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## Excess Wing in the Dielectric Loss of Glass Formers: A Johari-Goldstein $\beta$ Relaxation?

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Dielectric loss spectra of glass-forming propylene carbonate and glycerol at temperatures above and below  $T_g$  are presented. By performing aging experiments lasting up to five weeks, equilibrium spectra below  $T_g$  have been obtained. During aging, the excess wing, showing up as a second power law at high frequencies, develops into a shoulder. The results strongly suggest that the excess wing, observed in a variety of glass formers, is the high-frequency flank of a  $\beta$  relaxation.

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In the frequency-dependent dielectric loss,  $\epsilon''(\nu)$ , of many glass formers, an excess contribution to the high-frequency power law of the  $\alpha$  peak,  $\epsilon'' \sim \nu^{-\beta}$ , shows up about 2–3 decades above the  $\alpha$ -peak frequency  $\nu_p$ . This excess wing can be reasonably well described by a second power law,  $\epsilon'' \sim \nu^{-b}$ , with  $b < \beta$  [1–3]. An excess contribution at high frequencies was already noted in the pioneering work of Davidson and Cole [4] and it is a common feature in glass-forming liquids without a well-resolved  $\beta$  relaxation (see below). The physical origin of the excess wing is commonly considered as one of the great mysteries of glass physics. Despite the fact that some theoretical approaches describing the excess wing have been proposed [5], up to now there is no commonly accepted explanation for its microscopic origin. In addition, some phenomenological descriptions have been proposed [3,6,7]. Most successful is the so-called Nagel scaling [6], which leads to a collapse of the  $\epsilon''(\nu)$  curves (including the excess wing) for different temperatures and various materials onto one master curve.

In various glass formers additional relaxation processes, usually termed  $\beta$  processes, are clearly seen in the loss spectra, showing up as a shoulder or even a second peak at  $\nu > \nu_p$  [7,8]. Such relaxations in supercooled liquids without intramolecular degrees of freedom were already systematically investigated three decades ago by Johari and Goldstein [8] and basically were ascribed to intrinsic relaxation phenomena of the glass-forming process. We recall that these Johari-Goldstein  $\beta$  relaxations are fundamentally different from  $\beta$  relaxations due to intramolecular degrees of freedom. It is commonly assumed that the excess wing and  $\beta$  relaxations are different phenomena [6,7], and even the existence of two classes of glass formers was proposed: “type A” with an excess wing and “type B” with a  $\beta$  process [7]. Based on experimental observations, it seems natural to explain the Johari-Goldstein  $\beta$  processes and excess wing phenomena on the same footing. Indeed such a possibility was already considered earlier [1,9–13], and from an experimental point of view it cannot be excluded that the excess wing is simply the high-frequency flank of a  $\beta$  peak, hidden under the dominating  $\alpha$  peak.

However, only the presence of a shoulder with a downward curvature can provide unequivocal proof for an underlying  $\beta$  peak. In materials with a well-pronounced  $\beta$  peak, the  $\alpha$ - and  $\beta$ -relaxation time scales increasingly separate with decreasing temperature. Therefore, within this picture it may be expected that at low temperatures the excess wing transfers into a shoulder, due to less interference with the  $\alpha$  peak. In marked contrast to this prediction, for various glass-forming liquids far below the glass temperature  $T_g$ ,  $\epsilon''(\nu)$  follows a well-developed power law, without any indication of a shoulder [1,7]. However, measurements of glass-forming materials at low temperatures near or below  $T_g$  suffer from the fact that thermodynamic equilibrium is not reached in measurements using the usual cooling rates. In addition, the loss becomes very low, yielding increasingly high experimental uncertainties. Clearly, high-precision equilibrium measurements are necessary to investigate the “true” behavior of the excess wing at low temperatures.

