Origin of the High-Frequency Contributions to the Dielectric Loss in Supercooled Liquids

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Dielectric loss spectra of four different glass formers revealing either β relaxation or excess wing are presented. We compare the effect of pressure and temperature on the mentioned processes. Our findings suggest that the excess wing and the β relaxation cannot be treated on the same footing.

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In the supercooled region the molecular dynamics of liquids slow down dramatically, and some characteristic relaxation processes can be observed. The major (α) relaxation process, reflecting structural rearrangement, is characterized by a broad, asymmetric absorption spectrum, along with deviation from an Arrhenius dependency of relaxation times on temperature or pressure.

For many liquids another relaxation process, called the secondary or β relaxation, is found near and below the glass transition temperature. The maximum of the secondary relaxation peak occurs at frequencies higher than the α peak, and above T_g both relaxations tend to bifurcate. First observations of the β relaxation were made in polymers, corresponding to the motion of sidegroups in polymers containing flexible pendant dipoles, or more generally local mode motions [1]. However, from the work of Johari and Goldstein [2], who observed the β relaxation in rigid, small molecules, this process is considered to be a near universal and intrinsic feature of the deeply supercooled and glassy states.

However, despite much debate, there is no general agreement about the origin of the secondary relaxation in supercooled liquids. It is still unknown if this process has an intermolecular or intramolecular origin, or whether it reflects small [3,4] or relatively large-angle jumps [5]. Another open issue is whether all molecules contribute to the relaxation, or only those residing in regions of density lower than the bulk. The latter idea was put forward by Johari and Goldstein [6], who referred to regions retaining motional degrees of freedom as "islands of mobility." On the other hand, the former idea can be found in many models. One of the most general concepts is embodied in the "coupling model" of Ngai [7]. He suggests that the secondary relaxation is a spatially uniform feature, with temporary fluctuations of density responsible for the motions underlying this process. This view, in which statistically all molecules contribute to the observed response, finds support in the work of Wagner and Richert on sorbitol [8] and of Vogel and Roessler on toluene [4].

It is well known that there are a number of molecular glass formers that do not exhibit a well-resolved β relaxation, either as a peak or shoulder [9,10]. Instead, the dielectric loss spectrum exhibits an excess wing on the high frequency side of the α-relaxation peak. This wing can be described by a second power law $\varepsilon'' \sim n^{-b}$ with $b < \beta$ (β being the exponent characterizing the high frequency side of the α relaxation in the vicinity of the loss maximum) [10,11]. There is no general agreement on whether the excess wing and the β relaxation have the same microscopic origin. The tendency to consider these as distinct processes is reflected in the proposition that liquids can be divided into two groups: type-*A* materials having an excess wing and type-*B* materials with a well-resolved β peak (toluene and sorbitol) [12].

During recent years, many efforts have been made to understand the relation between the β relaxation and the "excess wing." Dixon *et al.* [9] postulated that the excess wing is an intrinsic feature of α relaxation, universal for all glass formers. In their opinion, its apparent absence in the case of type-*B* liquids is due to masking by a dominant β peak. Wu [13] postulated that even in cases in which the β peak is well resolved, any fitting procedure should employ a function which includes the excess wing. There are also theoretical models, such as Chamberlin's dynamically correlated domains [14] which are consistent with the suggestions of Dixon *et al.*

A completely different approach is suggested by, among others, Ngai's coupling model [7]. He postulates that the excess wing is simply the high-frequency flank of a secondary peak, the latter unresolved due to the presence of the dominating α peak close to the β-peak maximum.

In support of the above thesis, Schneider carried out a very interesting experiment on the two best-known representatives of type-*A* materials (i.e., glycerol and propylene carbonate [15]. Based on observations that the well-resolved β peak is far less sensitive to temperature than the α relaxation, they suggested that if the excess wing is indeed a secondary relaxation process, it should be possible to separate it from the α process by probing deep into the glassy state, followed by appropriate long time annealing to reach equilibrium.

