



Isochronal temperature–pressure superpositioning of the α -relaxation in type-A glass formers

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Received 13 August 2002; in final form 30 August 2002

Abstract

Dielectric spectra were obtained at ambient and elevated pressures for three ‘type-A’ glass formers, which exhibit excess intensity on the high frequency side of the structural relaxation peak. The response to pressure of the peak maximum and the excess wing suggests categorization of such glass formers into two groups: associated liquids, in which the α -relaxation and the excess wing have a different pressure dependence, and van der Waals liquids, which at fixed value of the α -relaxation time, conform to temperature–pressure superpositioning. This distinction is believed to arise from the change in the number of intermolecular bonds (non-dispersive interactions) with volume.

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1. Introduction

Structural relaxation in supercooled liquids remains one of the more intriguing aspects of the dynamics in dense fluids. In addition to the primary α -relaxation, the dielectric spectrum of many liquids (so-called type-B glass formers [1]) reveals a higher frequency process, the β -relaxation. When the motion underlying this β -relaxation involves intermolecular degrees of freedom, it is referred to as a Johari–Goldstein relaxation [2]. The behavior of such β -processes is related to the highly cooperative α -relaxation [3,4], although the details of the relationship remain problematic. Commonly,

secondary relaxations are regarded as Johari–Goldstein processes if they exhibit certain properties, for example, an Arrhenius temperature dependence below T_g , and merging with the α -relaxation at a characteristic temperature, $T_\beta \sim 1.3T_g$, at which $\tau_\beta = \tau_\alpha$. This merging temperature is associated with myriad properties changes, evidencing a change in the cooperative nature of the dynamics [5–9].

Notwithstanding the universal properties of the Johari–Goldstein secondary relaxation, in some supercooled liquids (type-A glass formers [1]), a distinct β -peak is absent from the loss spectrum. Instead, an excess intensity is observed, also towards the high frequency side of the structural relaxation peak. This wing appears as a power-law deviation from the (steeper) power-law characterizing the α -process beyond the peak maximum. Recent debate has focussed on identification of

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this excess wing. One possibility is that it is an inherent part of the α -relaxation, as suggested by Dixon–Nagel scaling of the spectra [10]. The idea that the α -peak and the excess wing are the same process is further supported by successful scaling of loss spectra measured at different pressures on two, structurally very similar, van der Waals liquids, phenylphthalein–dimethylether (PDE) [11] and cresolphthalein–dimethylether (KDE) [11,12]. The alternative possibility is that the excess wing is a different process, overlapping with but distinct from the α -relaxation. Consistent with this interpretation, physical aging, which preferentially shifts the α -peak to lower frequencies, has been shown to transform the respective excess wings in the spectra of propylene carbonate and glycerol into nascent secondary peaks [13]. The fact that an excess wing is often found in liquids whose relaxation function has a small degree of non-exponentiality of the α -relaxation function [3,12,14] supports the idea that the excess wing is merely an unresolved secondary relaxation.

Although these conflicting interpretations of the excess wing phenomenon are each consistent with certain experimental facts, both cannot be correct. This suggests the possibility that the properties of the excess wing may vary among materials; that is, a sub-classification of type-A glass formers according to their behavior may be required. Establishing the existence of a putative connection between an excess wing and the β -relaxation relies on an unambiguous determination that the latter is a Johari–Goldstein relaxation (i.e., intermolecular, involving restricted reorientation of all molecules [2,4,15]). For example, while the secondary relaxation in 1,1'-bis(*p*-methoxyphenyl)cyclohexane (BMPC) shows attributes of a Johari–Goldstein relaxation, NMR experiments reveal that the underlying process is flipping of the phenyl rings [16]. It was also recently reported that the secondary relaxation times of BMPC are invariant to pressure [17]. The implication is that such local motion, not involving the entire molecule, may not be a Johari–Goldstein process. Contrarily, τ_β for sorbitol [18] and for chlorobenzene/decalin mixtures [19], both increase with pressure, and are clearly Johari–Goldstein processes.

