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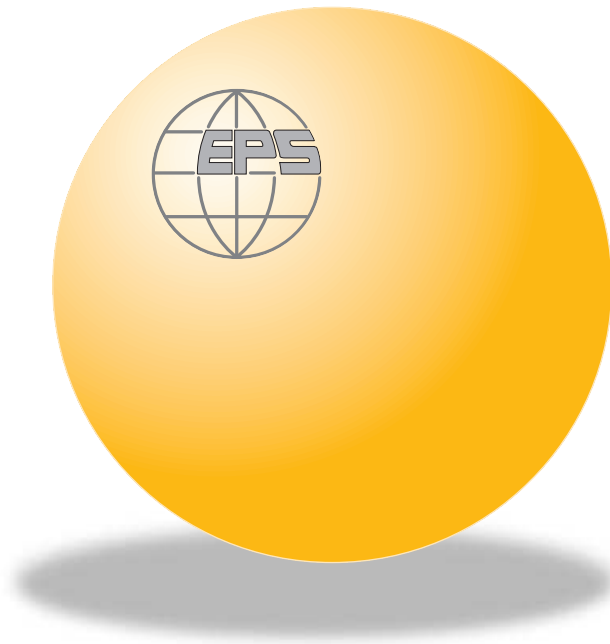
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in the dielectric loss of glass-formers**

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R. BERGMAN, J. MATTSSON, C. SVANBERG,
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Confinement effects on the excess wing in the dielectric loss of glass-formers

R. BERGMAN(*), J. MATTSSON(**), C. SVANBERG,
G. A. SCHWARTZ and J. SWENSON

*Department of Applied Physics, Chalmers University of Technology
SE-412 96 Göteborg, Sweden*

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Abstract. – We present results from dielectric spectroscopy on four molecular glass-formers, both in bulk and in confined geometry. For systems exhibiting a well-resolved secondary (β) relaxation, the confinement induces a relative enhancement (compared to the main α relaxation) of the effective dielectric strength of the β process. In bulk systems without a well-separated β process a similar relative enhancement is found also for the contribution to the dielectric loss identified as the excess wing. The latter effect results in a bimodal loss, which suggests that the excess wing should be attributed to a relaxation process separate from, and thus not a feature of, the α relaxation. The results hence provide an explanation for the much debated excess wing often observed in the dielectric response of glass-formers.

When a liquid or polymer is cooled below its melting point, while avoiding crystallization, it enters the supercooled state. As temperature is further decreased, the viscosity and the accompanying characteristic time for structural relaxation will increase dramatically, reaching values typical for solid materials at the glass transition temperature, T_g . An interesting and fundamental question in this important field of physics [1] concerns the shape of the relaxation function [2] related to the glass transition. The relaxation processes are generally much broader than what is expected from a simple Debye behavior and, in the case of the α relaxation, they are well described by a stretched exponential, *i.e.* a Kohlrausch-Williams-Watts (KWW) function: $\phi(t) \propto \exp[-(t/\tau)^{\beta_{\text{KWW}}}]$ [3, 4]. Here τ is the characteristic relaxation time and $0 < \beta_{\text{KWW}} \leq 1$ is the so-called stretching parameter. It has recently been shown [5] that the KWW function can be well represented in frequency domain by the following equation:

$$\varepsilon''(\omega) = \frac{\varepsilon_p''}{\frac{(1-|a-b|)}{a+b} (b(\omega/\omega_p)^{-a} + a(\omega/\omega_p)^b) + |a-b|}, \quad (1)$$

with $a = 1$ and $b = \beta_{\text{KWW}}$. In eq. (1) ε_p'' is the dielectric loss at ω_p , the angular peak frequency. This function, as well as other commonly used empirical functions for the frequency response

(*) E-mail: f5xrb@fy.chalmers.se

(**) Present address: Department of Physics and DEALS, Harvard University - Cambridge, MA 02138, USA.