Under such extreme conditions, it is indeed possible to obtain a well-resolved relaxation peak in place of the excess wing. Moreover, relaxation times calculated from the data do not follow the Arrhenius, but rather the Vogel-Fulcher-Tammann, law. The authors concluded that the β relaxation and the excess wing should be considered on the same footing. This implies that the division of glass formers as type A or B should be carried out not based on the presence or absence of a secondary relaxation, but rather according to the temperature dependence of the β-relaxation times. These findings motivated us to investigate whether the secondary relaxation, when manifested as an excess wing, can indeed be treated as the "normal" β relaxation.

All the conclusions discussed above arise from isothermal studies. However, more definitive postulates require new experimental facts, such as from the use of pressure as a variable. The effect of pressure on the dynamics is determined by the activation volume and its dependence on pressure, whereas temperature influences the relaxation behavior through evolution of the activation energy. Unfortunately, until now, there have been no systematic studies on the effect of pressure on the β relaxation or the excess shoulder.

Accordingly, we use dielecric spectroscopy to investigate the behavior of these processes under conditions of high compression, comparing the results with isobaric experiments. The materials are two glass formers exhibiting a well-resolved β process [diisobutyl phthalate (DIBP) and bis(methoxyphenyl)cyclohexane (BMPC)] and two liquids with an excess wing [cresolphthalein-dimethylether (KDE) and phenolphthalein-dimethylether (PDE)].

Very recently, we reported a detailed study of the dynamical properties of KDE [16]. Herein we focus on the effects of temperature and pressure on the excess shoulder in relation to the alpha relaxation. As one can see in Fig. 1(a), good scaling between the spectra is observed for KDE. Comparing the strength of the excess wing, one observes that it becomes more visible as T approaches T_g (or p approaches p_g). This means that although the peak maxima lie close to each other, their separation is possible due to the different temperature dependencies of the α and β processes.

Another material exhibiting an excess wing is PDE, whose chemical structure resembles that of KDE. In this case one can also observe exact agreement between the shape of pressure- and temperature-dependent dielectric loss spectra [Fig. 1(b)]. Thus, we postulate that for both cases, the effect of either variable on the excess wing is the same.

It should be mentioned that the width of the alpha peak in both KDE and PDE changes significantly upon approaching the glass transition. In this respect, the scaling of the curves (i.e., the main peak and the excess wing) representing different temperatures and pressures (see Fig. 12 in Ref. [16]) is remarkable. It suggests that the shapes, positions, and relative amplitudes of the main peak and the excess wing are determined by a single parameter, the α peak position. This leads to the conclusion that the excess wing is strongly correlated with the α process.

