

Revealing the rich dynamics of glass-forming systems by modification of composition and change of thermodynamic conditions

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Abstract

Secondary relaxations have been classified into two types, depending on whether they are related to the structural α -relaxation in properties or not. Those secondary relaxations that are related to the α -relaxation may have fundamental importance, and are called the Johari-Goldstein (JG) β -relaxations. Two polar molecular glass-formers, one flexible and another rigid, dissolved in apolar host with higher glass transition temperature are studied by broadband dielectric spectroscopy at ambient and elevated pressure. The neat flexible glass-former diethylphthalate (DEP) has a resolved secondary relaxation which unlike the α -relaxation is insensitive to pressure and hence not the JG β -relaxation. In the solution, the JG β -relaxation of DEP shows up in experiment and its relaxation time τ_β is pressure and temperature dependent like τ_α . The result supports the universal presence of the JG β -relaxation in all glass-formers, and the separation between τ_α and τ_β is determined by intermolecular interaction. The rigid glass-former is cyano-benzene (CNBz) and its secondary relaxation involves the entire molecule is necessarily the JG β -relaxation. The dielectric relaxation spectra obtained at a number of combinations of pressure and temperature at constant τ_α show not only unchanged is the frequency dispersion of the α -relaxation but also τ_β . The remarkable results indicate that the JG β -relaxation bears a strong connection to the α -relaxation, and the two relaxations are inseparable when considering the dynamics of glass-forming systems. Experimentally, τ_α has been found to be a function of the product variables, T/ρ^γ , where ρ is the density and γ is a material constant. From the invariance of the ratio, τ_α/τ_β , to change of thermodynamic conditions seen in our experiment as well in other systems, it follows that τ_β is also a function of T/ρ^γ , with the same γ at least approximately. Since the JG β -relaxation is the precursor of the α -relaxation, causality implies that the T/ρ^γ -dependence originates from the JG β -relaxation and is passed on to the α -relaxation.

Keywords: Glass transition, binary mixtures, pressure, secondary relaxation, intermolecular relaxation

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1. Introduction

Relaxation dynamics of glass-forming systems presents a complex scenario, characterized by numerous relaxation processes over a very broad frequency window of more than 12 decades. Among these processes manifested over wide temperature or broad frequency range, the structural or α -relaxation process traditionally had been considered as the most important. Therefore research on glass transition was usually centred around this slow α -relaxation process alone, and inadvertently the other faster secondary relaxations are often thought to have no fundamental role. In the early years, secondary relaxation in general were considered as originating from some intramolecular degree of freedom, and hence cannot be related to the intermolecularly cooperative α -relaxation. Historically this is perhaps the primary reason for trivializing the role of secondary relaxations in glass transition.

There are two research developments separated by almost three decades and together they have changed the attitude towards the secondary relaxations. In 1970, Johari and Goldstein shocked the research community by showing the existence of secondary relaxation in a totally rigid small molecular glass-former [1]. Starting from 1998, Ngai [2-4], Ngai and co-workers [5-26], and other workers [27-33] found secondary relaxations belonging to a special class have properties bearing strong connection to the α -relaxation in glass-formers of various chemical and physical compositions. For non-polymeric glass-formers in general that can be flexible or not totally rigid, the secondary relaxation in the special class has to involve the entire molecule or the basic relaxation unit. For polymeric glass-formers, the secondary relaxation in the special class must involve also some motion of the backbone of the repeat unit. This discovery since 1998 was motivated by the Coupling Model (CM) [4,34-37]. **The CM is based on the primitive relaxation, which is a local and independent relaxation involving the motion of the entire molecule and acting as the precursor of the cooperative α -relaxation.** The primitive relaxation time, τ_0 , rigorously related to the α -relaxation time, τ_α , given by the time honoured equation,

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

where t_c is about 1 to 2 ps for molecular and polymeric glass-formers, and $(1-n)$ is the fractional exponent in the Kohlrausch correlation function of the α -relaxation,

$$\phi(t) = \exp[-(t/\tau_\alpha)^{1-n}]. \quad (2)$$

Existence of strong connections in properties and dependencies on variables between the primitive relaxation and the α -relaxation is immediate consequence of Eq.(1). Since by definition secondary relaxation of the special class is also a local and independent process, involving the motion of the entire molecule, and having connections with the cooperative α -relaxation in properties, the approximate relation, $\tau_0 \approx \tau_\beta$, between τ_0 and the relaxation time, τ_β , of the secondary relaxation is expected. On combining this approximate relation with Eq.(1), we have the *approximate* relations

$$\tau_\beta \approx \tau_0 = (t_c)^n (\tau_\alpha)^{1-n}, \quad (3)$$

or the *approximate* relation between τ_α and τ_β

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

Either (3) or (4) predicts not only the values of τ_α and τ_β are related quantitatively, but also their dependencies on temperature T and pressure P or other variables are related, albeit approximately. The various predictions coming out from these approximate relations have been amply verified in many glass-formers and non-glassformers since the start in 1998 (see Ref.[4] for a comprehensive review).

Certainly, all totally rigid molecular glass-formers investigated by Johari and Goldstein (JG) belong to this special class because there is only one secondary relaxation, and it necessarily involves the entire rigid molecule. With the intent to honour JG for their

important findings three decades ago, the glass-formers belonging to the special class are summarily called the JG β -relaxations by Ngai and co-workers [2-26]. This usage of the term has to be distinguished from some workers in the field who still refer to any secondary relaxation as JG β -relaxation, irrespective of whether it has connection to the α -relaxation or not. Moreover, secondary relaxation of this special class is universal and found in all kinds of glassformers, organic molecular, polymeric, metallic, inorganic, ionic, colloidal, and plastic crystalline [4]. Most remarkable is the finding of the secondary relaxation in metallic glasses [38,39], which are atomic particles devoid of rotational degree of freedom, and in plastic crystals which have no translational degree of freedom [40-42].

In the earlier years, relations (3) and (4) have been mainly the criteria used to verify whether the secondary relaxation is the JG β -relaxation or not. If the approximate relations (3) or (4) are satisfied, the connection between τ_β and τ_α becomes obvious. Not only the value of τ_β approximately predicted by (3) is verified quantitatively, but also the dependence of τ_α on any variable λ , including temperature T and pressure P , are related to the corresponding dependence of τ_β on λ . An example is that τ_β of JG β -relaxation has to be pressure dependent because τ_α is invariably pressure dependent. These expanded criteria for JG β -relaxation were summarized in the paper of 2004 [6] as one of the methods to classify secondary relaxations. An important advance was made by Böhmer and co-workers in 2006 [27,28]. Using spin-lattice relaxation weighted stimulated-echo spectroscopy, they were able to suppress the contributions of some sub-ensembles of the JG β -relaxation above the glass transition temperature in ortho-terphenyl, D-sorbitol, and cresolphthaleindimethylether, and it was found that the α -relaxation is modified. The findings provide direct experimental support for the strong connection between the α - and the JG β -relaxation.

The advance of broadband dielectric relaxation spectroscopy in making measurements at elevated pressure up to 2 GPa and compensated by increasing temperature has helped immensely to bring out the strong connection of the JG β -relaxation to the α -relaxation, and hence its fundamental importance was not appreciated before. This experimental advance is complemented by elegant molecular dynamics simulations of polymers [33]. Another research trend of recent years is the study of the modification of the relation between the JG β -relaxation and the α -relaxation of a glass-former by mixing with another glass-former having significantly different T_g [14,25,32,43]. The presence of the other component alters the coupling parameter n of the α -relaxation, and in turn the approximate relation between τ_α and τ_β according to relation (4). By combining the two new research trends (*i.e.* studying the dynamics of a component in binary mixtures under elevated pressure), deeper insight is gained into the fundamental role played by the JG in the dynamics of glass-formers and in glass transition. In this paper we present new results from such combined experimental study of component dynamics of novel binary mixtures at ambient and elevated pressure. The far reaching implications of the results on the physics of the dynamics of glass-forming systems as well as the impact on other current research efforts are brought out.