of disordered materials, has a power law behavior at limiting frequencies. Power laws are normally observed in experimental dielectric loss data at frequencies far from ω_p [6]. For some glass-formers, however, if measured over a wide enough frequency range, a crossover from $\varepsilon'' \propto \omega^{-\beta_{\text{KWW}}}$ to a second power law, $\varepsilon'' \propto \omega^{-\gamma}$, with an exponent γ less than β_{KWW} , is often observed at high frequencies [7]. This so-called excess wing (excess compared to the KWW contribution) has been proposed to be an intrinsic feature of the α relaxation [7, 8]. Dixon *et al.* [7] have shown that it is possible to scale α relaxation dielectric responses, even those including the excess wing, into one master plot. It has to be emphasized, however, that the physical explanation for this scaling is still lacking and its apparent success might simply be due to the way the data is presented; *i.e.* fixing the high- and low-frequency behavior and reducing possible differences around the actual peak.

An alternative hypothesis [9–11] for the origin of the excess wing is that it is due to a relaxation process separate from the α relaxation. A possible candidate is the so-called Johari-Goldstein β relaxation, which is faster than the α process and normally has an Arrhenius temperature dependence of its relaxation time. In contrast to the α loss, the β relaxation normally shows a symmetric loss on a logarithmic frequency axis. β processes are often supposed to be rather local compared to the α relaxation, and for polymers they have often been identified with side-group motions. However, Johari and Goldstein [12] showed that molecular glass-formers without intra-molecular degrees of freedom also show dielectric β responses. This suggests that β relaxations are general features of glassy dynamics.

Interestingly, a correlation has been found between the β_{KWW} -parameter and the relaxation time of the β relaxation at T_g [13, 14]. This relation suggests that the β relaxation at T_g is slower for glass-formers with high β_{KWW} -values. Based on this correlation it has been suggested that the excess wing is simply a β relaxation partly hidden by the α peak in liquids with large β_{KWW} -values [15]. One way to determine if the excess wing is due to a hidden β relaxation is to study the response at low temperatures, below T_g , as we then expect the α and β relaxations to be more separated.

Recently, Schneider *et al.* [9] performed dielectric relaxation experiments on glycerol and propylene carbonate (PC) at temperatures below T_g . Thermodynamic equilibrium was reached by the use of long-time annealing. It was observed that, during annealing, the excess wing developed into a shoulder, suggesting an underlying separate relaxation process. Furthermore, it has also recently been shown that for homologous oligomer series the excess wing observed for the monomer gradually transforms into a clear and well-separated β relaxation for higher M_w [16, 17].

Another way to investigate if the excess wing is due to an underlying secondary relaxation process is to use geometrical confinement. The different nature of the α and β relaxations suggests different sensitivities to confinement, something which might facilitate a separation of the two relaxational contributions. Additionally, in dielectric experiments on a liquid in confinement the α and β relaxations should be affected differently due to effective medium effects [18].

Based on these ideas, we chose to study the dielectric loss of four molecular glass-formers. Two glass-formers, exhibiting well-separated β peaks: dipropylene glycol (2-PG) and 3-fluoroaniline (3-Fa), and two glass-formers lacking clear β peaks, but instead showing excess wings, propylene carbonate (PC) and propylene glycol (PG) were studied. All samples were measured both in the bulk and when confined to the inter-platelet galleries of a Na-vermiculate clay. The structure of the vermiculate clay is a stack of essentially two-dimensional silicate platelets with very thin galleries (3–5 Å) in between [19]. The clays were loaded by submersion into the respective liquid, and the mass uptake was monitored. The macroscopic (10 × 10 mm²) clay pieces were placed with the platelets parallel to the electrodes (20 mm in diameter) of a

