Do Theories of the Glass Transition, in which the Structural Relaxation Time Does Not Define the Dispersion of the Structural Relaxation, Need Revision?

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Upon decreasing temperature or increasing pressure, a noncrystallizing liquid will vitrify; that is, the structural relaxation time, τ_α, becomes so long that the system cannot attain an equilibrium configuration in the available time. Theories, including the well-known free volume and configurational entropy models, explain the glass transition by invoking a single quantity that governs the structural relaxation time. The dispersion of the structural relaxation (i.e., the structural relaxation function) is either not addressed or is derived as a parallel consequence (or afterthought) and thus is independent of τ_α. In these models the time dependence of the relaxation bears no fundamental relationship to the value of τ_α or other dynamic properties. Such approaches appear to be incompatible with a general experimental fact recently discovered in glass-formers: for a given material at a fixed value of τ_α, the dispersion is constant, independent of thermodynamic conditions (T and P); that is, the shape of the α-relaxation function depends only on the relaxation time. If derived independently of τ_α, it is an unlikely result that the dispersion of the structural relaxation would be uniquely defined by τ_α.

1. Introduction

Vitrification, the dramatic slowing down of kinetic processes such as molecular reorientation, is a general phenomenon found in organic, inorganic, metallic, and polymeric materials. On decreasing temperature T or increasing pressure P, the structural relaxation time τ_α becomes long and eventually the liquid cannot reach its equilibrium configuration. The importance of vitrification and glassy behavior in science and technology has inspired continued research efforts over many decades, with the goal of understanding the underlying dynamics and ascertaining the governing factors therein. Those factors that have been identified are incorporated into present-day theories and models of the glass transition. The most notable dynamic property (and the immediate cause of vitrification) is the divergence of τ_α with decreasing temperature at constant pressure. This temperature dependence can be represented in the vicinity of the glass transition by the Vogel−Fulcher−Tammann−Hesse (VFTH) equation[1−3] or the equivalent Williams−Landel−Ferry (WLF) equation.[4] The factor governing the divergence of τ_α was identified as unoccupied volume in the free volume model,[4,5] and configurational entropy in the Adam and Gibbs[6] model.

An increase of pressure, similar to a temperature decrease, reduces both the unoccupied volume and the configurational entropy, thus slowing down structural relaxation. The free volume model has been extended to consider the effect of hydrostatic pressure,[4,7] and an extension of the Adam−Gibbs model for elevated pressures has been proposed.[8] More sophisticated offshoots of these two celebrated models have appeared but are based essentially on the same controlling factors.

Despite differences in the physics underlying the various theories and models of the glass transition, one trait common to all is that the dispersion (time or frequency dependence) of the structural relaxation bears no relation to the structural relaxation time and does not govern the dynamic properties. Instead, the dispersion is either not considered or is derived as a separate consequence of the model based on other factors, possibly entailing additional assumptions. Consequently, the dispersion and τ_α are obtained independently as separate and unrelated predictions. Certainly τ_α can be constant for different combinations of temperature and pressure because of compensating effects on the molecular mobility, even though the specific volume, configurational entropy, and static structure factor may change. However, if the dispersion of the structural relaxation is derived independently of τ_α, it is not expected to be constant for these same combinations of T and P since the two quantities do not necessarily have the same dependence on volume, entropy, static structure factor, high-frequency shear modulus, etc.

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In this paper we present representative experimental results for various glass formers to show that the dispersion of the structural relaxation remains unchanged for widely different combinations of temperature and pressure, provided τ_α is constant. This apparently general property implies that the dispersion of the structural relaxation is defined by τ_α, or at least τ_α and the dispersion have to be coupled predictions of any viable theoretical interpretation. If the dispersion of the structural relaxation is derived independently of τ_α, it is unlikely to be a unique function of τ_α. This observation and the conclusions drawn from it have important consequences for studies of the glass transition and the dynamic properties of glass-forming materials. Newly analyzed experimental data, along with some previously published results, are presented herein to support these conclusions.