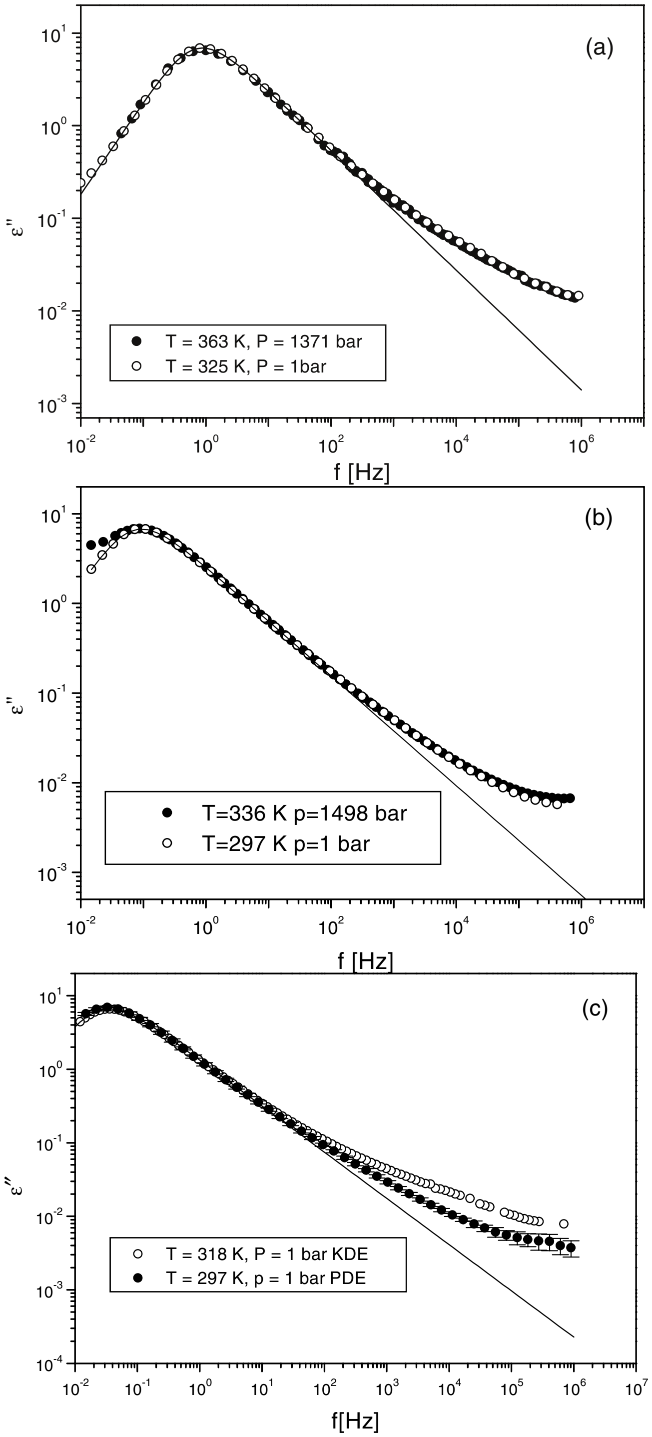

FIG. 1. A comparison of the shapes of the dielectric absorption spectra obtained from isothermal and isobaric measurements for KDE (a) and PDE (b). On panel (c) comparison of the strength of the excess wing in KDE and PDE is shown. In each case spectra have almost the same frequency of the a peak.

In the previous work on KDE [16], we suggested that the unusual aspects of the dynamics of that compound are caused by its characteristic five-member ring, which includes an oxygen, with neighboring vinyl carbons bonded to another oxygen (for chemical formula, see Ref. [17]).

However, the excess wing phenomenon has to involve not only the ring moiety, but the entire molecule. This follows from the comparison of the relative strengths of the excess wing in KDE and PDE. From Fig. 1(c) it is clear that the excess shoulder is less visible in PDE than in KDE, a consequence of either a lower amplitude or less splitting of the primary and the secondary relaxation.

Distinctly different behavior can be observed in materials having a well-pronounced β relaxation. Figure 2 presents the temperature and pressure evolution of the dielectric loss for BMPC. It is evident that, although the β relaxation moves towards lower frequencies with decreasing temperature, the relaxation time is independent of pressure. This effect can be seen more clearly in Fig. 3, depicting the temperature and pressure dependencies. As expected, the temperature dependence of the relaxation times follows an Arrhenius behavior. On the other hand, an increase of pressure has no measurable effect on the relaxation process. This observation is in agreement with the findings of Williams [18], who noticed similar behavior in the β relaxation in polymers. A possible explanation of our pressure results is found in the recent work of Vogel and Roessler [4]. They suggested that the β relaxation is due to "molecular axis jumps on the edge of a cone with a small opening angle." Their findings suggest that the effect of pressure on relaxation times should be negligible, due to very small volume requirements of such motion.

For comparison, we studied another low molecular glass former, DIBP, whose detailed dynamics in the supercooled state were presented some years ago [19]. This material also exhibits a pronounced β-relaxation peak. Figure 4 compares two spectra from temperature-dependent experiments with two spectra from pressure-dependent measurements. We chose to superimpose these particular spectra because maxima of the respective α-relaxation peaks coincide. Note the lack of scaling between the respective β relaxations. The secondary relaxation is better resolved by the application of pressure. The implication is that the effect of pressure in DIBP is negligible, similar to the case of BMPC, suggesting that the underlying processes have the same origin.

