Beta-relaxation of non-polymeric liquids close to the glass transition

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Dielectric beta-relaxation in a pyridine-toluene solution is studied close to the glass transition. In the equilibrium liquid state the beta loss peak frequency is not Arrhenius (as in the glass) but virtually temperature-independent, while the maximum loss is strongly temperature-dependent. Both loss peak frequency and maximum loss exhibit thermal hysteresis. A new annealing-state independent parameter involving loss and loss peak frequency is identified. This parameter has a simple Arrhenius temperature-dependence and is unaffected by the glass transition.

Viscous liquids are characterized by relaxation times that increase strongly upon cooling towards the glass transition. The relaxation time of molecular rotation is monitored by dielectric relaxation experiments probing the linear response to a periodic external electric field. The dominant relaxation process is referred to as the alpha-process. For most viscous liquids, upon cooling the alpha process bifurcates just before the glass transition and an additional minor loss peak appears at higher frequencies. This is traditionally referred to as beta-relaxation (now sometimes termed Johari-Goldstein beta-relaxation to distinguish it from the mode-coupling theory’s “cage-rattling” at much higher frequencies). Beta-relaxation has also been observed in mechanical and thermal relaxation experiments. Here, we limit ourselves to dielectric beta-relaxation. Our purpose is to show that the conventional view that beta-relaxation is unaffected by the glass transition is not confirmed by experiments on non-polymeric liquids. We have not studied beta-relaxation in polymers, but believe based on the literature that beta-relaxation in non-polymeric liquids is probably not affected by the glass transition.

Beta-relaxation was first seen in polymers, where it was attributed to side-chain motion. In 1970 Johari and Goldstein found beta-relaxation in a number viscous liquids of rigid molecules and conjectured that beta-relaxation should be considered as “a characteristic property of the liquid in or near the glassy state.” However, for some glass-forming liquids (e.g., glycerol) no beta-relaxation has been observed. Today, viscous liquids are sometimes classified according to whether or not they exhibit beta-relaxation, although there are recent intriguing speculations that beta-relaxation indeed is universal with the beta-peak sometimes hiding under the alpha-peak.

There is no general agreement about the cause of beta-relaxation. It is unknown whether every molecule contributes to the relaxation or only those within “islands of mobility.” Similarly, it is not known whether small angle jumps or large angle jumps are responsible for beta-relaxation. Of course, a possible explanation of these disagreements is that beta-relaxation is non-universal.

As traditionally reported in the literature (see, e.g.,), beta-relaxation is characterized by a broad loss peak with Arrhenius temperature-dependent loss peak frequency and only weakly temperature-dependent maximum loss. In this picture, which is mainly based on measurements in the glassy phase, the glass transition has no effect on the temperature-dependence of the beta loss peak frequency. In our opinion, it is unlikely that the temperature-dependence of the loss peak frequency is unaffected by the glass transition, considering the well-known fact that the strength of the beta process in the glassy state decreases during annealing (in some cases to below resolution limit). Actually, no detailed investigations of beta-relaxation in the equilibrium liquid phase of non-polymeric liquids have been carried out. This may be because studying beta-relaxation above the glass transition temperature is difficult since there is only a tiny temperature-window (if any) where alpha and beta-relaxations are well-separated.

Motivated by the above arguments, one of us recently investigated beta-relaxation in sorbitol and found that the temperature-dependence of both loss peak frequency and loss magnitude in the equilibrium liquid state is indeed different from what is found in the glassy state. This result was obtained on a system which - like most others - has a beta-relaxation that in the equilibrium liquid phase is not very well separated from the alpha-relaxation. The sorbitol results were mainly based on annealing experiments below and the results were to some extent inconclusive. Below, we present data for beta-relaxation in a liquid with a strong beta-peak which is well separated from the alpha-peak in a range of temperatures above . The liquid is a mixture of pyridine and toluene, a system first studied by Johari. Toluene molecules have only a small dipole moment, so dielectric spectra mainly reflect motion of the pyridine molecules acting as probes of the overall dynamics of the solution.

The dielectric measuring cell used is a 22-layer gold-plated capacitor with empty capacitance 68 pF (layer distance 0.1 mm). The dielectric constant was measured...
over 9 decades of frequency using standard equipment: From 100 Hz to 1 MHz a HP4284A precision LCR meter was used, from 1 mHz to 100 Hz a HP3458A multimeter in conjunction with a Keithley 5 MHz, 12-bit, arbitrary waveform generator was used. The dielectric loss was determined with at precision better than $10^{-4}$ in the whole frequency-range. The measurements were carried out in a cryostat designed for long time annealing experiments, keeping temperature variations below 5 mK.