2. Experimental Section

Mixing polar aromatic molecules with oligomers of styrene is an ideal strategy to have very good glass-formers with a good miscibility range. The presence of aromatic rings, in fact, improve the solubility of the polar probes in the apolar oligo-styrene system due to the affinity of the π - π interactions. The study of the dielectric response of such binary mixtures can selectively reveal the rotational dynamics of the polar component alone, even when the polar component is dilute. Actually the permanent dipole moment of the styrene

repeating unit ($\mu=0.2$ D) is very small compared to the strong permanent dipole moment of the solute (in our case μ is in the range between 2.5 and 5 D). Since the dielectric strength, i.e. the intensity of the loss peak, scales as $N\mu^2$ (where N is the number of dipoles per unit volume and μ is the permanent dipole moment), we can affirm that the dynamics of the polar component dominates the dielectric response of the mixtures presented in this paper, having a molar concentration of the polar component of $X_M=0.1$.

Cyanobenzene (CNBz, $M_W=103$ g/mol) and diethylphthalate (DEP, $M_W=222.2$ g/mol) were purchased at high purity grade from Sigma-Aldrich and used as received. CNBz was mixed at molar fraction $X_M=0.1$ with tristyrene (PS370) ($T_g=234$ K, $M_W=370$ g/mol, obtained from Polymer Standard Service). DEP was mixed at molar fraction $X_M=0.1$ with and oligostyrene of $M_W=820$ g/mol, $M_w/M_n=1.01$, (PS800) ($T_g=282$ K, obtained from Scientific Polymer Product). All samples were stored and handled in a dry nitrogen atmosphere.

Novocontrol Alpha-Analyzer was used for dielectric measurements, both at atmospheric and at high pressure, in the frequency interval from 10 mHz to 10 MHz. The sample cell consisted in a parallel plate capacitor separated by a quartz spacer (empty capacitance ~ 90 pF) and filled by the sample in the liquid state. For atmospheric pressure measurements the temperature was controlled using a dry nitrogen-flow Quatro cryostat ($T=100\text{--}360$ K) with a temperature accuracy of better than 0.1 K. For high pressure measurements, a sample-holder multi-layer capacitor (empty capacitance ~ 30 pF) was separated from the pressurizing fluid (silicon oil) by a Teflon membrane. The high pressure chamber (Cu-Be alloy), provided by UNIPRESS, was connected to a hydraulic pump able to reach 700 MPa and controlled in the interval 195–360 K within 0.1 K by means of a thermally conditioned liquid flow.

3. Results and Discussion

3.1 Johari-Goldstein relaxation of flexible polar probes in apolar solvents

In the Introduction, we mention the existence of the special class of secondary relaxations, namely the Johari-Goldstein (JG) β -relaxations, which involves the motion of the entire molecule or some motion of the backbone in the case of polymers and opposed by the intermolecular energy barrier. Although the JG β -relaxation is not of cooperative in character, its relaxation time τ_β is sensitive to change in density, although to a smaller extent than the cooperative α -relaxation [6]. In contrast, intra-molecular secondary relaxations albeit in an intermolecular environment are governed by intra-molecular energy barrier, and are not affected **either at all or to a much lesser extent** by the reduction of density. **JG β -relaxations have to overcome intermolecular barrier, and are more affected by pressure.**

A survey of publications in the literature as well as from our own laboratory shows there is no concrete evidence of the presence of the JG β -relaxation in some well studied small molecular glass-formers composed of flexible molecular units. This casts doubts on the universality of the JG β -relaxation in glass-formers and their importance in the research of glass transition. An example is diethyl phthalate (DEP) which has a single well resolved secondary relaxation, whose dynamics have been proven to be insensitive to applied pressure [44], and hence not the JG β -relaxation we are looking for. By comparing spectra with the same loss maximum frequency for the α -peak, obtained with different combination of T and P , Pawlus and co-workers [44] found that the shape of the α -relaxation as well as the excess wing present on the high frequency flank of the α -peak does not change with density, whereas the prominent secondary process, here named the γ -relaxation, becomes more and

more separated from the α -relaxation on increasing density. At 293 K, by applying a pressure of more than 1.2 GPa, while the α -relaxation slows down and DEP becomes vitrified, the relaxation time τ_γ remain constant at 0.1 μ s. This fact is not unexpected from the γ -relaxation of the DEP and **higher members** of the dialkyl phthalates family because it originates from fluctuations of $-C=O-$ dipole moment in the presence of the very mobile alkyl chains. This intramolecular degrees of freedom can fluctuate without the need of a large activation volume and thus they can be quite insensitive to density reduction. Considering that the α -loss peak is **rather** narrow, and near T_g it can be well fitted by the Fourier transform of the Kohlrausch function with non-exponentiality parameter $n=0.36$, the CM relation (4) would suggest that the JG β -relaxation near T_g should be located at a frequency few tens of Hz, and therefore it is obscured by the high frequency flank of the α -peak, and manifests itself as an “excess wing”.

A way to increase the coupling parameter n is to change the intermolecular environment. The method that has been explored [14,16,18,22,31,32,43] is to mix the polar molecule in a solvent with a slower dynamics, that could enhance the degree of cooperativity of the rotational relaxation, thus increasing n and separating the timescale of the JG relaxation from that of α -process according to the CM relation (4). In the research reported in this paper, we dissolved DEP in an apolar host with higher T_g like PS800 at low molar fraction ($X_M=0.1$). **In this way, the α -relaxation associated with the DEP component is enhanced in intermolecular coupling and cooperativity and is slowed down and separated further from the prominent γ -process, and making it possible for a new secondary relaxation to appear in between. We will show that this slower secondary relaxation has the characteristics of the JG β -relaxation.**

Fig.1 shows the loss spectra of DEP at five selected temperatures from the entire set of measurements. The top two temperatures are above the T_g observed via the DEP component, and the other three temperatures are below T_g . At the two lowest temperatures, the loss spectra show two well resolved secondary relaxations, β and γ . At higher temperatures, the faster γ -relaxation moves out of the experimental frequency window, but the slower β -relaxation continues to be observed even above T_g .