2. Invariance of the α-Dispersion to Different Combinations of *T* and *P* at Constant τ_α

Due largely to experimental convenience, studies of molecular dynamics have focused on the effect of temperature, wherein isobaric measurements of relaxation times and viscosities are carried out as a function of *T*. Recently, pressure has been employed as an experimental variable, with the resulting data leading to discovery of new facts having important insights into the dynamics of glass-forming liquids and polymers. Some of these new findings concerning the dynamic properties are widely applicable and have immediate impact on understanding the glass transition. One example is the dielectric loss spectra measured at atmospheric and elevated pressures for a large number of glass-formers.[9-36] A given value of the structural relaxation time τ_α or frequency ν_α at ambient pressure can be maintained upon increases in pressure *P* by raising the temperature. Various combinations of *P* and *T* can be chosen for which the α-loss peak frequency ν_α will remain the same. In cases where the height of the α-loss peak, ϵ''_{max}, changes, the dispersions at a fixed ν_α are compared after the amplitude of the dielectric loss $\epsilon'(\nu)$ has been normalized by ϵ'_{max}. Remarkably, for the same α-loss peak frequency there is no change in the frequency dispersion of the α-loss peak with varying pressure and temperature. In other words, for a given material at a fixed value of τ_α, the α-relaxation function is constant, independent of thermodynamic conditions (temperature and pressure). Stated differently, temperature−pressure superpositioning works for the dispersion of the structural α-relaxation at constant τ_α. Lack of superposition may occur at frequencies sufficiently higher than ν_α. Such deviations are attributed to contributions to the dielectric loss from secondary relaxations (which may not be resolved from the primary α-peak), whose relaxation time and dielectric strength do not have the same *P* and *T* dependences as the α-relaxation.

To demonstrate convincingly this general experimental fact, we use newly analyzed experimental data and provide additional data on previously investigated glass formers. We present dielectric relaxation loss curves measured at different *P* and *T* combinations that have more than one value of ν_α or τ_α (and thus different breadths for the dispersion[37]). These results show that for a given material, the invariance of the structural relaxation function for fixed τ_α is valid for a broad range of τ_α. The materials investigated herein include molecular glass formers (Figure 1) and amorphous polymers (Figure 2) of diverse chemical structure; all show the property of temperature−pressure superpositioning of the α-dispersion at constant τ_α.

3. Results

Molecular Glass Formers. We first consider small-molecule, glass-forming liquids that have narrow dispersions of the α-relaxation and an excess wing on the high-frequency flank, but otherwise no other resolved secondary relaxations in their dielectric spectra. There are experimental results[38-42] indicating that the excess wing is an unresolved Johari−Goldstein secondary relaxation.[43-46] These materials include cresolphthalein-dimethyl ether (KDE),[9] phenylphthalein-dimethyl ether (PDE),[10] propylene carbonate (PC),[11] chlorinated biphenyl (PCB62),[12] phenyl salicylate (salol),[13] 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BPTCDaH),[14] and 1,1′-di(4-methoxy-5-methyl-phenyl)cyclohexane (BMMPC).[15] For these materials, due to the unresolved secondary relaxation, a strong dependence of the shape of the dispersion on *T* and *P* (with τ_α varying) is especially evident; see for example refs 9 and 12. The fact that at a fixed value of τ_α the dispersion of the α-relaxation is constant, independent of *T* and *P*, is demonstrated in Figure 1a for KDE, Figure 1b for PC, and Figure 1c for PCB62 (experimental details of these measurements can be found respectively in refs 9, 11, and 12). In each figure, previously unpublished data are used to show that this property holds for more than one value of τ_α. The same results are found (but not shown herein) for PDE, BPTCDaH, BMMPC, and salol.