Figure 1a shows the dielectric loss at 125K, 126K, and 127K. The alpha- and beta-peaks are quite well separated. Despite this a procedure is needed to eliminate the alpha-tail influence on the beta-peak. From Fig. 1a we find that the alpha-peak follows a high-frequency power-law decay with exponent -0.47. In order to arrive at the “true” beta-peak this alpha-tail was subtracted by applying the following procedure: At each temperature the magnitude of the subtraction was uniquely determined by requiring that the beta-peak follows a low-frequency power-law. We used a power-law fit \((\star\star)\) because a Gaussian, as sometimes used to fit beta-peaks \((\star\star\star)\), cannot fit our data. This way to eliminate the alpha-contribution involves the following assumptions: 1) The dielectric spectrum is a simple sum of alpha- and beta-relaxation and not, e.g., a Williams-convolution \((\star\star\star\star)\); 2) In the relatively narrow temperature-interval under study the alpha-tail’s power-law decay has an exponent which is temperature-independent. Figure 1b shows eight normalized alpha-peaks (119K-126K) after subtraction of alpha-tails. The figure shows that the subtraction procedure is consistent: The “corrected” beta-peaks do follow a low-frequency power-law to a good approximation.

Figure 2a shows beta loss peak frequency \(f_{\text{max}}\) (\(\bigcirc\)) and maximum loss \(\epsilon_{\text{max}}\) (\(\bigtriangleup\)) as function of inverse temperature for a cooling taking the equilibrium liquid into the glassy state at a rate of 1 K/h. The system was cooled in steps of 0.5 K. Dielectric loss was measured after annealing 30 minutes at constant temperature, immediately before cooling another 0.5 K. At high temperatures - in the equilibrium liquid state - the loss peak frequency is almost temperature-independent \((\bigstar)\) while the loss decreases sharply during the cooling \((\bigstar\star)\). At low temperatures, the well-known Arrhenius temperature-dependence of loss peak frequency is observed and the maximum loss is much less temperature-dependent than in the liquid.

Figure 2b shows beta loss peak frequency \(f_{\text{max}}\) and maximum loss \(\epsilon_{\text{max}}\) (\(\bigtriangleup\)) as function of inverse temperature during a cooling through the glass transition followed by a subsequent faster reheating. Starting in the equilibrium liquid state the sample was cooled in steps of 0.5 K with measurements carried out after annealing 30 minutes at each temperature. The cooling continued until 119 K was reached. The sample was then heated in steps of 1.0 K every 30 minutes. The figure shows hysteresis like that found for all other quantities changing their temperature-dependence at the glass transition. The figure also shows \((\bigtriangleup)\) the temperature-dependence during both cooling and subsequent reheating of the following quantity

\[
X = f_{\text{max}}(\epsilon_{\text{max}})^{\gamma}.
\]  

Here, \(\gamma = 1.19\) is an empirical exponent. There is just one curve marking the temperature-dependence of \(X\), showing that \(X\) exhibits no thermal hysteresis. In particular, \(X\) is independent of annealing-state. Surprisingly, \(X\) has an Arrhenius temperature-dependence.

We have found similar behavior for sorbitol, DBP, DEP, DMP, and PPG, although these liquids have beta-peaks that are less well-separated from the alpha-peak in the liquid state. The exponent \(\gamma\) is non-universal (varying from 1 to 2). We have no model for these findings. Speculating, we note that the case \(\gamma = 1\) may be modelled by an asymmetric two-level system: If the large barrier is temperature-independent \(X\) is Arrhenius \((\bigstar)\). However, in order to explain the findings of Fig. 2, a rather peculiar temperature-dependence of the highest of the two energy minima must be assumed \((\bigstar\star)\).

In conclusion, we have shown that the loss peak frequency of beta relaxation in a pyridine-toluene solution is almost temperature-independent above \(T_g\) where, on the other hand, the maximum loss is strongly temperature-dependent. Thus, beta relaxation in the equilibrium liquid state has characteristics that are opposite of those found in the glassy state, where loss peak frequency is Arrhenius and maximum loss is only weakly temperature-dependent. It has furthermore been shown that the quantity \(X\) of Eq. \((\bigstar)\) is Arrhenius; in particular \(X\) exhibits no thermal hysteresis around \(T_g\). These results contradict the traditional view of beta-relaxation as being unaffected by the glass transition and show the need for further experimental as well as theoretical work in this field. The recent surprising findings by Wagner and Richert that liquids like o-terphenyl and salol, previously believed to have no beta-relaxation, do exhibit beta-relaxation deep in the glassy state after very fast quenchings \((\bigstar\star\star\star,\bigstar\star\star)\) emphasize the need for further work in this field.