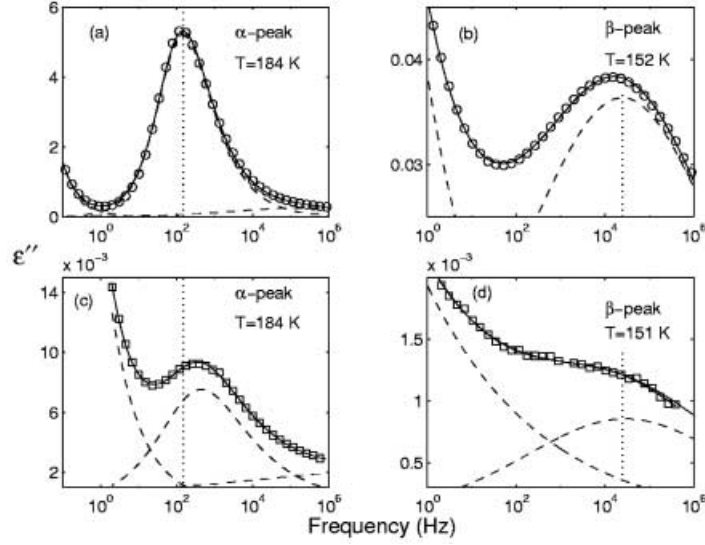


Fig. 1 – Imaginary part of the dielectric response, $\varepsilon''(f)$, at (a) $T = 184$ K and (b) $T = 152$ K for bulk 3-Fa, and (c) $T = 184$ K and (d) $T = 151$ K confined in Na-vermiculite clay. The α and β relaxations are shown together with the curve fits described in the text.

high-resolution and broad-band (10^{-2} – 10^7 Hz) dielectric spectrometer (Novocontrol Alpha). The complex dielectric permittivity, $\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f)$, was recorded isothermally every second or third degree in the relevant temperature ranges with a temperature stability better than 0.1 K.

In fig. 1 we show typical spectra of 3-Fa in bulk and in the clay. For the bulk system, the pronounced α process as well as the weaker β process is clearly seen. The data for the 3-Fa and 2-PG bulk samples can both be well described by a sum of three terms: one low-frequency power law for the DC conductivity, a second term given by eq. (1) and a third term given by the imaginary part of the symmetric Cole-Cole (CC) function [20]: $\varepsilon''(\omega) = \Delta\varepsilon_\beta/[1 + (i\omega\tau_\beta)^\alpha]$, where the exponent α is a shape parameter that quantifies the symmetric broadening. The relaxation time τ_β is inversely related to the peak frequency and $\Delta\varepsilon_\beta$ is the relaxation strength of the CC relaxation. We thus assume that the relaxational response is composed of an α relaxation of the KWW type and a faster symmetric β relaxation. Even though the strength of the signal from the relaxation processes were much lower and the conductivity more pronounced for the confined samples, the data could be satisfactorily described with the same three terms as used for describing the bulk samples, see fig. 1(c) and (d). The pronounced low-frequency contribution could be well described using a power law with an exponent ≈ -0.5 . This imperfect conductivity is most likely due to charge buildup at the clay platelets. Even though a reasonable fit was obtained using a KWW function for the data of the confined samples, clear deviations were found in the low-frequency part of the α peak and better fits were obtained using eq. (1) without the restriction $a = 1$.

As seen in fig. 2, the temperature evolution of the relaxation times for both the α and β processes are very similar in confinement and in the bulk. The confined samples, however, show consistently slightly faster α relaxations and for 3-Fa, the activation energy for the β process appears to have a somewhat lower value. We find slightly lower values of the low-frequency power law exponent of the α relaxation in the confined samples (≈ 0.85 compared with 1

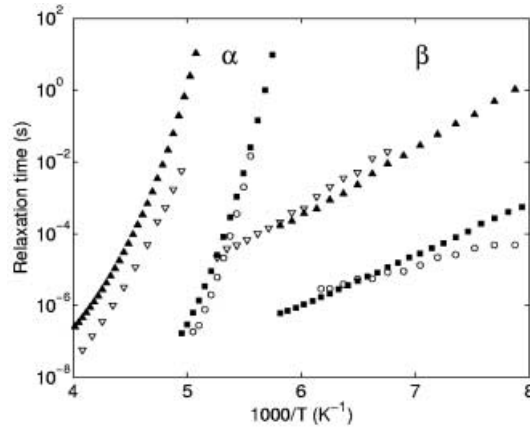


Fig. 2 – Relaxation times for 2-PG (triangles, up and down), and 3-Fa (squares and circles). Open symbols are for the confined samples and filled symbols for the bulk samples.