There are molecular glass formers that have a resolved secondary relaxation whose peak frequency is pressure independent; these are not Johari−Goldstein (JG) processes (according to the definition given in ref 42). The slower JG relaxation is not resolved from the α-relaxation in the equilibrium liquid state, but in some cases it can be observed as a distinct peak in the glassy state. Such liquids include 1,1′-bis-(p-methoxyphenyl)cyclohexane (BMPC),[16] diethyl phthalate, (DEP),[17] di-*n*-butyl phthalate (DBP),[18] diisobutyl phthalate (DiBP),[18] di-isooctal phthalate (DiOP),[19] decahydroisoquinoline (DHIQ),[20] dipropyleneglycol dibenzoate (DPGDB),[21] benzoin-isobutyl ether (BIBE),[22] the epoxy compounds including di-glycidyl ether of bisphenol A (EPON828),[23] 4,4′-methylenebis-(*N,N*-diglycidylaniline) (MBDGA),[24] bisphenol A-propoxylate-(1 PO/phenol)diglycidyl ether (1PODGE),[25] *N,N*-diglycidyl-4-glycidyloxyaniline (DGGOA),[26] and *N,N*-diglycidylaniline (DGA).[26] For all members of this class of glass formers, a constant dispersion is associated with a fixed value of τ_α, independent of thermodynamic conditions (*T* and *P*). We show this (for more than one value of τ_α) with previously unpublished data in Figure 1d for DiBP, Figure 1e for DPGDB, and Figure 1f for BIBE. The experimental details for these can be found, respectively, in refs 18, 21, and 22. The same property holds also for BMPC, DiBP, DEP, DiOP, DHIQ, EPON828, 1PODGE, MBDGA, DGGOA, and DGA (results not shown).

Earlier dielectric studies under elevated pressure[47-51] found temperature−pressure superpositioning at constant τ_α for a few molecular glass formers, including *ortho*-terphenyl (OTP), di-(2-ethylhexyl) phthalate, tricresyl phosphate, polyphenyl ether, and a naphthenic mineral oil; however, the temperature and pressure ranges were not as wide as herein.

