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Scaling of β -relaxation in the equilibrium liquid state of sorbitol

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Abstract

The Johari–Goldstein dielectric β -relaxation has been studied in the molecular liquid, sorbitol. In the narrow temperature interval in which α - and β -relaxation are separated (still being in the equilibrium liquid state), it is shown that β -relaxation has a temperature-dependence of loss peak frequency and magnitude, which differs from what is found in the glassy state. Within experimental error the β -peak is “time–temperature invariant” (i.e., shape and loss peak frequency are temperature-independent), while the magnitude increases with temperature following an Arrhenius equation. Finally, for non-equilibrium states we find that loss peak frequency and magnitude show a simple isothermal correlation, which is independent of thermal history. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The ubiquity of β -relaxation in simple liquids was pointed out by Johari and Goldstein [1]. It is generally assumed that β -relaxation can be described by an Arrhenius function even above T_g . Below T_g it has been shown [2] that the magnitude of the β -peak depends on annealing time, but to our knowledge no systematic studies of the scaling behavior of β -relaxation above T_g in simple liquids have been carried out. This is the subject of interest here. One problem is that the interference between α - and β -relaxation in the merging region is not well understood. Different models have been applied for the merging, leading to different temperature-dependencies of the β -peak itself. To avoid the merging problem the β -peak must be studied at temperatures where the two peaks are

well separated. If we assume that the rate of equilibration is of the same order of magnitude as the loss peak frequency for the α -relaxation, $f_{p\alpha}$, a separate study of β -relaxation in the equilibrium liquid state is limited to a rather narrow temperature interval (depending, of course, on the magnitude of the β -loss peak frequency, $f_{p\beta}$).

In a prior paper [3] time–temperature scaling of the α -peak in dibutylphthalate was discussed. It was shown that at temperatures where the α - and β -peaks are separated, time–temperature scaling of the α -peak is obeyed, with only a minor vertical (i.e., magnitude direction) shift. Here we find an even simpler scaling law for the β -peak, namely only a vertical and no horizontal (i.e., frequency direction) shift; we refer to this as “time–temperature invariance”. If this scaling law applies also in the temperature range where α - and β -peak merge, the β -peak may be scaled to higher temperatures measuring only the high frequency tail of this peak (which is, of course, best separated from the α -peak).

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Sorbitol is a good candidate for studying the scaling behavior of the β -peak, because the magnitude of the β -peak is only one decade smaller than that of the α -peak at temperatures where they are well separated in the equilibrium liquid state. The high frequency α -tail follows an approximate power law with exponent -0.3 . If we demand at least a one decade suppression of the α -peak at $f_{p\beta}$, $f_{p\alpha}$ should be more than 7 decades below $f_{p\beta}$. As $f_{p\beta}$ is about 10 kHz, one has to anneal the sample for more than 1000 s. Since $f_{p\alpha}$ changes half a decade per Kelvin, measurements are very time consuming. The conclusions of this work are based on measurements on the equilibrium liquid obtained in a narrow temperature interval (258–263 K), but are supported by a detailed description of the annealing behavior.

2. Experimental

D-Sorbitol was purchased (Alfa Chemicals) as a powder (98% purity). The sample was prepared by clearing the melt at 390 K for 4 h. After loading into a multilayer gold-plated capacitor (22 layer, 68 pF), the sample was placed in a cryostat filled with an N_2 atmosphere and then cooled to 270 K. Nothing was done to dry the sample, but the N_2 atmosphere prevents contamination during the measurements. The time constant for the temperature control of the sample was 300 s. The temperature was kept constant within 5 mK with an absolute uncertainty <0.2 K. Dielectric measurements were carried out in the frequency range between 10 mHz and 100 kHz applying a HP3458A digital multimeter and a network analyzer (HP4192A) with a preamplifier, and between 100