Therefore we performed high-precision dielectric measurements, keeping the sample at a constant temperature, some K below  $T_g$ , for up to five weeks which ensured that thermodynamic equilibrium was indeed reached. The experiments were performed on two prototypical glass formers known to exhibit well-pronounced excess wings, propylene carbonate (PC,  $T_g \approx 159$  K) and glycerol ( $T_g \approx 185$  K). For the measurements, parallel plane capacitors having an empty capacitance up to 100 pF were used. Because of the approach of the fictive [14] towards the real temperature during aging, a thermal contraction of the sample may occur. Its magnitude in one dimension can be estimated at  $\Delta l/l \leq 3 \times 10^{-3}$ , which has a negligible effect on the results. High-precision measurements of the dielectric permittivity in the frequency range  $10^{-4} \text{ Hz} \leq \nu \leq 10^6 \text{ Hz}$  were performed using a Novocontrol alpha analyzer. It allows for the detection of values of  $\tan \delta$  as low as  $10^{-4}$ . At selected temperatures and aging times, additional frequency sweeps at  $20 \text{ Hz} \leq \nu \leq 1 \text{ MHz}$  were performed with the autobalance bridges Hewlett-Packard HP4284 and HP4285. To keep the samples at a fixed temperature for up to five weeks, a closed-cycle refrigerator system was

used. The sample was cooled from a temperature 20 K above  $T_g$  with the maximum possible cooling rate of about 3 K/min. The final temperature was reached without any temperature undershoot. As zero point of the aging times reported below, we took the time when the desired temperature was reached, about 200 s after passing  $T_g$ . The temperature was kept stable within 0.02 K during the five week measurement time.

Figure 1 shows  $\epsilon''(\nu)$  of PC and glycerol at temperatures some K below  $T_g$  during aging. A strong dependence of the spectra on aging time  $t$  is observed. The spectra measured after the maximum time of  $t = 10^{6.5}$  s (squares) are identical to those obtained after  $t = 10^6$  s (stars), clearly demonstrating that equilibrium was reached. In Fig. 2 these equilibrium spectra are shown, together with equilibrium curves taken at higher temperatures, partly published earlier [15]. Obviously, in the frequency window of Fig. 1, mainly the excess wing region is covered; the  $\alpha$  peak is located at much lower frequencies, leading to a somewhat steeper increase towards low frequencies only. In Fig. 1, for both materials, indeed the typical power law, characteristic of an excess wing, is observed for short  $t$ . However, with increasing  $t$  the excess wing successively develops into a shoulder. This behavior strongly suggests that a relaxation is the origin of the excess wing observed at shorter times or higher temperatures (Fig. 2). Admittedly, for glycerol the curvature in  $\log_{10}\epsilon''(\log_{10}\nu)$  is quite

subtle (Fig. 1b). However, further evidence is provided by Fig. 3, where the derivatives of the lowest curves in Figs. 1 and 2 are shown. A maximum is observed, clearly indicative of a  $\beta$  process [7]. In the region of the shoulder, the values of  $\tan\delta$  ranging between  $5 \times 10^{-3}$  and  $2 \times 10^{-2}$  are well above the resolution limits of the measurement. In addition, for both materials, the measurements using the autobalance bridges (not shown) agree well with those obtained with the alpha analyzer. Finally, the response of the empty capacitor was measured at the temperatures of Fig. 1. The resulting loss of  $\epsilon'' < 1.5 \times 10^{-4}$  in the region of  $10 \text{ Hz} \leq \nu \leq 100 \text{ kHz}$  excludes a nonintrinsic origin of the observed shoulder.

The results of Fig. 1 are interpreted as follows: During aging the fictive temperature [14] successively approaches the "real" temperature, leading to a strong shift of the  $\alpha$  peak towards lower frequencies. The relaxation times of  $\beta$  processes usually exhibit a weaker temperature dependence than those of the  $\alpha$  process. Therefore the  $\beta$  process causing the excess wing can be expected to be less affected by the aging. The different aging dependences of the  $\alpha$  and the  $\beta$  process can also be easily deduced from the fact that the spectra at different aging times cannot be scaled onto each other by a horizontal shift in Fig. 1. In addition, aging experiments reported by Johari and Goldstein [8] revealed a negligible change of the  $\beta$ -peak frequency with aging time [16]. Overall, with increasing aging time, respectively decreasing effective temperature, the time scales