This suggests that a fruitful approach to identify the nature of the excess wing in glass formers is from their response to pressure. Accordingly, we have measured the dielectric spectra, as a function of pressure for three type-A glass formers. Our objective was to compare the effect of pressure on the α -peak and the wing, in order to establish whether any connection exists between the motions underlying these two spectral features.

2. Experimental

Salol (phenyl salicylate, from Sigma-Aldrich) BMMPC (1,1'-bis(*p*-methoxymethylphenyl)cyclohexane from H. Sillescu of the University of Mainz), and a polychlorinated biphenyl (Monsanto's Aroclor 1242, obtained from J. Schrag of the University of Wisconsin) were all used as received. For dielectric measurements, the sample was contained between parallel plate electrodes in a Manganin pressure cell (Harwood Engineering). Dielectric spectra were obtained using two spectrometers, a Novocontrol Alpha ($10^{-2} < f$ (Hz) $< 10^7$) and an IMass TDS ($10^{-4} < f$ (Hz) $< 10^4$). Pressures as high as 640 MPa were applied, using a manually operated pump (Enerpac), in combination with a pressure intensifier (Harwood Engineering).

3. Results

In Fig. 1 is shown the dispersion in the dielectric loss for salol, a prototypical type-A glass former. Since broadening of the structural relaxation peak as temperature approaches T_g is commonly observed (and indeed, can be one signature of the change in dynamics occurring below T_β [6,7]), the spectra are compared at a constant value of the relaxation time, defined as $\tau_\alpha = (2\pi f_m)^{-1}$, where f_m is the frequency of the maximum in the dielectric loss. The ambient pressure measurements were obtained at a temperature 4 °C above T_g . Extrapolation using a power-law on the high frequency side of the peak delineates the excess wing. Superimposed on the ambient pressure measurement are dielectric loss curves obtained at elevated pressures, and temperatures such that the $\tau_\alpha(T, P)$

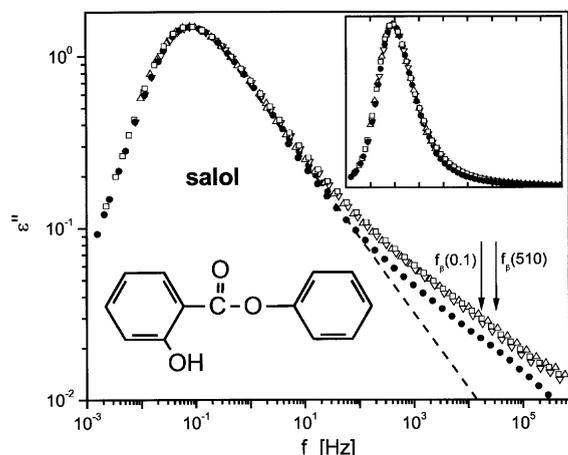


Fig. 1. Structural relaxation peak for salol [(●) $T = 223$ K, $P = 0.1$ MPa; (∇) $T = 297$ K, $P = 380$ MPa; (□) $T = 309$ K, $P = 510$ MPa; (△) $T = 323$ K, $P = 640$ MPa]. The dashed line represents extrapolation of the power-law for frequencies just past the maximum. The arrows denote the calculated frequency of the secondary relaxation for ambient pressure (arrow on left) and at 510 MPa (arrow to the right). The inset shows the data over the same frequency range, but using a linear ordinate scale.

are approximately equal. Since the dielectric strength decreases with temperature (and increases with pressure), the spectra were vertically scaled ($<10\%$) to superimpose. Slight shifting along the frequency axis, by less than 20%, was also necessary to bring the α -peaks into coincidence. Note that of the three glass formers investigated herein, salol exhibits the weakest pressure dependence of τ_α .