Amorphous Polymers. Dielectric relaxation measurements under pressure have been carried out on several amorphous polymers and for all cases the dispersion of the local segmental relaxation (i.e., the α-relaxation) conforms to temperature−pressure superpositioning at constant τ_α. These polymers include polyvinylmethyl ether (PVME),[27] poly(vinyl acetate) (PVAc),[28] poly(ethylene-*co*-vinyl acetate) (EVA, having 70 wt % vinyl acetate),[29] polymethylphenylsiloxane (PMPS),[30] poly(methyl-tolylsiloxane) (PMTS),[31] polyvinylethylene (PVE, also referred
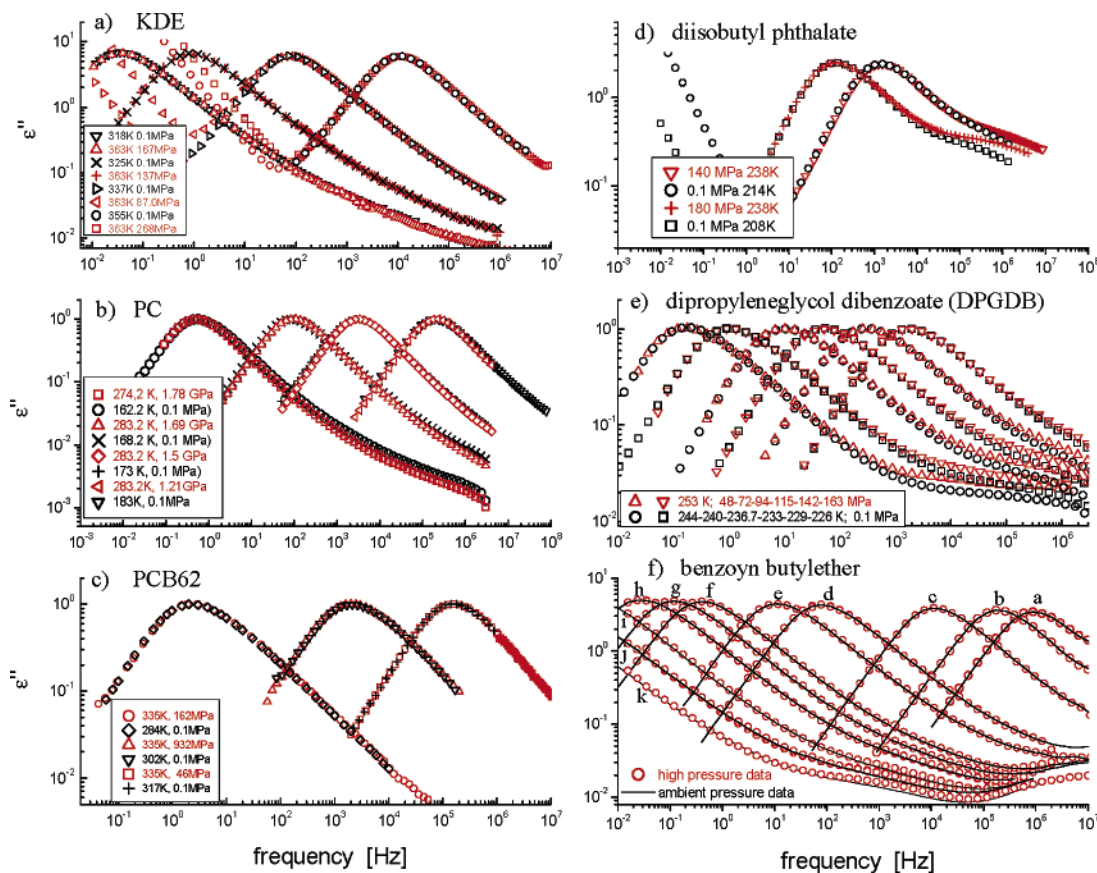
Figure 1. Dielectric loss data at various combinations of temperature and pressure (as indicated) to demonstrate the invariance of the dispersion of the α-relaxation at constant α-loss peak frequency ν_α or equivalently at constant α-relaxation time τ_a. (a) Cresolphthalein-dimethylether (KDE). (b) Propylene carbonate (PC) (loss normalized to the value of the maximum of the α-loss peak measured at ambient pressure). The two ambient pressure spectra at higher frequency are from ref 38. (c) Chlorinated biphenyl (PCB62). (d) Diisobutyl phthalate (DiBP). (e) Dielectric loss of dipropyleneglycol dibenzoate (DPGDB) normalized to the value of the maximum of the α-loss peak. The d.c. conductivity contribution has been subtracted. Red triangles are isothermal measurements at $T = 253$ K and $P = 48, 72, 94, 115, 142, 163$ MPa (from right to left). Black symbols are isobaric measurements made at $P = 0.1$ MPa and $T = 244, 240, 236.7, 233, 229, 226$ K (from right to left). The spectrum at $T = 226$ K has been shifted along *x*-axis by multiplying frequency by a factor 1.3. (f) Dielectric loss of benzoyn butyl ether (BIBE) at different *T* and *P*. The d.c. conductivity contribution has been subtracted. Spectra obtained at higher *P* are normalized to the value of the maximum of the loss peak obtained at the same frequency at atmospheric pressure. From right to left: black lines are atmospheric pressure data at *T* (K) = 271 (a), 263 (b), 253 (c), 240 (d), 236 (e), 230 (f), 228 (g), 226 (h), 223 (i), 220.5 (j), 218 (k) K. Symbols are high-pressure data: $T = 278.5$ K and $P = 32$ (a), 65 (b), 118 (c), 204 (d), 225 (e), 320 (h), 370 (j), 396 (k) MPa; $T = 288.2$ K and $P = 350$ (f), 370 (g), 423 (i), 450 (j) MPa, and $T = 298$ K and $P = 330$ (d), 467 (h) MPa.

to as 1,2-polybutadiene),[32] poly(phenyl glycidyl ether)-*co*-formaldehyde (PPGE),[33] 1,4-polyisoprene (PI),[34] poly(propylene glycol) (molecular weight: 4000 Da) PPG-4000,[35] and poly-(oxybutylene) POB.[36] Including some previously unpublished data, constant dispersions at a fixed value of τ_α independent of thermodynamic conditions (*T* and *P*) are shown for more than one τ_α in Figure 2a for PVAc, in Figure 2b for PMTS, in Figure 2c for PPGE, and in Figure 2d for POB. Experimental details for these measurements can be found in refs 28, 31, 33, and 36, respectively. Note that for POB there is a dielectrically active normal mode at lower frequencies, which has different *P* and *T* dependences than the local segmental mode. The *T*−*P* super-position at fixed τ_α holds also for PVME, EVA, PMPS, PVE, and PPG-4000 (data not shown).