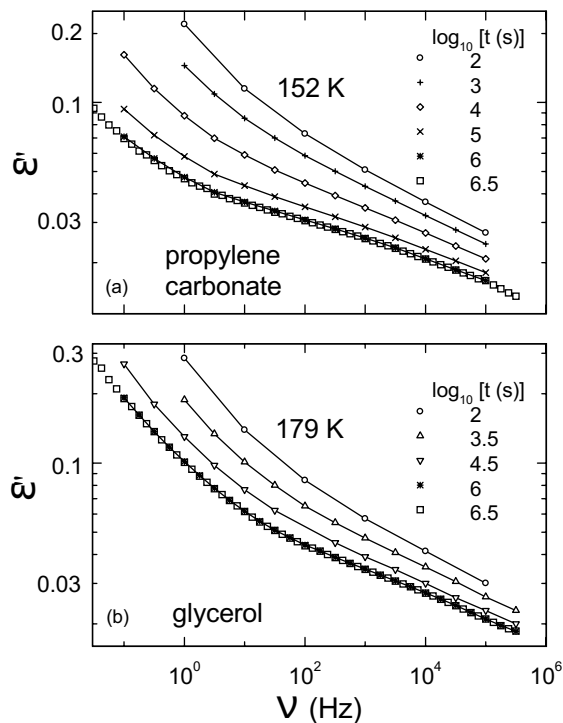


FIG. 1. Frequency-dependent dielectric loss of PC (a) and glycerol (b) for different aging times  $t$  (not all shown). The lines connect the symbols for  $t \leq 10^6$  s. The spectra for the maximum aging time of  $10^{6.5}$  s ( $\square$ ) have been taken in an extended frequency range.

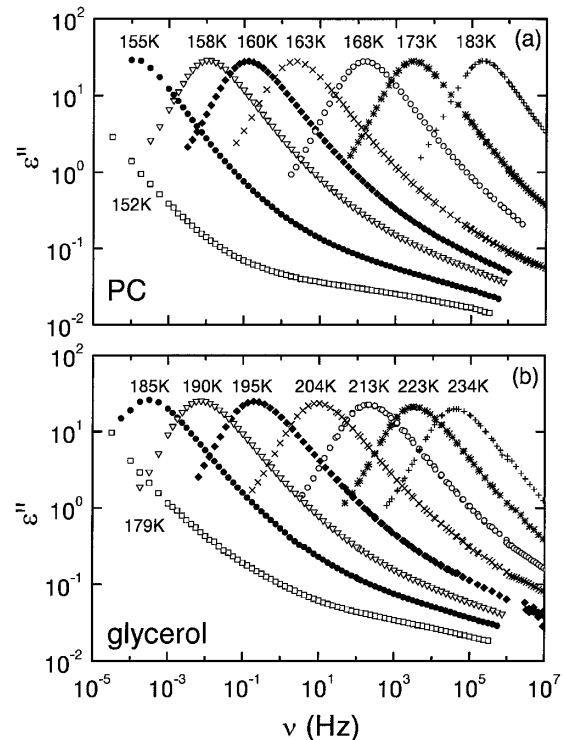


FIG. 2. Frequency-dependent dielectric loss of PC (a) and glycerol (b) for different temperatures. All curves were taken in thermodynamic equilibrium.