Evident in the figure is a marked difference between the intensity of the excess wing measured at low (ambient) pressure and its intensity at high pressure. Since the α -peak maxima superimpose, this indicates that while both spectral features are sensitive to pressure, the responses of α -relaxation and the excess wing are not the same. Thus, for salol, the molecular motion underlying the excess wing is not identical to the structural relaxation process; the former is a separate, albeit related, process.

While the maxima of the primary α -peaks coincide in Fig. 1, there is a modest broadening with increase in pressure. The full width at half maximum (FWHM) of the atmospheric pressure peak is 1.77 decades, while at 510 MPa the FWHM =

1.84 decades. The α -peak can be described using the transform of the derivative of the Kohlrausch function

$$\varepsilon''(2\pi f) = \Delta\varepsilon \int_0^\infty dt \left[\frac{-d}{dt} \exp - (t/\tau_K)^{\beta_K} \right] \sin(2\pi ft)$$

(in which $\tau_K \sim 0.8 \times \tau_\alpha$ for salol). From measurements of an analogous broadening in salol as a function of temperature at atmospheric pressure, Dixon [20] obtained a relationship between the FWHM and the stretch exponent, $\beta_K = 1.047w^{-1} - 0.047$, where w is the FWHM normalized by the Debye width (= 1.142 decades). From the Dixon relation, we obtain $\beta_K = 0.63$ ($P = 0.1$ MPa) and 0.60 ($P = 510$ MPa).

The only quantitative relationship between τ_α and τ_β is due to Ngai [7,14,21], who proposed that $\tau_\beta = t_c^{1-\beta_K} \tau_\alpha^{\beta_K}$, where t_c is a temperature-independent constant taken to equal 2 ps. We calculate $f_\beta (= 1/2\pi\tau_\beta)$ for $P = 0.1$ and for 510 MPa, with the results indicated in Fig. 1. The respective frequencies fall within the range of the excess wing. More significantly, the predicted separation of the f_β is comparable to the displacement of the excess wing induced by elevated pressure. This result supports the interpretation of the excess wing in salol as a distinct secondary process. It is related to, but not an inherent component of the α -relaxation.

Fig. 2 shows the dielectric loss for BMMPC, measured at 3 °C above T_g and $P = 0.1$ MPa, along with spectra for two higher temperatures and pressures. The latter loss curves were vertically scaled $\leq 20\%$ to account for the changing dielectric strength; the frequencies are as measured. There is a prominent excess wing, which superimposes for all three spectra; that is, the α -relaxation and the wing respond identically to changes in pressure and temperature. We also note that the breadth of the primary peak is constant for a given value of τ_α . Both properties are different from those of salol noted above.

Dielectric spectra of Aroclor 1242 are shown in Fig. 3. The behavior is quite similar to that of BMMPC. The excess wing position and intensity, relative to the main α -peak, is unaffected by pressure; thus, when compared at equal τ_α , the spectra can be superimposed. Since for both BMMPC and Aroclor, there is no change in the α -relaxation

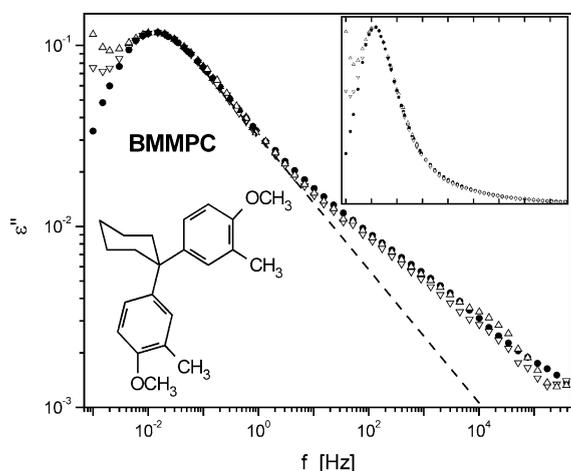


Fig. 2. Structural relaxation peak for BMMPC [(●) $T = 264$ K, $P = 0.1$ MPa; (▽) $T = 279$ K, $P = 50$ MPa; (△) $T = 308$ K, $P = 173$ MPa]. The dashed line represents extrapolation of the power-law for frequencies just past the maximum. The inset shows the data over the same frequency range, but using a linear ordinate scale.