Some years ago, BMPC was studied by Meier *et al.* [20]. They suggested, on the basis of NMR experiments and computer simulations, that the β relaxation observed in BMPC has an intramolecular origin, arising from a 180° phenyl ring flip. This type motion, being thermally activated, will be affected by a change of temperature. Such an interpretation, similar to that of Vogel

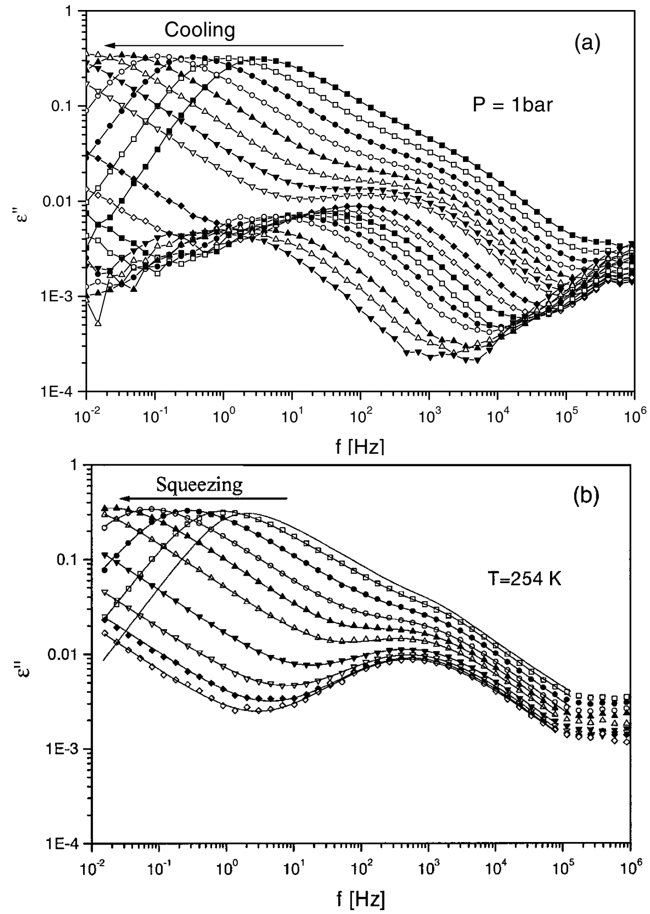

FIG. 2. Dielectric loss spectra of BMPC measured as a function of frequency at different temperature (a) and pressure (b).

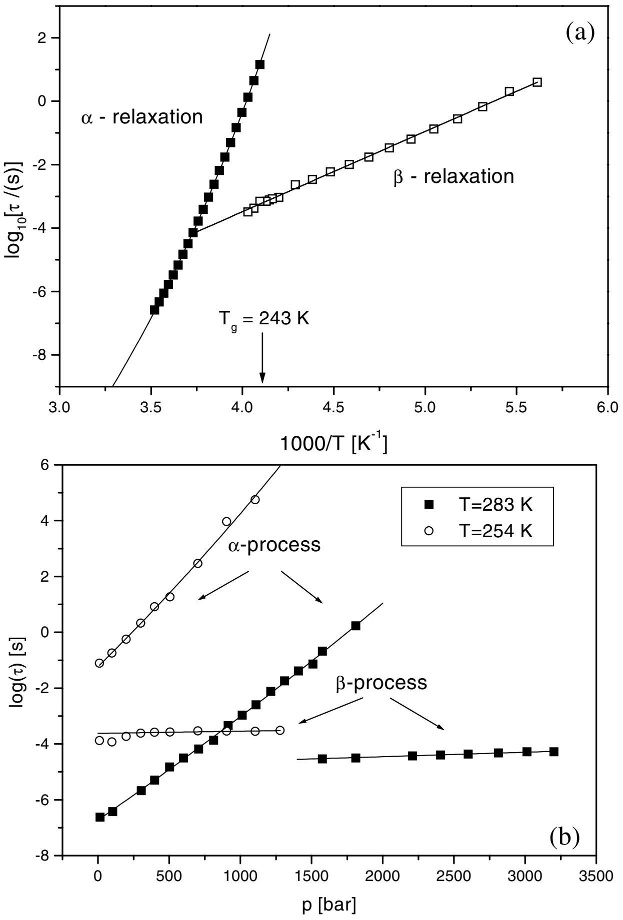

FIG. 3. A comparison of temperature (a) and pressure (b) dependence of α- and β-relaxation times for BMPC.

