by the CM based on  $n_\alpha$  being larger than the translational coupling parameter  $n_t$  [132, 133], which holds irrespective of the temperature dependence of  $n$  below  $T_B$  as long as there is the onset of stronger intermolecular coupling below  $T_B$  which invariably holds [132, 133]. This CM explanation works in other cases [134, 135] where the spatial heterogeneous explanation fails. An analog of breakdown of the Debye–Stokes–Einstein (DSE) relation is found in many glass-formers when comparing translational diffusion of impurity ions from dc conductivity  $\sigma_{\text{dc}}$  and rotational relaxation time  $\tau_\alpha$  of the host molecules measured by dielectric spectroscopy [70]. Instead of  $\sigma_{\text{dc}}\tau_\alpha = \text{constant}$ , independent of  $T$  and  $P$ , the fractional DSE relation

$$\sigma_{\text{dc}}(\tau_\alpha)^s = \text{constant} \quad (5)$$

is found with  $s < 1$ . Usually, the fractional exponent  $s$  is the same for variations of  $T$  (isobaric measurements) as for variations of  $P$  (isothermal measurements), although there are a few exceptions [70]. There is enhancement of the translational motions over the rotations, and the degree of decoupling (or  $s$ ) is the same for the  $T$ - and  $P$ -dependences. This property is consistent with the CM explanation of the decoupling based on the difference of the coupling parameters for rotation  $n_\alpha$  and translation. This is because the CM has already explained the property discussed in section 2 (i) that  $n_\alpha$  is the same for the same  $\tau_\alpha$ , and similarly  $n_t$  is the same for the same  $\sigma_{\text{dc}}$ . The CM prediction of the same fractional exponent  $s$  for variations of  $T$  (isobaric measurements) as for variations of  $P$  (isothermal measurements) then follows from the same property for the two coupling parameters  $n_\alpha$  and  $n_t$ .

The Johari–Goldstein  $\beta$ -relaxation appears to start splitting off from the structural  $\alpha$ -relaxation when temperature falls below a temperature  $T_\beta$ , which is also near  $T_B$ . Equation (3) of the CM, when rewritten as

$$\log(\tau_\alpha(T)) - \log(\tau_{\text{JG}}(T)) = n(T)[11.7 + \log(\tau_\alpha(T))], \quad (6)$$

indicates that the separation between  $\tau_\alpha$  and  $\tau_{\text{JG}}$  in the logarithmic scale is proportional to  $n$  at constant  $\tau_\alpha$ . Hence, one requirement of the onset of splitting of the JG  $\beta$ -relaxation from the  $\alpha$ -relaxation at  $T_\beta$  is a sufficiently large value of  $n$  below  $T_B$ . The separation,  $\log(\tau_\alpha) - \log(\tau_{\text{JG}})$ , has a small value at  $T_\beta \approx T_B$  and increases monotonically with decreasing temperature. This is consistent with equation (6) because of the factor  $n(T)[11.7 + \log(\tau_\alpha(T))]$  on its right-hand side. This factor increases with  $\log(\tau_\alpha(T))$  on decreasing temperature, independently of whether  $n(T)$  increases or remains constant below  $T_\beta \approx T_B$ .

Another characteristic of  $T_B$  is that it marks the temperature at which the linear relation between  $\log \tau_\alpha$  and the reciprocal of the product  $TS_c$  of temperature and configurational entropy  $S_c$  predicted by the Adam–Gibbs model [136] breaks down. Found in many different glass-formers,  $\tau_\alpha$  has different dependences on  $TS_c$  above and below

$T_B$  [137, 138]. The Adam–Gibbs model makes no explicit consideration of the many-body interactions, at least that part giving rise to the dynamic heterogeneity and nonexponentiality inherent to the supercooled state of glass-formers. As we have seen in the discussion of other properties, the change in dynamics on crossing  $T_B$  is due to changes in the many-body relaxation dynamics. However, the Adam–Gibbs model is based solely on thermodynamic considerations. Therefore, the Adam–Gibbs model cannot account for the change in dynamics on crossing  $T_B$ , and the predicted linear relation between  $\log \tau_\alpha$  and  $(TS_c)^{-1}$  does not hold both below and above  $T_B$ . On the other hand, the logarithm of the calculated primitive relaxation time,  $\log \tau_0$ , was found to be a linear function of  $(TS_c)^{-1}$  [115, 138]. This suggests that  $\tau_0$  as well as  $\tau_{JG}$  is already dependent on entropy, which is an important point in the construction of a fundamental theory of glass transition [31].