for the bulk samples). The main effect that the confinement has on the measured response, however, is that the effective strength of the α and β processes decreases considerably in confinement. Importantly, the relative ratio of the amplitudes changes in favour of the β relaxation. For the 2-PG sample, the ratio between the α and the β peak value at T_g change from the bulk value of ~ 335 to ~ 48 in confinement. For 3-Fa this effect is even more pronounced, with the corresponding values being 106 and 8, respectively. Hence, apart from a generally lower effective signal, there is a significant relative enhancement of the β relaxation when these glass-formers are subject to the present confinement. The observed shift in the relaxation times and at least a significant part of the decrease in the dielectric strength can be accounted for by effective medium effects [18].

Next, we turn to the results for the glass-formers without resolved β peaks, instead displaying excess wings. In fig. 3(a) we show a typical spectrum of $\varepsilon''(f)$ for bulk PC at $T = 164$ K, which is close to T_g (160 K). The strong α peak dominates the spectrum. However, at high frequencies there is an extra contribution, the so-called excess wing discussed above, and it is visible as an extra linear contribution at high frequencies in the double logarithmic plot shown in the inset of fig. 3(a). As in the case of 2-PG and 3-Fa, we parameterize the relaxational response by a sum of one asymmetric (KWW) term and one symmetric (CC) term. The CC contribution only appears as a wing of the dominant KWW contribution (see inset of fig. 3(a)). The dielectric loss of PC confined in the near-2D interplatelet galleries of the Na-vermiculite clays is shown in fig. 3(b), which reveals a bimodal shape of the spectra. We analyze the data using the same approach as for the bulk, except that a low-amplitude high-frequency process (CC) had to be added in order to describe the data well at high frequencies. The two main loss contributions were robust with regard to how this additional feature was described in the fitting procedure. Comparing fig. 3(a) and (b), it is clear that the two relaxation processes can be described using the same main contributions with similar shapes and peak positions (see the inset to fig. 3(b)) in bulk and in the clay. There is, however, as expected from the results of 2-PG and 3-Fa, a marked difference in the relative amplitudes. The same analysis was performed also for PG, with identical observations.

For both PG and PC, the obtained shape parameters for the KWW contribution are very similar in bulk and in the clay. However, the CC contribution becomes narrower in the clay. The obtained relaxation times are shown in the inset of fig. 3(b). Evidently, the relaxation