and Roessler [4], suggests that the effect of pressure on the β relaxation in BMPC should be negligible. However, we believe that Meier's conclusions concerning the origin of the secondary relaxation in BMPC is at odds with the experimental results *in toto.* The temperature behavior of relaxation times and the shape of the β peak in BMPC are compatible with the properties of a J-G relaxation from which we infer that the mechanism of the relaxation process is the same as for rigid molecules.

High pressure experiments on rigid molecules are necessary to definitively resolve this issue. It is worth noting that if pressure effects on the relaxation times were different from what was obtained in our experiments, it would facilitate distinguishing the two types of well-resolved β relaxations, i.e., processes which exhibit the same temperature response notwithstanding a different microscopic origin.

We have compared temperature- and pressure-dependent dielectric loss spectra of four low-molecule weight, glass forming liquids, near or in the glassy state. Two of the materials exhibit an excess wing, while the other two have a well-resolved β relaxation. We find that the different dependences of relaxation time on temperature (a normal β relaxation has an Arrhenius behavior, whereas excess wing relaxations are well described by the VFT law, as shown by Schneider *et al.* [15]) is not the only distinction between these two processes. A different sensitivity to pressure also is seen. The effects of temperature and pressure on the excess wing relative to α process, are equivalent. Contrarily, at least for the two liquids considered herein, the effect of pressure on the well-resolved β relaxation is negligible in comparison with the temperature effect, when the data are scaled by the α process. For BMPC, we find additionally that the β relaxation is pressure independent. Thus, these two phenomena cannot be treated collectively, and a division into type-A and type-B materials is valid. This point of view is also subscribed to by Hofmann *et al.* [21]; however, their suggestion is based only on the analysis of the temperature-dependent data. Hence, our findings provide a new and corroborative perspective on this issue.

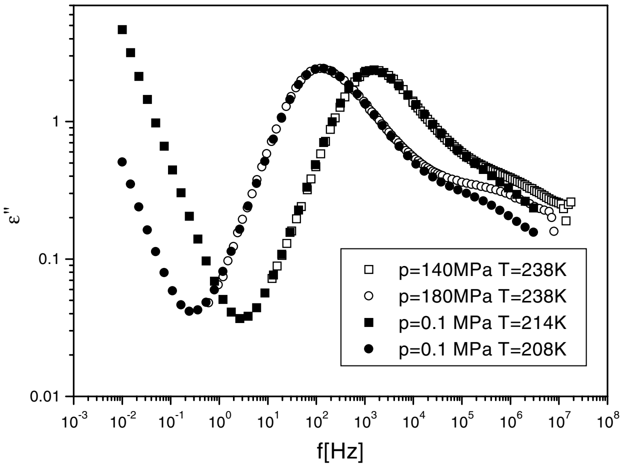

FIG. 4. A comparison of the dielectric spectra obtained from isothermal and isobaric measurements for DIBP.

Two hypotheses can account for the observed phenomena. (i) Both phenomena are secondary relaxations but have a different origin. The well-resolved relaxation is a Johari-Goldstein mechanism, which depends only weakly on pressure in dielectrically rigid molecules, because of the small angle of reorientation. In this case the mechanism of the excess wing relaxation is unclear. The use of the term β relaxation for well-resolved secondary relaxations is then ambiguous and indicates only the existence of a high-frequency process (possibly having both intramolecular and intermolecular origin). (ii) The excess wing is an intrinsic feature of the α relaxation, and type-A materials simply lack a β relaxation.

It remains to be seen whether the well-resolved β relaxation observed in rigid molecules exhibits the same sensitivity to pressure as does the excess wing. To assess these two propositions, further experiments must be carried out, especially on rigid molecules with a well-resolved β peak.

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