Hydrogen bonded networks or clusters, if present, are modified at elevated pressure and temperature, changing the physical structure of the glass-former. This occurs, for example, in glycerol,[52] propylene glycol dimer (2PG),[40] and m-fluora-niline.[53] These hydrogen bonded glass formers do not obey temperature−pressure superpositioning at constant τ_α, since the physical structure of the material changes at elevated pressure/elevated temperature.[54]

4. Discussion

We now discuss the impact of this general property on theories and models of the glass transition. The primary concern of most theories is to explain the temperature and pressure dependences of the structural relaxation time. The dispersion of the structural relaxation is either not addressed or else is drawn separately from additional considerations not involved in arriving at τ_α. For example, the original free volume models[4,5] and the Adam−Gibbs model[6] treat the variation of relaxation times with *T* but do not predict the distribution of molecular relaxation rates. Additional input such as a specific fluctuation of some parameter must be introduced to generate a distribution of relaxation times. It is not difficult for any of these theories to find combinations of *T* and *P* such that the predicted $\tau_\alpha(T,P)$ is constant. However, it is unlikely that the same combinations will also yield an invariant dispersion. For a single glass former it may be possible to introduce additional assumptions to force both τ_α and the dispersion to be simultaneously constant. However, this would not be a worthwhile undertaking since τ_α and the dispersion are simultaneously constant for so many glass-formers, with different physical and chemical structures, and greatly different sensitivities to temperature and density.[55,56]

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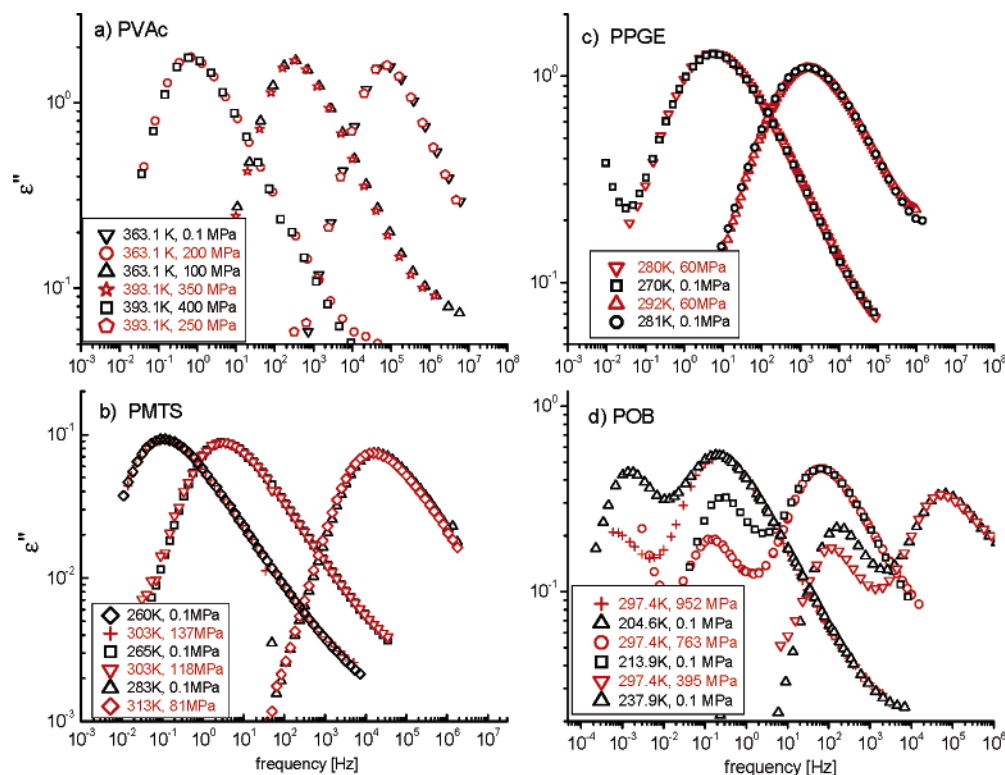

Figure 2. Dielectric loss data at various combinations of temperature and pressure (as indicated) to demonstrate the invariance of the dispersion of the α-relaxation at constant α-loss peak frequency ν_α or equivalently at constant α-relaxation time τ_α. (a) Poly(vinyl acetate) (PVAc); (b) poly(methyltolylsiloxane) (PMTS); (c) poly(phenyl glycidyl ether)-*co*-formaldehyde (PPGE); (d) poly(oxybutylene) (POB). In all cases, spectra obtained at higher *P* are normalized to the value of the maximum of the loss peak obtained at the same frequency at atmospheric pressure.