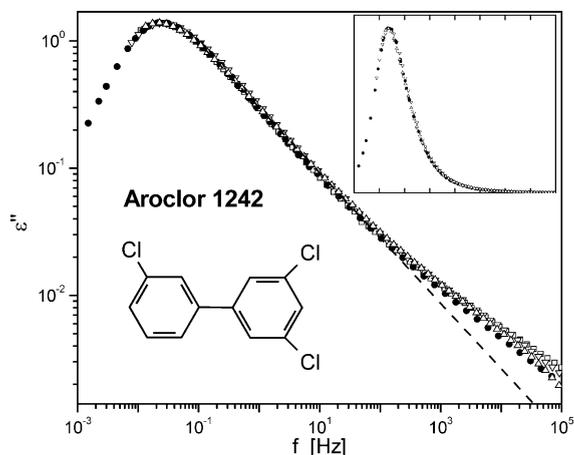


Fig. 3. Structural relaxation peak for Aroclor 1242 [(●) $T = 224$ K, $P = 0.1$ MPa; (▽) $T = 263$ K, $P = 180$ MPa; (□) $T = 273$ K, $P = 235$ MPa; (△) $T = 283$ K, $P = 291$ MPa]. The dashed line represents extrapolation of the power-law for frequencies just past the maximum. The inset shows the data over the same frequency range, but using a linear ordinate scale. The structure shown is a representative isomer of trichlorobiphenyl.

(i.e., no broadening or narrowing), the argument given for salol implies conversely that the entire dispersion (peak and excess wing) for these materials retain the same shape, as observed in Figs. 2 and 3.

4. Discussion

The behavior of salol in Fig. 1 is very similar to that of glycerol. As recently reported [22], the α -peak broadens and there is an apparent shifting of the excess wing when glycerol is subjected to large (0.9 GPa) pressure. Thus, like salol, the excess wing in glycerol cannot be identified as an inherent part of the primary α -relaxation. A similar conclusion was drawn by Schneider et al. [13] from physical aging experiments, which cause glycerol to develop a shoulder in the vicinity of the excess wing. (The same effect was reported in [13] for propylene carbonate, which is highly polar, but lacks hydrogen bonding. Since the spectral changes induced by aging are subtle, dielectric measurements on propylene carbonate under elevated pressure would be useful.) We also note that the excess wing in propylene glycol, although not shown to have different characteristics than the α -relaxation, has been identified as a submerged β -process. This conclusion came from analysis of dielectric spectra taken on propylene glycol oligomers of varying molecular weight [14]. Decreasing the number of monomers in polypropylene glycol reduces the separation of the α - and β -peaks. Extrapolation to one monomer unit implies an encroachment on the high frequency side of the structural relaxation, as observed for propylene glycol. Thus, we can identify at least some glass formers in which separation of the excess wing from the α -relaxation demonstrates that the former is not a component of the latter.

On the other hand, in addition to BMMPC and Aroclor, there are two other type-A glass formers for which the response of the excess wing and the α -process to pressure are known to be the same, PDE [11] and (the structurally very similar) KDE [11,12]. We list in Table 1 all type-A materials mentioned herein, with the salient issue being the origin of the two forms of excess wing behavior. One distinguishing characteristic of the type-A liquids in Table 1 whose excess wing can be separated from the α -peak is their capacity for hydrogen bonding. The four species with isochronal temperature–pressure superimposable dielectric spectra, however, are strictly van der Waals liquids.