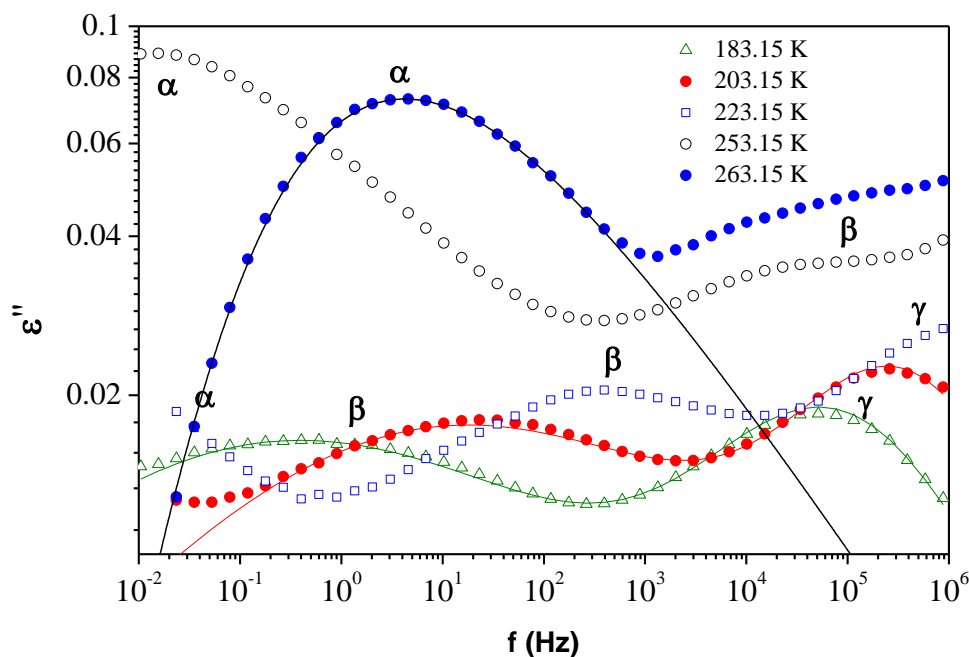


Figure 1. Dielectric loss spectra of DEP dissolved in PS800 mixture ($X_M=0.1$). Black continuous line is the Fourier transform of a KWW function ($n=0.70$) fitted to the α -peak. Other lines represents fitting to the spectra in the glassy state obtained as a superposition of Cole-Cole functions.

For this system, at temperatures near T_g the α and the β relaxations usually appear within the experimental frequency window, and well separated from each other so that the α -loss peak can be isolated and well fitted by the Fourier transform of the KWW function (Eq.2) and the n parameter can be extracted. The fit to the α -loss peak was performed in a semi-logarithmic scale, choosing the same footing for all the spectra as the region of the full width half maximum (FWHM). **A Filon trapezoidal algorithm was used for calculating the KWW Fourier Transform contribution. A simplex optimization algorithm was used to minimize the mean squared deviation between data and fitting function.** Alternatively, dielectric spectra can be well fitted in the whole temperature range by a superposition of Havriliak-Negami (for α -process) and Cole-Cole (for β - and γ -processes) functions. In this way the contribution of each process can be singled out by a simple superposition fitting procedure [45], and the most probable relaxation times of the single processes, τ_α , τ_β , τ_γ can be obtained as $\tau_m=(2\pi f_m)^{-1}$, the reciprocal of the loss peak maximum angular frequencies f_m related to the α -, β - and γ -relaxation, respectively. The relaxation frequencies of the α -relaxation and the two secondary relaxations deduced from the spectra obtained at all temperatures are plotted against $1000/T$, and the results are presented in Fig.2. Shown also in the same figure are the relaxation frequencies of the α - and the γ -relaxations of neat DEP taken from the published data of ref.[44]. The T -dependence of f_α can be represented by $f_\alpha=f_\infty \exp[-B/(T-T_0)]$, the Vogel-Fulcher-Tamman (VFT) function, whereas the temperature dependence of secondary relaxation frequency is of the Arrhenius type.

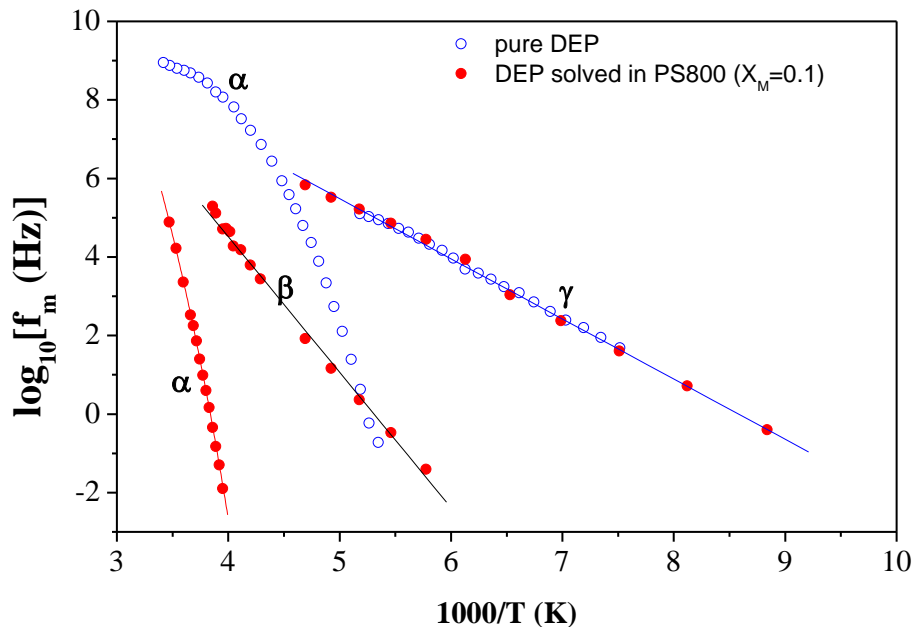


Figure 2. Relaxation map for DEP pure (open symbols) from Ref.[44] and DEP dissolved in PS800 (filled symbols). Black straight lines are representing fitting with Arrhenius laws, while red curve is a fit using VFT function.

The relaxation frequencies of the faster secondary relaxation of DEP in the mixture are almost the same as the γ -relaxation times of neat DEP at the same temperature and has the same activation enthalpy of 29.3 kJ/mol. The coincidence indicates that the faster secondary relaxation in the mixture is the same motion as the γ -relaxation in neat DEP. The insensitivity of its relaxation times to mixing supports that the γ -relaxation originates from local motion of the alkyl chains about the oxygen linkage with dielectric strength derived from the dipole moment of the polar carboxyl group. On the other hand, having a much high activation enthalpy of 66.1 kJ/mol than the γ -relaxation, the slower secondary relaxation observed in the mixture must involve in addition other parts of the DEP molecule, and is the JG β -relaxation of DEP that we are looking for. It is clear in Fig.2 that the presence of the higher T_g PS800 in the mixture does increase the separation between the γ -relaxation time and the α -relaxation time of DEP above and below T_g , making room for the JG β -relaxation of DEP to be resolved and observed.

Actually for the JG relaxation we have a temperature dependence of the type $f_\beta = f_\alpha \exp(E_{JG}/RT)$ in the glassy state but it crosses over to stronger temperature dependence in vicinity of T_g . This change of temperature dependence of f_β at T_g is similar as that of the α -process when it crosses from a structurally arrested state (below T_g) to the equilibrium liquid state. The similar property indicates that the JG β -relaxation is sensitive to change of density or entropy dependence on crossing the glass transition temperature.