#### 4. Conclusions

The results from the recent flourish of studies on the dynamics of glass-formers under elevated pressures have had a great impact on the glass transition research frontier. Striking and yet general and fundamental properties have been found. Some examples of these properties are summarized and discussed in this paper. They must be taken into consideration in any serious attempts to solve the long-standing problem of glass transition. The implication of these properties is that intermolecular coupling and many-molecule relaxation dynamics are important factors that control the dynamic properties, in addition to volume, entropy, pressure, and temperature. This conclusion is evident from the prominent role played by the width of the dispersion of the  $\alpha$ -relaxation or equivalently the Kohlrausch nonexponentiality parameter  $n$ , which is a measure of the degree of intermolecular coupling. Any theoretical model must include both thermodynamics and many-body dynamics in order to accurately describe the general properties of the glass transition including those discovered by applying pressure. At the present time, among the different theories and models, only the coupling model has predictions that are consistent with these experimental facts. This is because the coupling model takes into account the effect of intermolecular coupling and the important relation of the Johari–Goldstein (JG)  $\beta$ -relaxation (or the primitive relaxation of the model) to the structural  $\alpha$ -relaxation. However, the coupling model is not a complete theory of glass transition. A complete theory would have to provide a first-principles account of the JG  $\beta$ -relaxation together with a rigorous treatment of intermolecular coupling, leading to the heterogeneous many-molecule dynamics of the  $\alpha$ -relaxation, together with the effects of volume, entropy, pressure, and temperature. Construction of such a complete satisfactory theory is understandably difficult and it may not be available in the near future.

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#### References

- [1] Bridgman P W 1926 *Proc. Am. Arts Sci.* **61** 57
- [2] Schug K U, King H E Jr and Böhmer R 1998 *J. Chem. Phys.* **109** 1472
- [3] Gilchrist A, Earley J E and Cole R H 1957 *J. Chem. Phys.* **26** 196
- [4] Williams G 1964 *Trans. Faraday Soc.* **60** 1548
- [5] Williams G 1979 *Adv. Polym. Sci.* **33** 60
- [6] McCrum N G, Read B E and Williams G 1991 *Anelastic and Dielectric Effects in Polymeric Solids* (New York: Dover)
- [7] Sasabe H and Saito S 1968 *J. Polym. Sci. Polym. Phys. Edn* **6** 1401
- [8] Sasabe H, Saito S, Asahina M and Kakutani H 1969 *J. Polym. Sci. Polym. Phys. Edn* **7** 1405
- [9] Johari G P and Whalley E 1972 *Faraday Symp. Chem. Soc.* **6** 23
- [10] Naoki M, Matsumoto K and Matsushita M 1986 *J. Phys. Chem.* **90** 4423  
Naoki M, Endou H and Matsumoto K 1987 *J. Phys. Chem.* **91** 4169
- [11] Naoki M and Katahira S 1991 *J. Phys. Chem.* **95** 431  
Naoki M, Ujita K and Kashima S 1993 *J. Phys. Chem.* **97** 12356
- [12] Fytas G, Dorfmueller Th and Wang C H 1983 *J. Phys. Chem.* **87** 5041
- [13] Fytas G, Patkowski A, Meier G and Dorfmueller Th 1982 *Macromolecules* **15** 21
- [14] Gapinski J, Paluch M and Patkowski A 2002 *Phys. Rev. E* **66** 011501
- [15] Paluch M, Roland C M, Casalini R, Meier G and Patkowski A 2003 *J. Chem. Phys.* **118** 4578
- [16] Patkowski A, Matos Lopes M and Fischer E W 2003 *J. Chem. Phys.* **119** 1579
- [17] Dreyfus C, Aouadi A, Gapinski J, Matos-Lopes M, Steffen W, Patkowski A and Pick R M 2003 *Phys. Rev. E* **68** 011204
- [18] Dreyfus C, Le Grand A, Gapinski J, Steffen W and Patkowski A 2004 *Eur. J. Phys.* **42** 309
- [19] Oliver W F, Herbst C A, Lindsay S M and Wolf G H 1991 *Phys. Rev. Lett.* **67** 2795
- [20] Frick B, Alba-Simionesco C, Andersen K H and Willner L P 2003 *Phys. Rev. E* **67** 051801
- [21] Tölle A 2001 *Rep. Prog. Phys.* **64** 1473
- [22] Cailliaux A, Alba-Simionesco C, Frick B, Willner L and Goncharenko I 2003 *Phys. Rev. E* **67** 010802
- [23] Frick B, Dosseh G, Cailliaux A and Alba-Simionesco C 2003 *Chem. Phys.* **292** 311
- [24] Atake T and Angell C A 1979 *J. Phys. Chem.* **83** 3218
- [25] Takahara S, Ishikawa M, Yamamuro O and Matsuo T 1999 *J. Phys. Chem. B* **103** 792  
Yamamuro O, Takahara S and Suga H 1995 *J. Non-Cryst. Solids* **183** 144
- [26] Alba-Simionesco C 1994 *J. Chem. Phys.* **100** 2250
- [27] Okuchi T, Cody G D, Ho-kwang Mao and Hemley R J 2005 *J. Chem. Phys.* **122** 244509
- [28] Ngai K L, Casalini R, Capaccioli S, Paluch M and Roland C M 2005 *J. Phys. Chem. B* **109** 17356
- [29] Ngai K L, Casalini R, Capaccioli S, Paluch M and Roland C M 2006 *Adv. Chem. Phys. Part B* vol 133 *Fractals, Diffusion and Relaxation in Disordered Complex Systems* ed Y P Kalmykov, W T Coffey and S A Rice (New York: Wiley) chapter 10, p 497
- [30] Ngai K L 2003 *J. Phys.: Condens. Matter* **15** S1107
- [31] Ngai K L 2005 *J. Non-Cryst. Solids* **351** 2635
- [32] Ngai K L and Paluch M 2004 *J. Chem. Phys.* **120** 857