Table 1
Classification of type-A glass formers

Liquid	Interactions	Excess wing	Reference
Salol	H-bonding	Distinct from α -process	Herein
Glycerol	H-bonding	Distinct from α -process	[13,22]
Propylene glycol	H-bonding	Distinct from α -process	[14]
BMMPC	van der Waals	T–P superimposable	Herein
Aroclor 1242	van der Waals	T–P superimposable	Herein
PDE	van der Waals	T–P superimposable	[11]
KDE	van der Waals	T–P superimposable	[11,12]

This suggests a possible mechanism underlying the differing behaviors. In the first category of type-A liquids, application of pressure reduces the extent of the intermolecular forces. Substantial compression of the liquid imposes space-filling demands which cannot be satisfied without sacrifice of the local orientation necessary for non-dispersive intermolecular interaction, such as H-bonding ('geometrically selective bonds' [23]). Indeed, it has been shown that pressure reduces the degree of hydrogen bonding in polyalcohols, such as glycerol and propylene glycol [24]. H-bond formation in alcohols can also be suppressed by imposing configurational restrictions on the molecular structure itself [25] or by the addition of ions [26–28]. Some highly associated liquids evidently have secondary relaxations that are too slow to be fully resolved from the α -process; however, alleviation of the H-bonding promotes their separation. This reduction in hydrogen bonding can be effected by increasing molecular weight, which directly changes type-A into type-B behavior in propylene glycols [14] and polyalcohols [29]. Our sub-classification of type-A materials is also consistent with the observation that physical aging causes the excess wing in glycerol to develop into a shoulder [13], since such aging reduces the unoccupied volume, analogous to the effect of pressure. However, for strictly van der Waals liquids, while compression may alter the magnitude of the interactions, this transpires without changing the number of intermolecular bonds; thus, at fixed τ_α , T–P superpositioning is maintained.

We point out that the proposed differentiation of type-A glass formers parallels a distinction found between van der Waals glass formers, for which thermal energy and free volume have a

comparable effect on the structural relaxation times (e.g., PDE [30], KDE [31], diglycidylether of bisphenol A [32], *o*-terphenyl [33], and poly-[(phenyl glycidyl ether)-coformaldehyde] [30]), and associated liquids, in which temperature is the dominant control variable (e.g., glycerol [34] and sorbitol [18]).

The question remains as to why a change in intermolecular bonding occasions the behavior distinguishing the two forms of type-A liquids. We suggest that the conformance to temperature–pressure superpositioning at fixed τ_α , as seen in van der Waals glass formers, does not demonstrate that the excess wing in those cases is an inherent component of the α -relaxation. Such superpositioning only indicates that the two processes have the same response to pressure. However, alteration of the number of non-dispersive intermolecular bonds affects the highly cooperative α -process more so than the less cooperative secondary process. Therefore, in associated liquids, the excess wing can be disjoined from the structural relaxation peak by volume changes, the latter induced by hydrostatic pressure or physical aging. As shown for alcohols [14,29], the excess wing can even be resolved into a separate peak, although pressure alone is evidently insufficient to bring this about. Of course, if they are distinct processes, at least in principle separation of the α -peak and the excess wing may be possible for van der Waals liquids as well. However, this evidently requires more severe conditions than imposed herein. As an example, it has been shown that changes in the relative shapes of the peak and the excess wing in Aroclor can be brought about by changing the number of chlorine atoms per molecule [35].

5. Summary

The behavior of type-A glass formers can be divided into two categories, those in which the excess wing responds to pressure in the same manner as the primary α -relaxation, and those in which the excess wing has a different response. The former correspond to van der Waals liquids, whose structural relaxation times are governed both by temperature and volume, while the latter group comprises associated liquids, for which temperature dominates the structural relaxation times. This does not mean that there is any fundamental difference in the dynamics underlying the excess wing of associated versus van der Waals glass formers. Rather, their differing behavior reflects the effectiveness of pressure (or molecular structure) in altering intermolecular interactions, and hence the response of intermolecularly cooperative processes.

Acknowledgements

We thank K.L. Ngai for insightful discussions and J.J. Fontanella for experimental assistance. The support of the Office of Naval Research and the Polish State Committee for Scientific Research (Project No. 5P03B 022 20) are gratefully acknowledged.

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