The α -relaxation of DEP in the mixture is much slower than in the neat state, reflected in the increase of T_g from 183 K of the neat system to 250 K of the mixture. At 250 K, their α -relaxation times differ by about 12 orders of magnitude. This is due to the fact that the α -relaxation of DEP in the mixture necessarily involves the host PS800 repeat units, which have significantly lower mobility. As a result, the α -relaxation of DEP in the mixture is stretched to longer times. If the Kohlrausch function is used to describe the correlation function of the α -relaxation, then τ_α is much longer and n is larger for DEP in the mixture than in neat DEP. This increase of n or width of the α -dispersion of DEP in the mixture originates from stronger intermolecular coupling [23,26,46]. This is the primary cause of the larger width the α -loss peak of DEP in the mixture than in neat DEP, according to the CM description of component dynamics in binary mixtures and polymer blends. There is however additional cause of broadening of the α -loss peak. Apparently, the concentration of the DEP in the mixture is not low enough to exclude the presence of concentration fluctuations of the two components. Moreover, there is a difference in mobility between chain ends and inner monomers of PS800. These factors introduce some distribution of environments and heterogeneous broadening of the α -relaxation of DEP in the mixture beyond that coming from intermolecular coupling. The heterogeneous broadening introduces a distribution of Kohlrausch functions each with different n_i and $\tau_{\alpha i}$, and each pair is related by the CM relation, $\tau_{\alpha i} = [t_c^{-n_i} \tau_0]^{1/(1-n_i)}$. As a special case, the most probable value of n_i in the distribution, \hat{n} , and the corresponding most probable observed α -relaxation time $\hat{\tau}_\alpha$ are related by $\hat{\tau}_\alpha = [t_c^{-\hat{n}} \tau_0]^{1/(1-\hat{n})}$. Furthermore from $\tau_{JG} \approx \tau_0$, we have the approximate relation between $\hat{\tau}_\alpha$ and τ_{JG} given by $\hat{\tau}_\alpha \approx [t_c^{-\hat{n}} \tau_{JG}]^{1/(1-\hat{n})}$. When there is no component concentration fluctuation like in neat glassformers, \hat{n} is simply n in the Kohlrausch function in Eq.(4), and the τ_{JG} calculated via CM relation is in good agreement with the observed value. In the mixture, the slower PS800 host stretch the α -relaxation of DEP to longer times, thereby the value \hat{n} can be significantly larger than $n=0.36$ of neat DEP. At temperatures near T_g of DEP in the

mixture, to fit the observed τ_{JG} by the calculated values of τ_0 via the CM equation Eq.(3) the value of \hat{n} required is 0.55 and is larger than 0.36 of neat DEP as expected. The α -loss peak of DEP in the mixture with $\hat{\tau}_\alpha$ near 0.1 s is much broader than the shape of the one-sided Fourier transform of the Kohlrausch function with $n=0.55$ (the actual value is 0.7) due to heterogeneous broadening as discussed in the above. The loss contributed by the JG β -relaxation is about half of the maximum α -loss. It severely broadens the high frequency side of the α -loss peak to the extent not seen before in neat glassformers. **The presence of the more mobile alkyl-chain units in DEP may have something to do with this. It is partly responsible for the larger value of 0.7 of \hat{n} required to fit the α -dispersion.**

A critical test to verify the character of the newly resolved β -relaxation in the DEP/PS800 mixture is to apply pressure. Selected spectra obtained in isothermal conditions are shown in Fig.3. Interestingly the newly resolved β -process is pressure sensitive, since it moves toward lower frequencies together with α -process. The fast γ -secondary process remains outside the experimental window over all the pressure range investigated, confirming the same behavior observed in the pure DEP system. The fitting of the α -loss peak of DEP in the mixture with the one-sided Fourier transform of the Kohlrausch function yields n around 0.7, confirming that density change does not change the relaxation loss peak shape.

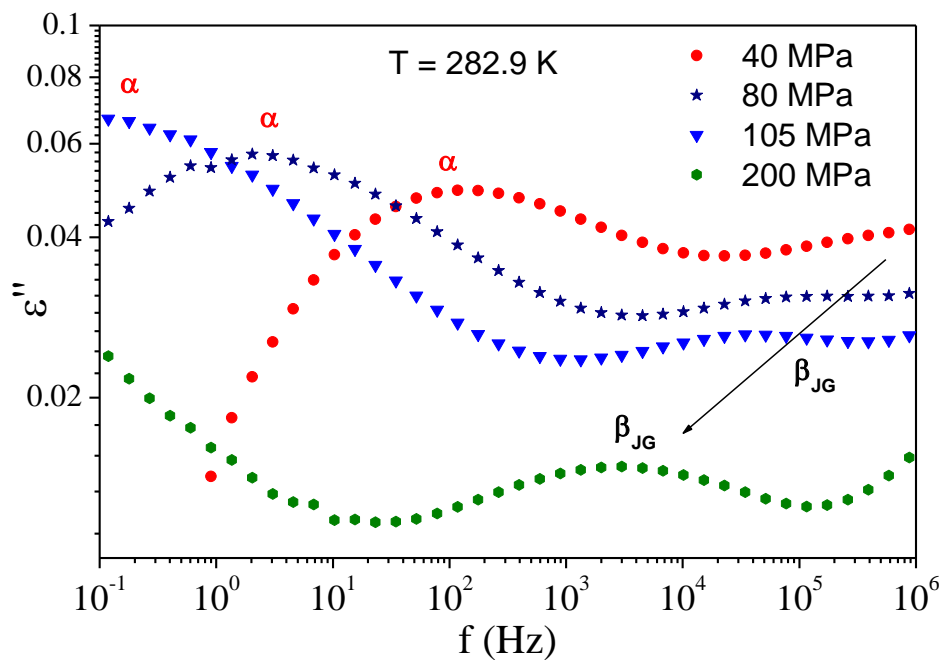


Figure 3. Selected dielectric loss spectra for DEP dissolved in PS800 mixture at constant temperature 283 K and different pressures. The arrow marks the increasing pressure trend.

It is interesting to compare the combined effect of T and P on the dynamics of the α - and β -process shown above. Cooling and compressing seem to have similar effect on α - and β -dynamics, both shifting the characteristic frequencies to lower values, even if each relaxation has its own different T - P dependence, as shown by the combined plots in Fig.4. A similar dynamic range has been shown, in order to compare the two effects. The isothermal diagram at 283 K in Fig.4b corresponds to the first point at the left in Fig.4a. It is clear that the γ -

relaxation never enter into Fig.4b, because at this temperature the frequency of the γ -loss maximum lies outside the experimental window and also because it is insensitive to pressure. Pressure decreases the frequency of the maximum of α -process in a non-linear way, with an activation volume increasing on approaching T_g . This behavior is the analogue of the well known VFT behavior for temperature. On the other hand, the pressure effect on the logarithm of β -relaxation frequency has an almost linear behavior, with an activation volume that changes on crossing P_g , reflecting the change of compressibility of the glassy state from that of the liquid. The most striking feature of Fig.4a and Fig.4b is the coincidence that can be found on comparing the position of the maximum frequency of the β -relaxation for the same α -relaxation frequency. In particular, choosing the glass transition condition as when $\tau_\alpha=100$ s, the frequency of β -relaxation is the same if evaluated either from the temperature dependence at constant pressure (Fig.4a) or from the pressure dependence at constant temperature (Fig.4b).