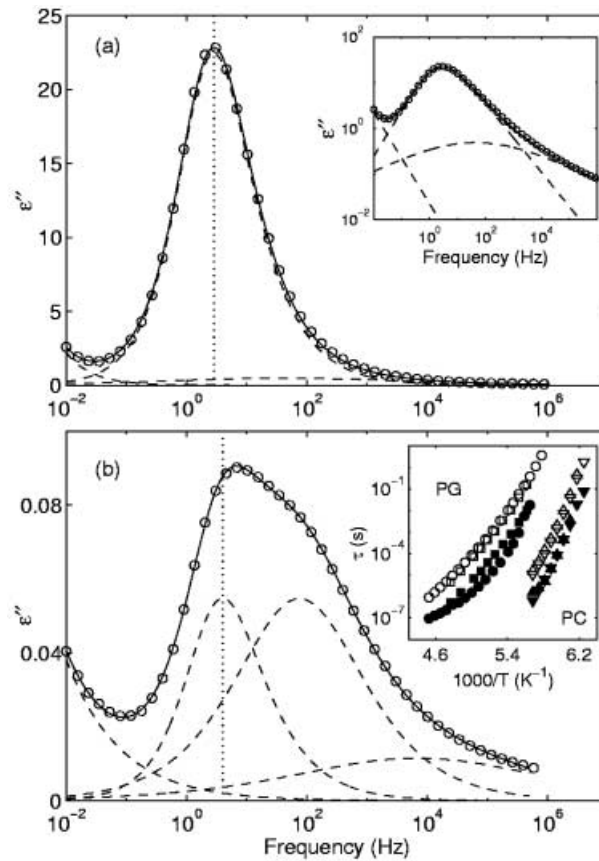


Fig. 3 – (a) Imaginary part of the dielectric response $\varepsilon''(f)$ for bulk PC at $T = 164\text{K}$. In the inset a double logarithmic plot of the same data clearly shows the excess wing at high frequencies. (b) Dielectric loss spectra $\varepsilon''(f)$ for PC confined in Na-vermiculite clay at the same temperature as in (a). In both spectra the full line indicates a least-squares fit using a sum of eq. (1) and a Cole-Cole function along with a low-frequency power law as discussed in the text. The individual contributions are shown as dashed lines. The inset shows the obtained relaxation times for bulk PC (triangles up), confined PC (triangles down), bulk PG (circles), and confined PG (squares). The α relaxation times are presented using open symbols and the β relaxation times with filled symbols.

times of the α relaxation are very similar in bulk and confined systems, indicating weak interactions both with the walls and the intercalated Na^+ ions for the molecules confined in the clay. This is in agreement with the results from the present 2-PG and 3-Fa studies and also other studies using the same confinement [21, 22].

The CC relaxation times of the faster peak in the clay coincide with the ones of the excess wing in the bulk sample. This indicates that the relaxation dynamics in both geometries are dominated by the same α and β relaxation processes. The obtained amplitudes, on the other hand, are much lower for the confined PC and PG but, importantly, the relative ratios change in favour of the CC contribution. In the bulk PC the peak height of the α relaxation is more than 30 times the height of the β relaxation, while they are almost equal for the PC in the confined geometry, see fig. 3. For bulk PG the ratio of relaxation amplitudes is roughly 100 at T_g , while in confinement, again, it is close to unity. For both PC and PG the major difference

in the spectra of confined and bulk systems is thus in the relative amplitudes of the KWW and CC contributions. This is consistent with what was observed for the 2-PG and 3-Fa systems as discussed above. The fact that the amplitudes of the primary and secondary relaxations have such markedly different sensitivity to confinement provides evidence that the excess wing is not an intrinsic feature of the α relaxation, but rather an underlying β relaxation.

For secondary relaxations (β relaxations), the dielectric strength is normally found to increase with increasing temperature. In this study the amplitudes of the observed β relaxations and excess wings show a clear increase with temperature in the studied bulk systems. Confined in the clay, three of the four studied samples show the same expected behaviour, while the fourth system, PG, first increases and then decreases with increasing temperature. It should be noted, however, that the amplitudes in the confined systems are considerably lower than in the bulk systems and since both relaxations are overlapping, an accurate determination of the individual amplitudes becomes difficult.

The behavior of the fast contribution, identified for PG and PC, thus behaves in the same manner as normal β relaxations. The feature that differs from well-separated β relaxations is that the CC relaxation time does not have an Arrhenius temperature dependence. Rather, it seems as if the relaxation time follows the temperature dependence of the α relaxation time. This could imply a close relation between α and β relaxations in materials exhibiting an excess wing [9]. An alternative, and more probable explanation, is that the excess wing is in fact the flank of an underlying effective β process, which is the convolution of the pure α and β processes according to Williams' ansatz [23]. The underlying β relaxation is then expected to have an Arrhenius temperature dependence, but the relaxation time of the experimentally observed effective process follows the α relaxation time if the α and β relaxation times are sufficiently close in time [24]. For PC and PG, with their relatively high β_{KWW} -values (~ 0.6 – 0.7), we indeed expect the α and β relaxation times to be close near T_g according to the correlation found by Ngai [13,14].

In summary, we have studied the high-frequency contribution of the dielectric loss, in both bulk and in geometrical confinement, for different glass-formers displaying either clear β peaks or excess wings. In the essentially 2D inter-platelet space of a Na-vermiculite clay, the observed spectra can be described with essentially the same parameters as in the corresponding bulk liquid, except for a strongly enhanced relative amplitude for the fast process, *i.e.* the β relaxation in 2-PG and 3-Fa and the excess wing in PC and PG, respectively. Our results thus support the idea that the excess wing is due to a secondary relaxation process, most likely a β process of the Johari-Goldstein type. In general, this suggests that the Johari-Goldstein β relaxation might be a fundamental feature of glass-formers.

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