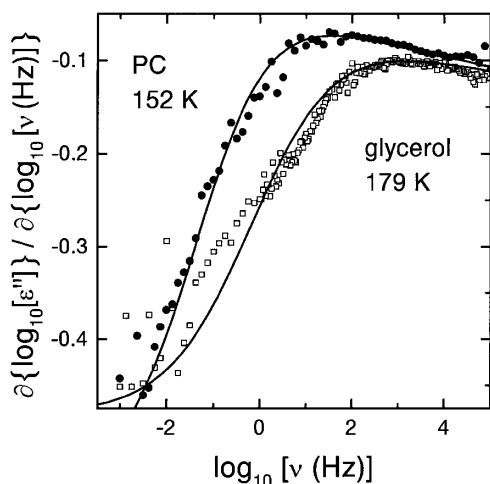


FIG. 3. Derivative of the dielectric loss spectra obtained after  $10^{6.5}$  s. The lines correspond to the fits shown in Fig. 4.

of the  $\alpha$  and  $\beta$  processes become successively separated, and finally the presence of a  $\beta$  relaxation is revealed by the appearance of a shoulder.

A close inspection of dielectric measurements at low temperatures, reported in literature, reveals some further evidence of a  $\beta$  relaxation being the origin of the excess wing: Already in the spectrum obtained by Leheny and Nagel [17], after aging of glycerol for  $2.5 \times 10^6$  s at 177.6 K, a vague indication of a shoulder is present. However, possibly due to doubt of its significance, these authors paid no attention to this feature. In addition, in various other published results, near or just below  $T_g$ , some indications of a shoulder show up [1,3,13,15,18], again being ignored in most of these publications. Except for [13], the thermal history was not reported in detail and it can be doubted if thermal equilibrium was reached. In the study of Wagner and Richert [13], in highly quenched Salol a strong secondary peak appeared below  $T_g$  which vanished after heating to  $T_g$ . In addition, in isochronal measurements of various quenched glass formers [19], nonequilibrium secondary relaxations were detected. From the results in [13,19] the question arises if the subtle indications for a  $\beta$  relaxation seen at about  $T_g$  in [1,3,13,15,18] are pure nonequilibrium effects and if this relaxation may completely vanish in equilibrium. Only the present aging experiments could prove that the excess wing is due to a  $\beta$  relaxation that is an equilibrium phenomenon. In Fig. 1 the amplitude of the  $\beta$  peak (only seen as an excess wing at short times) may be suspected to diminish with aging. Interestingly, in systems with well-resolved  $\beta$  relaxations a similar behavior was observed [8,9]. Finally, it should be mentioned that in Ref. [20] evidence of a  $\beta$  relaxation in various systems without a clearly resolvable second relaxation peak (including PC) was found by using a “difference isochrone” method. In addition, in glycerol a high-frequency shoulder was detected by performing high-pressure dielectric experiments [21]. Further evidence for

$\beta$  relaxations in typical excess-wing glass formers has also been obtained from other experimental methods, e.g., calorimetry [22] or nuclear magnetic resonance [23]. A strong corroboration of the present results is also provided by our recent results in ethanol, which prove that the well-pronounced excess wing in this glass former is also due to a  $\beta$  relaxation [24].

What further information on the  $\beta$  relaxation causing the excess wing can be gained from the present data? The  $\alpha$  peaks in PC and glycerol can well be fitted using the empirical Cole-Davidson (CD) function [4,15]. In materials with well-pronounced  $\beta$  peaks their spectral shape often can be described by the Cole-Cole (CC) function [25]. In Fig. 4 we demonstrate that the equilibrium curves of Fig. 1 can be well fitted by using a sum of a CD and a CC function. Similar analyses were performed in [1,10–12]. In Fig. 3 the corresponding derivatives are shown—again a reasonable agreement can be stated. Also the present spectra at higher temperatures (Fig. 2) can be described in the same way [26]. The resulting characteristics of the  $\beta$  relaxations in PC and glycerol can be summarized as follows: (i) The relaxation strength increases with  $T$ . This is often found for well-resolved  $\beta$  relaxations, e.g., in [7]. (ii) The width of the relaxation peaks becomes smaller with  $T$ , which is also a common property of well separated  $\beta$  relaxations [7]. (iii) Despite some difficulty in obtaining precise information on the temperature development of the  $\beta$ -relaxation time,  $\tau_\beta$ , the analysis reveals significant deviations from thermally activated behavior [26]. Therefore one may have objections to using the term “ $\beta$  relaxation” in this case, as  $\tau_\beta$  is commonly assumed to follow an Arrhenius behavior. However, there is no principal reason that  $\beta$  processes should always behave as thermally