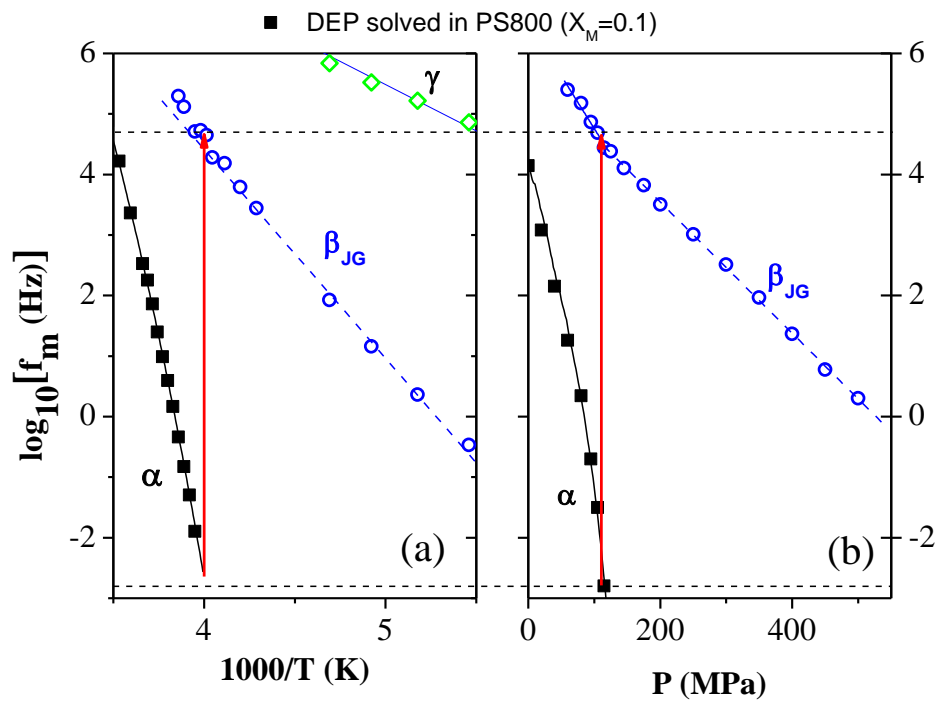


Figure 4. Relaxation maps for DEP dissolved in PS800 comparing the effects of (a) isobaric cooling at 0.1 MPa and of (b) the isothermal compression at 283 K. Black solid squares represent data for α -relaxation, open blue circles are for the β -relaxation data, γ -relaxation data are indicated by green open diamonds. Lower dashed horizontal line marks the frequency corresponding to the glass transition ($\tau_\alpha(T_g)=100$ s), while higher dashed horizontal line mark the frequency of the β -relaxation at T_g . Black curves represent the fitting of α -relaxation frequencies with VFT function (panel a) and VFT-like function for pressure (panel b). Straight dashed lines represent fitting the pressure activated behavior.

The fact that the β -relaxation frequency is the same when obtained at different T and P but with the same structural α -relaxation frequency f_α or time τ_α (isochronal spectra) shows additional evidences of the correlation or connection between the β -relaxation and the structural α -relaxation. The same result applied also if both T and P were varied over wide ranges. Increasing pressure increases the α -relaxation time τ_α , but the increase can be compensated by raising temperature. Naturally, widely different combinations of P and T can be found to have the same α -relaxation time τ_α , which are accompanied by significant

variations in the density. This correlation can be easily explained by the CM relations (3) or (4). If the coupling parameter n does not change appreciably, once τ_α is fixed, the τ_β or f_β is approximately the same. Thanks to these additional results, we can confirm the new secondary relaxation resolved in the DEP/PS800 mixture is the JG β -relaxation of DEP in the mixture. A better test of the correlation will be shown in the next sub-section for a rigid polar molecule in an apolar glass-forming solvent, like the mixture of chlorobenzene in *cis*-decalin used by Johari-Goldstein many years ago.

3.2 Johari-Goldstein relaxation of rigid polar probes in apolar solvents

Cyanobenzene (CNBz) has a very strong dipole moment ($\mu= 5.0$ D) and a putative glass transition temperature that should be in the range of those of halogenated benzenes, i.e. below 150 K. A suitable apolar solvent for this polar rigid probe is PS370 or tristyrene, that has a higher T_g (232 K) than CNBz. **Since tristyrene is a compact small molecule, when mixed with CNBz it does not introduce heterogeneity to the dynamics of CNBz, unlike the previous case of DEP dissolved in PS800 which has the chain ends which are more mobile than the internal repeat units. Thus, this is the ideal mixture to study the effects due to change of intermolecular coupling when CNBz is mixed with tristyrene.**

The dielectric response of the mixture of CNBz in PS370 at molar fraction $X_M=0.1$ shows a bimodal relaxation scenario, with α - and β - relaxation well separated but still visible within the same experimental frequency window. Selected dielectric loss spectra of the mixture of CNBz in PS370 at molar fraction $X_M=0.1$ are shown in Fig.5 under isothermal condition at different pressures.

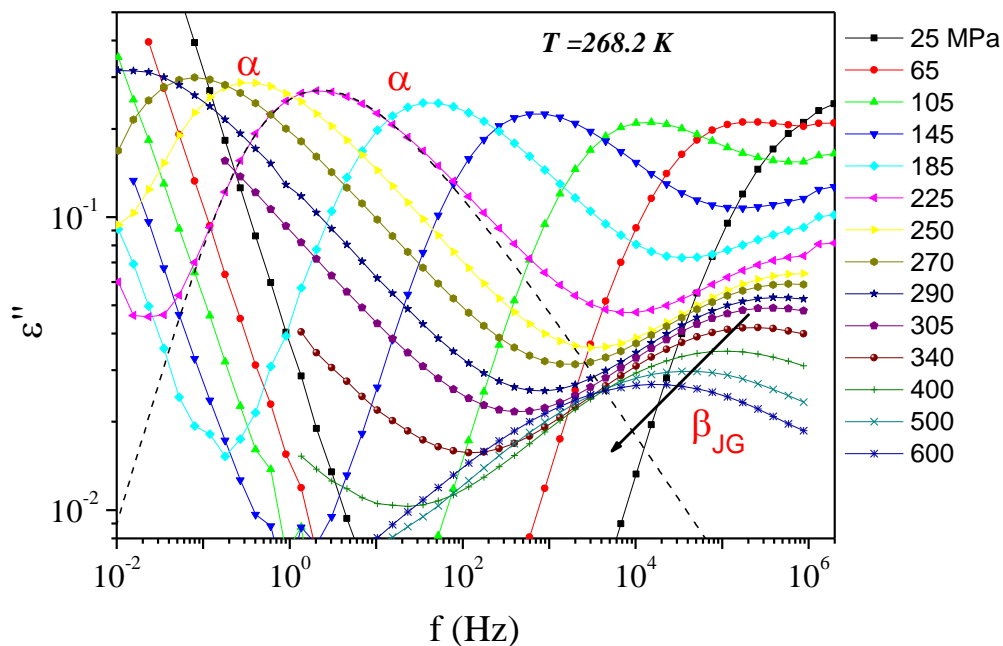


Figure 5. Selected dielectric loss spectra for CNBz dissolved in PS370 mixture at constant temperature 268.2 K and different pressures. The arrow marks the increasing pressure trend. Black dashed line is a KWW function ($n=0.55$) fitted to the α -peak.

Like DEP/PS800, the β -process of CNBz (henceforth referred to as the JG β -relaxation, because for sure it involve the entire molecule and is intermolecular since CNBz is a rigid polar molecule) appears to be very sensitive to pressure. Applying a fitting procedure as mentioned before, it is possible to single out the contributions of the α - and β -relaxations. A

relaxation map for the loss maximum frequencies of both processes under temperature and pressure variations can be found in Fig.6.