- [33] Ngai K L and Tsang K Y 1999 *Phys. Rev. E* **60** 4511
- [34] Ngai K L 2001 *IEEE Trans. Dielectr. Electr. Insul.* **8** 329
- [35] Alegria A, Gomez D and Colmenero J 2002 *Macromolecules* **35** 2030
- [36] Floudas G 2003 *Broadband Dielectric Spectroscopy* ed F Kremer and A Schönhals (Berlin: Springer) chapter 8
- [37] Roland C M, McGrath K J and Casalini R 2006 *Macromolecules* **39** 3581
- [38] Mierzwa M, Pawlus S, Paluch M, Kaminska E and Ngai K L 2008 *J. Chem. Phys.* **128** 044512
- [39] Kessairi K, Capaccioli S, Prevosto D, Lucchesi M, Sharifi S and Rolla P A 2008 *J. Phys. Chem. B* **112** 4470
- [40] Roland C M and Ngai K L 1991 *Macromolecules* **24** 2261
- [41] Roland C M and Ngai K L 1992 *Macromolecules* **25** 363
- [42] Roland C M and Ngai K L 2000 *Macromolecules* **33** 3184
- [43] Roland C M and Ngai K L 1995 *Macromolecules* **28** 4033
- [44] Alegria A, Colmenero J, Ngai K L and Roland C M 1994 *Macromolecules* **27** 4486
- [45] Capaccioli S and Ngai K L 2005 *Phys. Chem. B* **109** 9727
- [46] Ngai K L and Roland C M 2004 *Rubber Chem. Technol. Rubber Rev.* **77** 579
- [47] Rivera-Calzada A, Kaminski K, Leon C and Paluch M 2008 *J. Phys. Chem. B* **112** 3110
- [48] Lunkenheimer P, Pimenov A and Loidl A 1997 *Phys. Rev. Lett.* **78** 2995
- [49] Ngai K L, Lunkenheimer P, Léon C, Schneider U, Brand R and Loidl A 2001 *J. Chem. Phys.* **115** 1405
- [50] Casalini R and Roland M 2004 *Phys. Rev. B* **69** 094202
- [51] Blochowicz T and Rössler E A 2004 *Phys. Rev. Lett.* **92** 225701
- [52] Capaccioli S, Kessairi K, Prevosto D, Lucchesi M and Ngai K L 2006 *J. Non-Cryst. Solids* **352** 4643
- [53] Capaccioli S, Kessairi K, Prevosto D, Lucchesi M and Rolla P A 2007 *J. Phys.: Condens. Matter* **19** 205133
- [54] Capaccioli S, Ngai K L and Shinyashiki N 2007 *J. Phys. Chem. B* **111** 8197
- [55] Kaminski K, Kaminska E, Paluch M, Ziolo J and Ngai K L 2006 *J. Phys. Chem. B* **110** 25045
- [56] Johari G P and Goldstein M 1970 *J. Chem. Phys.* **53** 2372
- [57] Johari G P 1973 *J. Chem. Phys.* **58** 1766
- [58] Johari G P 1976 *Ann. New York Acad. Sci.* **279** 117
- [59] Johari G P, Powers G and Vij J K 2002 *J. Chem. Phys.* **116** 5908
- [60] Hensel-Bielowka S, Paluch M and Ngai K L 2005 *J. Chem. Phys.* **123** 014502
- [61] Morineau D, Alba-Simionesco C, Bellisent-Funel M C and Lauthie M F 1998 *Europhys. Lett.* **43** 195
- [62] Kessairi K, Capaccioli S, Prevosto D, Sharifi S and Rolla P A 2007 *J. Non-Cryst. Solids* **353** 4273
- [63] Prevosto D, Capaccioli S, Sharifi S, Kessairi K, Lucchesi M and Rolla P A 2007 *J. Non-Cryst. Solids* **353** 4278
- [64] Capaccioli S, Kessairi K, Prevosto D, Lucchesi M and Rolla P A 2007 *J. Non-Cryst. Solids* **353** 3984
- [65] Angell C A 1985 *Relaxation in Complex Systems* ed K L Ngai and G B Wright (Washington, DC: Naval Research Laboratory)
- [66] Böhmer R, Ngai K L, Angell C A and Plazek D J 1993 *J. Chem. Phys.* **99** 4201
- [67] For a list of such attempts see Niss K, Dalle-Ferrier C, Tarjus G and Alba-Simionesco C 2007 *J. Phys.: Condens. Matter* **19** 076102
- [68] Wang L-M, Velikov V and Angell C A 2003 *J. Chem. Phys.* **117** 10084
- [69] Martinez L-M and Angell C A 2001 *Nature* **410** 663
- [70] Ngai K L and Yamamuro O 1999 *J. Chem. Phys.* **111** 10403
- [71] Johari J P 2002 *J. Chem. Phys.* **116** 2043