ACKNOWLEDGMENTS

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[41] This conclusion is not changed if the beta-relaxation is determined from a Williams-convolution: If this procedure is applied, compared to what we find, the beta loss peak frequency is slightly lower at high temperatures (and unaffected at low temperatures). Thus an even more dramatic change of the temperature-dependence of the beta loss peak frequency is found.
[42] A. Kudlik, C. Tschirwitz, T. Blochowicz, S. Benkhof, and E. Rössler, J. Non-Cryst. Solids 235-237, 406 (1998).
[43] In an asymmetric two-level system, where all 3 energy differences (of the 2 minima and the maximum between them) are much larger than $k_BT$, the activation energy of the loss peak frequency is the small barrier and the loss magnitude is Arrhenius with activation energy equal to the energy difference between the two minima. The sum of this energy difference and the small barrier is the large barrier. Thus, if the large barrier is temperature-independent the product of loss peak frequency and loss magnitude is Arrhenius, corresponding to the case $\gamma = 1$ of Eq. (1). In order to reproduce the findings of Fig. 2 it must furthermore be assumed that above $T_g$ the small barrier is proportional to temperature, while below $T_g$ the energy difference between the minima is proportional to temperature. However arbitrary these ad hoc assumptions seem, they do make sense in one respect: The prefactor of the Arrhenius maximum loss above $T_g$ (Fig. 2a) is $10^3$, but in the above model this prefactor is the product of a exponential factor coming from the small barrier being proportional to temperature and a “real” prefactor which is 0.6, a physically much more reasonable value. Similarly, the model reduces the prefactor of the loss peak frequency in the glassy phase from $10^{13.6}$Hz to $10^{12.6}$Hz.
[44] R. Richert, unpublished.

**Fig. 1.**

Log-log plot of dielectric loss as function of frequency for a 71%/29% mixture of pyridine in toluene at 125 K, 126 K, and 127 K (16 measured points per decade, no smoothing applied). The large low-frequency peak is the alpha-relaxation process, the small high-frequency peak is beta-relaxation. The fact that the entire alpha-peak is visible at 126 K and 127 K signals that these measurements were taken in the equilibrium liquid phase, i.e., above the glass transition. In contrast to most other viscous liquids the system is characterized by a clearly visible beta-peak in the equilibrium liquid. The alpha-relaxation is characterized by a power-law tail, proportional to $f^{-0.47}$.

**Fig. 1b:**
Log-log plot of the normalized beta-peak at eight temperatures (T=119-126K) after subtraction of the high-frequency alpha-tail $\propto f^{-0.47}$. The magnitude of the subtraction was determined uniquely from requiring that the beta-peak follows a low-frequency power-law (leading to the power-law $\propto f^{0.45}$ at all temperatures). The figure shows that the assumptions behind this procedure are consistent, the assumptions being: 1) simple additivity of alpha- and beta-relaxation, 2) alpha-tail given by a power-law decay with a temperature-independent exponent, and 3) beta-relaxation at low-frequencies following a power-law. Deviations are found at low frequencies for the highest temperatures (here the alpha-peak is so close to the beta-peak that the power-law alpha-tail subtraction overestimates the alpha-contribution).

**Fig. 2.**

**Fig. 2a:**
Logarithm of beta loss peak frequency (□) and maximum loss (◇) as function of inverse temperature for a cooling from 126.5 K to 119.0 K (raw data before subtraction of alpha-tail marked by dots). The system was cooled in steps of 0.5 K with dielectric measurements carried out after annealing for 30 minutes at each temperature immediately before stepping down another 0.5 K. The figure shows a clear change of behavior at the glass transition which takes place around $x=8.1$, corresponding to $T_g \approx 123.5$ K. Above $T_g$ (in the equilibrium liquid) the loss peak frequency is almost temperature-independent while maximum loss is Arrhenius, below $T_g$ the opposite is the case.

**Fig. 2b:**
Logarithm of beta loss peak frequency (□) and maximum loss (◇) for a cooling from 126.5 K to 119.0 K at 1 K/h as in Fig. 2a and reheating at the double rate. Both quantities exhibit hysteresis as expected for quantities that change their temperature-dependence at the glass transition. The symbol △ marks the quantity $X = f_{\text{max}} (\epsilon'_{\text{max}})^{1.19}$ for both cooling and subsequent reheating. $X$ exhibits no hysteresis, is insensitive to the glass transition, and is Arrhenius temperature-dependent.