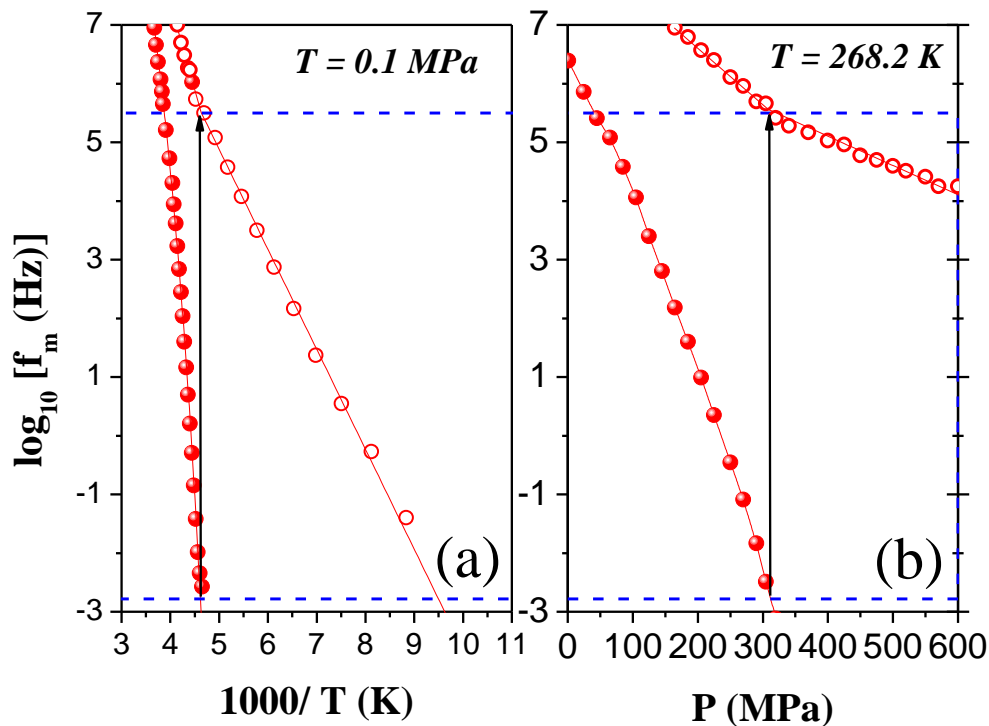


Figure 6. Relaxation maps for CNBz dissolved in PS370 comparing the effects of (a) isobaric cooling at 0.1 MPa and of (b) the isothermal compression at 268.2 K. Red solid circles represent maximum frequencies for α -relaxation, open red circles are for maximum frequencies of the β -relaxation. Lower dashed horizontal line marks the frequency corresponding to the glass transition ($\tau_\alpha(T_g)=100$ s), while higher dashed horizontal line mark the frequency of the β -relaxation at T_g . Red curves represent the fitting of α -relaxation frequencies with VFT function (panel a) and VFT-like function for pressure (panel b). Straight dashed lines represent fits to the pressure activated behavior.

As the case shown in §.3.1, pressure decreases the frequency of the maximum of the α -process in a non-linear way, with an activation volume (i.e. its pressure derivative) increasing on approaching T_g . The logarithm of β -relaxation frequency has an almost linear behavior, with an activation volume that changes on crossing T_g , reflecting the change of compressibility of the liquid on vitrification. It is noteworthy that the ratio between the pressure slope of $\log(f_\beta)$ over that of $\log(f_\alpha)$ is almost 0.5, if both are calculated above and near T_g . Again the frequency of the β -relaxation maximum obtained by either isothermal compression or isobaric cooling is the same at glass transition defined by $f_\alpha=1/2\pi\tau_\alpha$ with $\tau_\alpha=100$ s. The coincidence of $\log(f_\beta)$ from isothermal compression or isobaric cooling can be extended to other values of f_α and different isochronal combinations of T and P . Moreover, the correlation between α - and JG β -relaxation can be also tested by comparing isochronal spectra. The comparison in Fig.7 of selected spectra of the system CNBz/PS370 obtained at various combinations of P and T but with the same structural α -relaxation frequency f_α or time τ_α shows additional evidences of the strong correlation or inseparable relation between the JG β -relaxation and the α -relaxation.

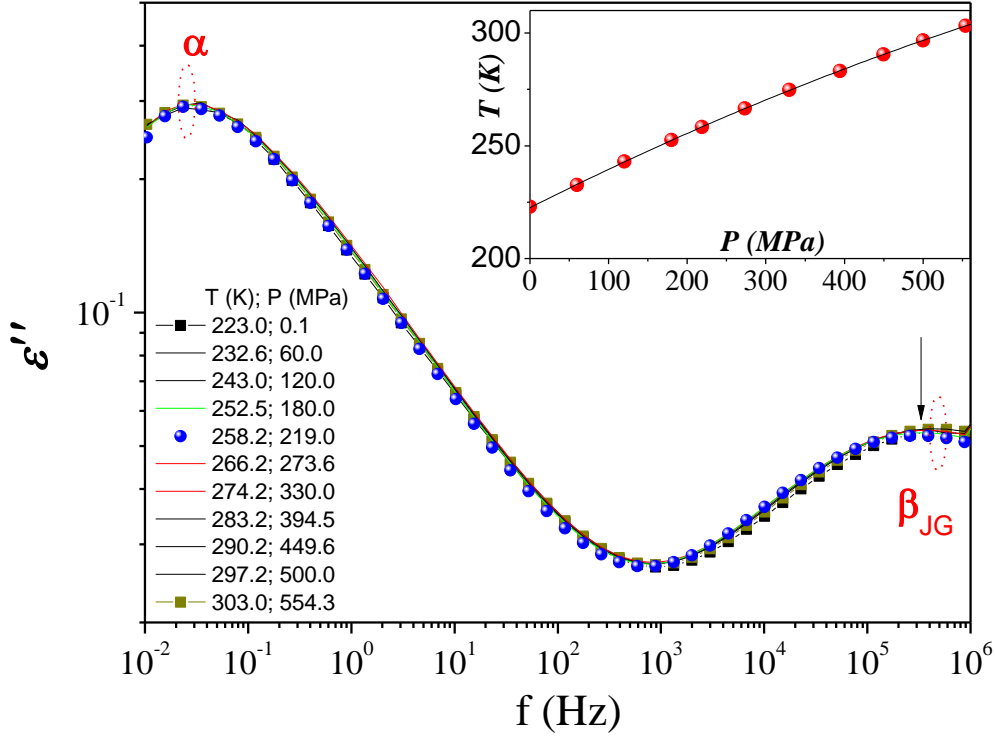


Figure 7. T - P superposition of loss spectra for CNBz/PS370 ($X_M=0.1$) measured at different T and P combinations but the same frequency $f_\alpha=29$ mHz. The arrow marks the CM prediction for the frequency maximum of the JG peak. The inset show the combinations of T and P used in the main plot for the isochronal comparison.

Spectra selected in Figure 7 are at various combinations of T and P that keep constant the most probable frequency of the structural α -process at $f_\alpha(T,P)=29$ mHz. Interestingly we got a remarkably perfect superposition of the entire spectra including the α -relaxation and the JG β -relaxation without any vertical shift of any data. Here T has been varied over the range from 223.0 K to 303.0 K and pressure increased from ambient pressure of 0.1 MPa to 554.3 MPa (see the inset of Fig.7). Such a huge variation of about 80 K in temperature and an increase of pressure by nearly 4 orders of magnitude are accompanied by significant changes in volume and entropy as expected. Still there is nearly perfect superposition of all relaxation processes at constant τ_α . It is noteworthy that, for the same f_α , also the shape (or the dispersion) of the α -peak is found invariant. The KWW function fits very well the loss peak with a value of $n=0.55$. This result can be restated as coinvariance of three quantities, τ_β , τ_α , and the α -dispersion or the fractional exponent, $(1-n)$, of the Kohlrausch correlation function for the α -relaxation to variations of P and T . Remarkably, the approximate relation (4) from the Coupling Model is in accord with the nearly perfect co-invariance found. Furthermore, the experimental value of τ_β is approximately the same as τ_0 calculated from Eq.(3) (shown by an arrow indicating the location of the corresponding maximum frequency $f_0=1/(2\pi\tau_0)$ with the values of τ_α and $(1-n)$ from the experimental data and $t_c=2$ ps and thus verifying the approximate correspondence between τ_0 and τ_β from the Coupling Model.