- [72] Yannopoulos S and Johari G P 2006 *Nature* **44** E2
- [73] Roland C M, Hensel-Bielowka S, Paluch M and Casalini R 2005 *Rep. Prog. Phys.* **68** 1405
- [74] Casalini R and Roland C M 2005 *Phys. Rev. E* **72** 031503
- [75] Bordat P, Affouard F, Descamps M and Ngai K L 2004 *Phys. Rev. Lett.* **93** 105502
- [76] Plazek D J 1965 *J. Phys. Chem.* **69** 3480
- [77] Ngai K L and Plazek D J 1995 *Rubber Chem. Technol.* **68** 376
- [78] Plazek D J 1996 *J. Rheol.* **40** 987
- [79] Schönhals A 1993 *Macromolecules* **26** 1309
- [80] Ngai K L, Schönhals A and Schlosser E 1992 *Macromolecules* **25** 4915
- [81] Plazek D J, Chay I-C, Ngai K L and Roland C M 1995 *Macromolecules* **28** 6432
- [82] Santangelo P G, Ngai K L and Roland C M 1996 *Macromolecules* **29** 3651
- [83] Ferry J D 1980 *Viscoelastic Properties of Polymers* 3rd edn (New York: Wiley)
- [84] Doi M and Edwards S F 1986 *The Theory of Polymer Dynamics* (Oxford: Clarendon)
- [85] Floudas G and Reisinger T 1999 *J. Chem. Phys.* **111** 5201
- [86] Roland C M, Casalini R and Paluch M 2004 *J. Polym. Sci. Polym. Phys. Edn.* **42** 4313
- [87] Casalini R and Roland C M 2005 *Macromolecules* **38** 1779
- [88] Ngai K L, Casalini R and Roland C M 2005 *Macromolecules* **38** 4363
- [89] Ngai K L, Plazek D J and Rendell R W 1997 *Rheol. Acta* **36** 307
- [90] Götze W 1991 *Liquids, Freezing and the Glass Transition* (Amsterdam: North Holland)
- [91] Zorn R, Richter D, Frick B and Farago B 1993 *Physica A* **201** 52
- [92] Patkowski A, Matos Lopes M and Fischer E W 2003 *J. Chem. Phys.* **119** 1579
- [93] Tölle A, Schober H, Wuttke J, Randl O G and Fujara F 1998 *Phys. Rev. Lett.* **80** 2374
- [94] Sokolov A P, Kisluk A, Novikov V N and Ngai K L 2001 *Phys. Rev. B* **63** 172204
- [95] Cang H, Novikov V N and Fayer M D 2003 *J. Chem. Phys.* **118** 2800
- [96] Ngai K L 2004 *Phil. Mag.* **84** 1341
- [97] Götze W and Sperl M 2004 *Phys. Rev. Lett.* **92** 105701
- [98] Sperl M 2006 *Phys. Rev. E* **74** 011503
- [99] Pardo L C, Lunkenheimer P and Loidl A 2007 *Phys. Rev. E* **76** 030502 (R)
- [100] Plazek D J and Magill J H 1966 *J. Chem. Phys.* **45** 3038
- [101] Magill J H and Plazek D J 1967 *J. Chem. Phys.* **46** 3757
- [102] Stickel F 1995 *PhD Thesis* Mainz University, Germany
- [103] Stickel F, Fischer E W and Richert R 1995 *J. Chem. Phys.* **102** 6251
- [104] Stickel F, Fischer E W and Richert R 1996 *J. Chem. Phys.* **104** 2043
- [105] Schneider U, Lunkenheimer P, Brand R and Loidl A 1999 *Phys. Rev. E* **59** 6924
- [106] Angell C A, Ngai K L, McKenna G B, McMillan P F and Martin S F 2000 *J. Appl. Phys.* **88** 3113
- [107] Rault J 2000 *J. Non-Cryst. Solids* **271** 177
- [108] Casalini R and Roland C M 2002 *Phys. Rev. B* **66** 180201
- [109] Novikov V N and Sokolov A P 2003 *Phys. Rev. E* **67** 031507
- [110] Casalini R and Roland C M 2005 *Phys. Rev. B* **71** 014210
- [111] Roland C M and Casalini R 2005 *J. Chem. Phys.* **122** 134505
- [112] Casalini R, Paluch M, Fontanella J J and Roland C M 2002 *J. Chem. Phys.* **117** 4901
- [113] Casalini R, Paluch M and Roland C M 2003 *J. Chem. Phys.* **118** 5701
- [114] Casalini R, Paluch M and Roland C M 2003 *J. Phys.: Condens. Matter* **15** S859
- [115] Paluch M, Ngai K L and Hensel-Bielowka S 2001 *J. Chem. Phys.* **114** 10872