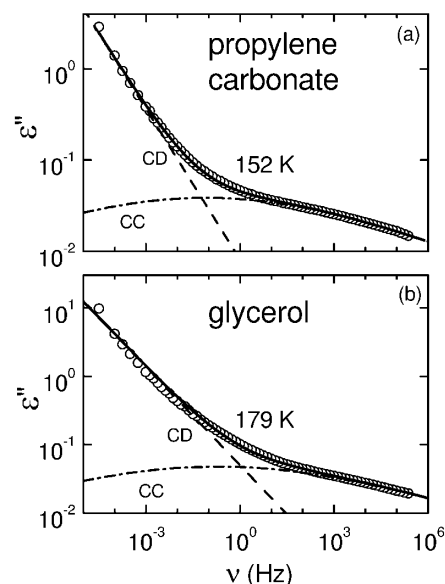


FIG. 4. Dielectric loss spectra obtained after  $10^{6.5}$  s. The solid lines are fits with a sum of a CD (dashed line) and a CC function (dashed-dotted line).

activated, especially as their microscopic origin is still unclear. Johari and Goldstein [8] already suspected that, in systems without a well-resolved  $\beta$  process, the relaxation times of the  $\alpha$  and  $\beta$  processes are closer together due to an uncommon temperature dependence of  $\tau_\beta$ . Maybe the only difference between type A and type B glass formers in the classification scheme of [7] is just the temperature evolution of the  $\beta$  dynamics: In the latter materials it is thermally activated, leading to a clear separation of the  $\alpha$  and  $\beta$  peaks at low temperatures. In contrast, in type A materials,  $\tau_\beta(T)$  follows  $\tau_\alpha(T)$  more closely (i.e., it deviates from Arrhenius), and only the high-frequency flank of the  $\beta$  peak—the excess wing—is visible. The Nagel scaling [6], which strongly suggests a correlation between the  $\alpha$  process and the excess wing in type A systems, is not opposed to this framework: It simply implies that in those materials the parameters characterizing both relaxation processes are intimately related.

In this context it is of interest that recently, for type B glass formers, a correlation of  $\tau_\beta$  and the Kohlrausch exponent  $\beta_{KWW}$  (describing the width of the  $\alpha$  peak), both at  $T_g$ , was found [27]:  $\log_{10}\tau_\beta(T_g)$  increases monotonically with  $\beta_{KWW}(T_g)$ . It was noted that those glass formers which show no well-resolved  $\beta$  relaxation (including PC and glycerol) have relatively large values of  $\beta_{KWW}(T_g)$ . Since the mentioned correlation implies that the  $\alpha$ - and  $\beta$ -time scales approach each other with increasing  $\beta_{KWW}(T_g)$ , the unobservability of a shoulder in those materials is easily rationalized. In [27] an explanation of this behavior within the coupling model (CM) [28] was proposed. Recently it was shown that the Nagel scaling can be explained within this framework [11] and even the deviation of  $\tau_\beta(T)$  from thermally activated behavior seems to be consistent with the CM.

In summary, by performing high-precision measurements below  $T_g$  in thermodynamic equilibrium we were able to resolve the presence of  $\beta$  relaxations in two typical excess-wing glass formers. Our results strongly suggest that the thus far mysterious excess wing, showing up at higher temperatures, is simply the high-frequency flank of the loss peaks caused by these  $\beta$  relaxations. Of course, the mere identification of the excess wing with a  $\beta$  relaxation provides no explanation, e.g., for the Nagel scaling [6] or for the question of why glass formers seem to fall into two classes: those with a well-separated  $\beta$  relaxation and those without [7]. But the knowledge of the true nature of the excess wing certainly is a prerequisite for any microscopic explanation of these phenomena (e.g., Ref. [11,27]), and hopefully will enhance our understanding of the glass transition in general.

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