3.3 Universality of the coinvariance, fundamental importance of the JG β -relaxation, and implication on the origin of density scaling

The approximate coinvariance was found before in dipropyleneglycol dibenzoate (DPGDB) [7], and benzoyn isobutylether (BIBE) [13], but in these neat glass-formers the β -relaxation was not well resolved [18]. Recently in a study of the conductivity relaxation dynamics of the room-temperature ionic liquid, 1-methyl-3-trimethylsilylmethylimidazolium tetrafluoroborate ([Si-MIm][BF₄]), a prominent and well resolved conductivity β -relaxation was observed [19]. The broadband conductivity (σ) relaxation measurements at ambient pressure and elevated pressures up to 600 MPa found approximate co-invariance of $\tau_{\sigma\beta}$, $\tau_{\sigma\alpha}$, and $(1-n)$ in this neat ionic liquid glass-former. Here $\tau_{\sigma\alpha}$ and $\tau_{\sigma\beta}$ stand for the conductivity α - and β -relaxation times. The CM is applicable to ion conductivity relaxation, and successful in accounting for experimental data in many ionically conducting materials [4,18,19,47-49] with the same equation (3) and relation (4), but with $\tau_{\sigma\alpha}$, $\tau_{\sigma\beta}$, and $\tau_{\sigma\alpha}$ replace the corresponding quantities in there. Thus, the co-invariance of $\tau_{\sigma\beta}$, $\tau_{\sigma\alpha}$, and $(1-n)$ found experimentally is consistent with the CM. Moreover in [Si-MIm][BF₄], there is approximate agreement between the primitive conductivity relaxation time $\tau_{\sigma\alpha}$ and $\tau_{\sigma\beta}$ from experiment. Conductivity relaxation is distinctly different from structural relaxation of glass-forming systems, and yet it has a conductivity β -relaxation, which bears the same strong relation to the conductivity α -relaxation. We submit that this conductivity β -relaxation should not be called JG β -relaxation because otherwise it is not the same. Notwithstanding, the generality of the phenomenon indicates the physics governing it is fundamental, as suggested by the CM.

There are two other binary mixture of polar probe molecules with apolar host that show well resolved β -relaxation. The mixtures are quinaldine dissolved in tristyrene [32], and picoline in tristyrene [14,43]. The dielectric spectra of the polar component measured with different combinations of P and T at constant α -loss peak frequency show the approximate coinvariance of τ_{β} , τ_{α} , and $(1-n)$. Moreover, molecular dynamics simulations of linear polymer melts represented by simple bead-necklace models were performed at ambient and elevated pressure by Bedrov and Smith, showing the same trend [33]. The torsional autocorrelation function (TACF) shows the presence of the JG β -relaxation at shorter times to be followed by the α -relaxation. The TACF obtained at $T=130$ K, $P=1$ atm matches the TACF obtained at $T=213$ K, $P=5000$ atm, and also the same for the TACF obtained at $T=60$ K, $P=1$ atm and $T=100$ K, $P=7000$ atm. There are also other combinations exhibiting the same effect. These results demonstrate the invariance of the time dependence of the correlation function of the α -relaxation as well as the ratio $\tau_{\alpha}/\tau_{\beta}$. Together, the two invariance can be restated again as approximate co-invariance of τ_{α} , n , and τ_{β} to change of thermodynamic conditions. In all the experiments and simulations considered in this paragraph, an approximate correspondence between τ_{β} and τ_0 calculated from the Eq.(3) of the Coupling Model has been found.

The remarkable and general property of approximate co-invariance of τ_{α} , n , and τ_{β} oblivious to changing thermodynamics conditions is another strong evidence that the JG β -relaxation is fundamentally important and it is strongly connected to the α -relaxation. This connection has impact on the interpretation of other experimental findings on dynamics of glass-forming systems. For example it has been shown by various authors that the α -relaxation times, τ_{α} , obtained at various T and P , superpose when plotted versus T/ρ^{γ} , where ρ is density and γ a material constant for many van der Waals liquids and polymers [50-54]. This T/ρ^{γ} -dependence of τ_{α} was obtained by combining the pressure-temperature-volume relation with τ_{α} deduced from the dielectric relaxation spectra measured at various

combinations of P and T . Since experiments and simulations have shown that for any τ_α that the ratio τ_α/τ_β is approximate constant independent of P and T , if τ_α is a function of T/ρ^γ , then it immediately follows that τ_β is also **approximately** a function of T/ρ^γ with the same γ . Actually in practice we have demonstrated that approximately τ_β is also a function of T/ρ^γ with the same γ as τ_α in diglycidyl ether of bisphenol-A (DGEBA) with molecular weight=380 g/mol, and other glass-formers. [20]. Since the JG β -relaxation is the precursor of the α -relaxation, causality implies that the dependence of τ_α on T/ρ^γ originates from the dependence of τ_β on T/ρ^γ . This has support from results of molecular dynamics simulations of binary Lennard-Jones systems, 1,4 polybutadiene, ionic liquids, and $2\text{Ca}(\text{NO}_3)_2 \cdot 3\text{KNO}_3$ (CKN) that the scaling exponent γ is related to the steepness of the repulsive part of intermolecular potential $U(r)$, evaluated around the distance of closest approach between particles in the case of Lennard-Jones systems, and less than the distance σ of the L-J potentials for non-bonded interactions in the case of 1,4 polybutadiene. **Such short distance is akin to the local and non-cooperative β -relaxation.** For details see Ref.[20].

Throughout the previous sections we emphasize that the relation (4) between τ_α and τ_β proposed by the Coupling Model is only approximate and not exact. We heighten the awareness of this fact by using therein the approximate equality sign ‘ \approx ’ instead of ‘ $=$ ’. The warning that the relation is only approximate had appeared in the first paper on this subject published in 1998 [2], many other papers following that such as Ref.[3], and review article [5] and book [4]. Since our relation between τ_α and τ_β is only approximate, τ_β is not expected to scale *exactly* for the *same* γ used to scale τ_α . A recent study of dielectric relaxation of a low molecular weight polymethylmethacrylate (PMMA) at various combinations of P and T found τ_α can be scaled to show that it is a function of T/ρ^γ over a range of 7 orders of magnitude change in τ_α [55]. On the other hand, the accompanying data of τ_β when scaled in the same way cannot be described *exactly* by a function of T/ρ^γ with the same γ as for τ_α over the same range. Notwithstanding, the scatters of the τ_β data from a plausible function of T/ρ^γ are all within ± 0.5 decade over the entire range of the scaling variable T/ρ^γ , where τ_α changes by 7 orders of magnitude (see fig.4 of Ref.[55]). Such small scatters of τ_β from a function of T/ρ^γ actually verify that the results of PMMA are consistent with the *approximate* relation (4). Unfortunately the authors mistakenly assert the exact equality (i.e. $\tau_\alpha = [t_c^{-n} \tau_\beta]^{1/(1-n)}$) is the prediction of the CM instead of the approximate relation (4). The mistake has led these authors to the wrong conclusion that their PMMA data contradict the CM, but actually the data are consistent with it. Nevertheless, the results from the experiment on PMMA [55] verify the prediction from relation (4) that the JG β -relaxation time obey approximately T/ρ^γ -scaling with the same γ as the α -relaxation time.