More serious revision is necessary to bring the conventional models into consistency with the general experimental property described herein.

As illustrated in some of the figures, the α-loss peaks are well represented by the one-sided Fourier transform of the Kohlrausch function,[57,58]

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

especially the main peak and its low-frequency flank.[37] The fractional exponent, *n*, can be used to characterize the dispersion of the α-relaxation. Thus, the experimental fact of constant dispersion of the α-relaxation at constant τ_α can be restated as the invariance of the fractional exponent or the Kohlrausch exponent, $(1-n)$, to different combinations of *T* and *P* that hold τ_α constant. The coupling model (CM)[59-63] is consistent with this experimental observation. In the CM, at any *T* and *P*, it is the heterogeneous many-molecule dynamics that slow the primitive relaxation rate, $1/\tau_0(T,P)$, and give rise to the Kohlrausch correlation function. The relaxation time $\tau_\alpha(T,P)$ and the fractional exponent *n* of the Kohlrausch function are linked by the relation $\tau_\alpha(T,P) = [t_c^{-n}\tau_0(T,P)]^{1/(1-n)}$. From this defining equation of the CM, it can be shown that τ_α and *n* are co-invariants for different combinations of *T* and *P*.

Not only does τ_α uniquely define the dispersion, as shown herein, but also many properties of τ_α are governed by the dispersion or the fractional exponent *n*. Examples of these properties are described in a review;[64] here a few are mentioned.

(*i*) The "fragility" index, $m \equiv d\log_{10}\tau_\alpha/d(T_g/T)|_{Tg/T=1}$, at ambient pressure increases with *n*.[64,65] However, there are well-known examples of violation of this correlation. This is because the temperature dependence of τ_α is governed not only by *n* (i.e., the breadth of the dispersion) but also by the specific volume, *V*, and entropy, *S*. Hence, *m* is not a fundamental quantity. Chemically different glass-formers can have widely different dependence of τ_α on *V* and *S*,[55] causing a breakdown of the correlation between *m* and *n*. Also for a given glass-former the correlation is found to break down under elevated pressure.[67] In general *m* decreases with *P*.[68] Since *n* or the dispersion is constant at $\tau_\alpha = 10^2$ s (a time customarily used to define T_g for any pressure), the fact that *m* decreases with *P* means that the correlation between *m* and *n* necessarily fails.

(*ii*) In quasielastic neutron scattering experiments, the dependence of τ_α on the scattering vector *Q* is given by $Q^{2/(1-n)}$.[64,69]

(*iii*) The separation, $[\log(\tau_\alpha) - \log(\tau_{JG})]$, of τ_α from the Johari–Goldstein relaxation time τ_{JG} at a fixed value of τ_α is proportional to *n*.[42,62,63,70]

(*iv*) The observed crossover at some temperature T_B above T_g of the temperature dependence of τ_α from one VFTH equation to another,[70-73] the apparent onset of bifurcation of τ_{JG} from τ_α,[39] and the decoupling of translational diffusion from viscosity[75] are all related to the small size of *n* at temperatures above T_B and the more rapid increase of *n* across T_B on decreasing the temperature.

(*v*) The ratio of the two values of τ_α at T_g given by the two VFTH equations used to fit τ_α at temperatures above and below T_B increases with increasing *n*.[74]

(*vi*) For polymers, there is also the correlation of the degree of thermorheological complexity with *n*, as exemplified by polystyrene and polyisobutylene.[64,76]

These properties are all consistent with the coupling model.[61]

5. Conclusion

A recently discovered, general experimental fact is that for virtually any glass formers at fixed τ_α, the shape of the α-dispersion is constant, independent of thermodynamic condi-

tions. If models of the glass transition derive the dispersion of the structural relaxation independently of τ_α, it is unlikely that τ_α would uniquely define the dispersion. With the exception of the coupling model, theories and models of the glass transition either do not address the dispersion or derive it independently of τ_α; hence, they are in need of revision.

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