- [111] Corezzi S, Beiner M, Huth H, Schröter K, Capaccioli S, Casalini R, Fioretto D and Donth E 2002 *J. Chem. Phys.* **117** 2435
- [112] Dixon P K 1990 *Phys. Rev. B* **42** 8179
- [113] León C and Ngai K L 1999 *J. Phys. Chem. B* **103** 4045
- [114] Ngai K L 1999 *J. Chem. Phys.* **111** 3639
- [115] Ngai K L and Roland C M 2002 *Polymer* **43** 567
- [116] Ngai K L 2000 *J. Non-Cryst. Solids* **275** 7
- [117] Schönhals A 2001 *Europhys. Lett.* **56** 815
- [118] Schönhals A, Kremer F, Hofmann A, Fischer E W and Schlosser E 1993 *Phys. Rev. Lett.* **70** 3459
- [119] Tyagi M, Alegría A and Colmenero J 2005 *J. Chem. Phys.* **122** 244909
- [120] Casalini R, Ngai K L and Roland C M 2003 *Phys. Rev. B* **68** 014201
- [121] Magill J H and Plazek D J 1967 *J. Chem. Phys.* **46** 3757
- [122] Magill J H and Plazek D J 1966 *Nature* **209** 70
- [123] Fujara F *et al* 1992 *Z. Phys. B* **88** 195
- [124] Cicerone M T and Ediger M D 1996 *J. Chem. Phys.* **104** 7210
- [125] Ngai K L, Magill J H and Plazek D J 2000 *J. Chem. Phys.* **112** 1887
- [126] Cicerone M T, Wagner P A and Ediger M D 1997 *J. Phys. Chem. B* **101** 8727
- [127] Richert R, Duvvuri K and Duong L J 2003 *J. Chem. Phys.* **118** 1828
- [128] Richert R 2005 *J. Chem. Phys.* **123** 154502
- [129] Rajian J R, Huang W, Richert R and Quitevis E L 2006 *J. Chem. Phys.* **124** 014510
- [130] For discussion of the NMR and light scattering data references see Mapes M K, Swallen S F and Ediger M D 2006 *J. Phys. Chem. B* **110** 507
- [131] Chakrabarti D and Bagchi B 2006 *Phys. Rev. Lett.* **96** 187801
- [132] Ngai K L 2007 *J. Non-Cryst. Solids* **353** 709
- [133] Ngai K L 1999 *J. Phys. Chem. B* **103** 10684
- [134] Comez L, Fioretto D, Palmieri L, Verdini L, Rolla P A, Gapinski J, Patkowski A, Steffen W and Fischer E W 1999 *Phys. Rev. E* **60** 3086
- [135] Ngai K L 1999 *Philos. Mag. B* **79** 1783
- [136] Adam G and Gibbs J H 1965 *J. Chem. Phys.* **43** 139
- [137] Richert R and Angell C A 1998 *J. Chem. Phys.* **108** 9016
- [138] Ngai K L 1999 *J. Phys. Chem. B* **103** 5895