The strong connection between the α -relaxation and the JG β -relaxation bought out by the invariance of τ_α/τ_β at constant τ_α for different combinations of P and T implies that the two relaxations are not independent. Fitting the data with the sum of the Fourier transform of the KWW function for the α -relaxation and the Cole-Cole loss peak for the JG relaxation is like treating the two processes as independent. In view of the strong connection between the two processes, this procedure is invalid. For well resolved β -loss peaks, the τ_β determined from this fit will not be too different from that of τ_β obtained simply from the reciprocal of the loss peak frequency. However, if the β -relaxation is not resolved, this unjustified fitting procedure can give spurious result for τ_β . An example of such practice is the analysis of the loss spectrum of the lower molecular weight (402 g/mol) PMMA taken at $T=294.8$ K and $P=367.4$ MPa, which exhibits a broad shoulder on the high frequency side of the α -loss peak [55]. A contrasting situation occurs in the mechanical relaxation measurements of the

metallic glasses, $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$, and $\text{Pd}_{30}\text{Ni}_{50}\text{P}_{20}$ [56]. As can be seen from the Arrhenius plot of $\log \tau_\alpha$ and $\log \tau_\beta$ in the paper [56], the separation between the two relaxations is small as indicated by $(\log \tau_\alpha - \log \tau_\beta) \leq 2$ for $T > T_g$. The loss from β -relaxation in these metallic glasses is not small compared with the high frequency flank of the α -loss peak as can be inferred from the isothermal spectra. Consequently the frequency dispersion of the α -relaxation is broadened by the encroaching β -relaxation at temperatures above T_g . There is no unambiguous way to separate out the loss contributed by the α -relaxation process from the raw data. Without doing that, it is meaningless to compare the broadened frequency dispersion of the α -relaxation in $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$, and $\text{Pd}_{30}\text{Ni}_{50}\text{P}_{20}$ with that of the two other Cu-containing metallic glasses, $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Pd}_{42.5}\text{Ni}_{7.5}\text{Cu}_{30}\text{P}_{20}$. The latter Cu-containing metallic glasses have β -relaxation well resolved and well separated from the α -relaxation, and hence the α -loss peak is not broadened by the β -relaxation. **Without taking into consideration of the difference in the relation between the two processes in these two types of metallic glasses**, comparison of their raw frequency dispersion data was made. Superficially the frequency dispersions of the α -loss peaks of all four glasses appear to be no different, and contradict the prediction of relation (4) that larger width of the α -dispersion (or larger n) corresponds to larger separation from the β -relaxation, found to hold in so many neat glass-formers and mixtures [2,26]. In reality, this comparison create no more than a confusion in interpreting the experimental data because the actual width of the α -relaxation in $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$, and $\text{Pd}_{30}\text{Ni}_{50}\text{P}_{20}$ is narrower than the raw data shown because of broadening by the β -relaxation **located** close by. In another similar paper on metallic glasses where the same $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ [57], less data and deeper in the glassy state are shown for τ_β , and the authors extrapolate these data by an Arrhenius fit to the temperature dependence a long way back to T_g and above. Shown as an inset to their Fig.10(b), the extrapolated value of $\tau_\beta(T_g)$ at $T=T_g=562$ K is about 4 s. This value of $\tau_\beta(T_g)$ are longer by several orders of magnitude from that given in the publication cited before for the same material [56]. Moreover, the activation energy, E_a , of the Arrhenius dependence of $\tau_\beta(T)$ used in the extrapolation is about 3206 K or 26.65 kJ/mol. Hence the ratio, E_a/RT_g , is equal to 5.7, much smaller than the nominal values of 25 and up for non-metallic and metallic glass-formers, and is unacceptable. Thus the Arrhenius extrapolation is problematic, and the value of $\tau_\beta(T_g)$ obtained is highly unreliable and should not be compared with any respectable model or theory. Despite these problems and the large uncertainties introduced by the long extrapolation, these authors compare their value of about 4 s for $\tau_\beta(T_g)$ to the CM prediction, and conclude by the irrelevant statement "... however, we find that the separation between the α and β processes in these cases is several orders of magnitude smaller than what is predicted from the CM.". Qiao and co-workers recognized the gross inconsistency in the extrapolation to get the value of $\tau_\beta(T_g)$ in their two papers, and rectify the inconsistency by publishing a new figure 10b in an erratum [58]. However, in the erratum they stated that "This correction does not require any change in the text of the paper.". This sentence in the erratum is incorrect because in the text of their paper [57], there is the negative remark on the CM (cited above), which no longer holds, and this blunder remains and requires change in the text of their paper [57].

4. Summary and Conclusion

The results from our study of the dynamics of two glass-formers presented in this paper serve several purposes. Diethylphthalate (DEP) is a flexible glass-former having a well resolved and prominent secondary relaxation. Calling it the JG β -relaxation has no meaning until there

is some criterion or criteria to distinguish it from the other garden variety of secondary relaxations. This is the reason why there is need to provide criteria to distinguish the JG β -relaxation of fundamental importance to glass transition from the rest of the secondary relaxations [6]. All criteria introduced before have to do with some properties of the JG β -relaxation that are related to the α -relaxation. One criterion emphasized in this paper is the pressure dependence of the secondary relaxation time τ_β . If τ_β is pressure independent unlike τ_α , this immediately shows that the secondary relaxation is not the JG β -relaxation. Dielectric relaxation study of DEP at elevated pressure has been done [44], and the secondary relaxation time τ_γ was found pressure insensitive, and hence the resolved secondary relaxation is not the JG β -relaxation. Since there is only one resolved secondary relaxation, the question that immediately follows is whether the JG β -relaxation exists or not in DEP. If not, the consequence is serious because then the JG β -relaxation is not a universal feature of glass-formers and hence not fundamental. The way to answer this question is motivated by another criterion for JG β -relaxation that it has τ_β approximately the same as the primitive relaxation time τ_0 of the CM, i.e. relation (3). Calculating by Eq.(1) with the relatively small value of the coupling parameter n of neat DEP, it turns out that $\tau_0 \approx \tau_\beta$ lies between τ_α and τ_γ , suggesting the JG β -relaxation is obscured by the more intense α - and γ -relaxations in the dielectric spectra. The way to resolve the JG β -relaxation from the α -relaxation, if it exists in DEP, is to increase the difference, $\log \tau_\alpha - \log \tau_0$, or the separation of the two processes. According to Eq.(2), this can be achieved by increasing the coupling parameter n of DEP, and experimentally this is done by dissolving DEP in solvent with much higher T_g . Elevating pressure will separate the JG β -relaxation from the non-JG γ -relaxation because the former is pressure dependent and the latter is not. By studying the dynamics of DEP in mixture with oligo-styrene at elevated pressure, we have resolved a new secondary relaxation, which has properties related to that of the α -relaxation, and is the JG β -relaxation of DEP.

The other glass-formers CNBz we studied is a rigid molecule and there is only one secondary relaxation. It is likely the JG β -relaxation because the one criterion that the motion involves the entire molecule is satisfied. We take advantage of this simpler situation of CNBz and study its dynamics with emphasis on the relation between the α -relaxation and the JG β -relaxation in mixtures with tristyrene and at different combinations of pressure and temperature. There is almost perfect superposition of the spectra at all frequencies for various combinations of P and T at constant τ_α . In other words, the frequency dispersions of the α -relaxation and the JG β -relaxation as well the processes intermediate between the two are invariant to change of P and T in this case. In particular, the ratio, τ_α / τ_β , is also invariant despite large changes in thermodynamic quantities including volume and entropy. **The same effects have been found in ionic conductivity relaxation. Thus, being independent of thermodynamic condition, these remarkable and general dynamic properties come from the evolution of the dynamics with time, which is solely governed by the intermolecular potential.** One consequence is that if τ_α is a function of T/ρ^γ , then τ_β is necessarily and approximately another function of T/ρ^γ , with the same γ . On the other hand, the primitive relaxation time τ_0 is exactly a function of T/ρ^γ in view of the CM Eq.(2). Since the JG β -relaxation or the primitive relaxation **has already taken place at times** before the α -relaxation, causality implies that the former is more fundamental, **and the T/ρ^γ -dependence actually originates from the JG β -relaxation or the primitive relaxation, and is passed onto the α -relaxation at later times in the manner as prescribed by relations (3) and (4) of the CM.**

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