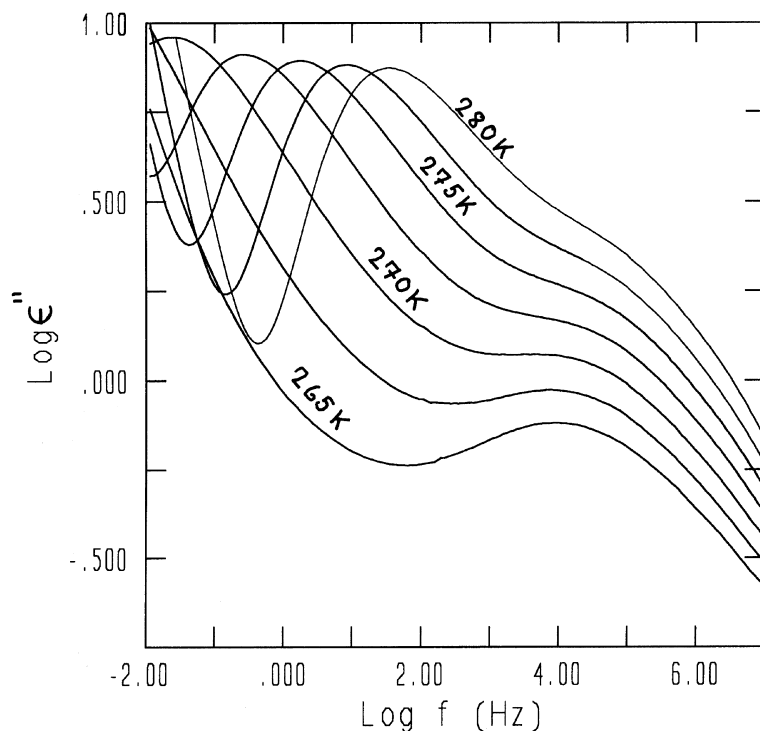


Fig. 1. ϵ'' of Sorbitol in the equilibrium liquid state at temperatures from 265 to 280 K in steps of 2.5 K. The β loss peak frequency is much less temperature-dependent than the α loss peak frequency, contrary to what is the case for the magnitudes of the two peaks. The temperature-dependence of the dielectric loss can therefore roughly be described as a horizontal resp. vertical shift with temperature for the α - resp. β component.

Hz and 10 MHz applying the analyzer as an impedance bridge. The dielectric constant is measured with an absolute error of $\pm 7\%$. Temperature and equipment for dielectric measurements were automatically controlled by a data acquisition program storing corresponding temperatures, frequencies, times, and dielectric constants. All annealing measurements were carried out in the frequency range between 100 Hz and 10 MHz only.

3. Results

To illustrate the overall temperature-dependence of dielectric relaxation in the equilibrium liquid state, the dielectric loss, ϵ'' , is shown in Fig. 1 at relatively higher temperatures. At lower frequencies, the contribution from DC-conductivity dominates; from the temperature-dependence

of the low frequency minimum it is seen that DC-conductivity and α -relaxation decouples. Above this minimum the α - and β -peaks are resolved. An approximate description of the temperature-dependence of the α - and β -relaxation is a horizontal shift of the α -peak and a vertical shift of the β -peak (at lower temperatures where the two peaks are separated). The next figures look into this picture of β -relaxation in more detail.

All measurements discussed below were carried out on the same sample. To avoid crystallization the sample was kept below 270 K until the last scan with temperatures at 290 K (Fig. 4). All measurements were reversible showing that no detectable crystallization takes place. By annealing for longer times the temperature interval probing the equilibrium liquid state was extended down to temperatures, where the α - and β -peaks are separated and the interference between them is negligible.

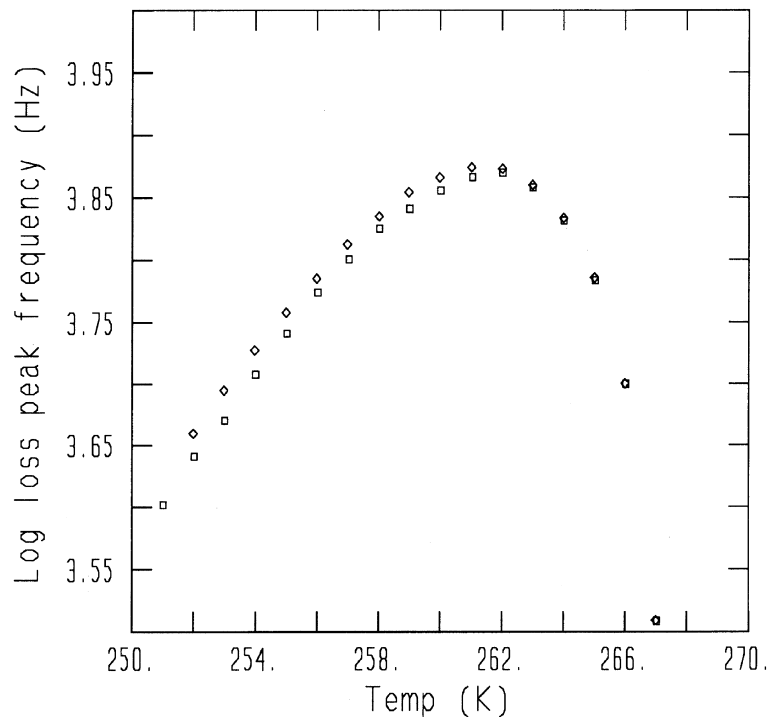


Fig. 2. The β loss peak frequency $f_{p\beta}$ as function of temperature in two temperature scans. In both scans the temperature was lowered in steps of 1 K, keeping the sample at 30 min at each temperature (\diamond), resp. 20 min at each temperature (\square). The figure shows that below the glass transition the loss peak frequency increases during annealing.

Fig. 2 shows the loss peak frequency, $f_{p\beta}$, as function of temperature ($f_{p\beta}$ is determined as the frequency at maximum of a second order polynomial fitted to data points covering one decade (21 points) around the maximum, the error in $f_{p\beta}$ and the maximum is 0.5% and 0.2%, respectively). The figure demonstrates that $f_{p\beta}$ changes with temperature differently, depending on equilibration time at each temperature. At temperatures far below the glass transition we expect $f_{p\beta}$ to be described by an Arrhenius function [2]. At higher temperatures aging of both α - and β -processes affects $f_{p\beta}$, and, near the glass transition, α - and β -relaxation starts to merge and interference dominates the temperature-dependence of $f_{p\beta}$ ($f_{p\beta}$ decreases with increasing temperature simply due to merging).

To study the non-equilibrium properties in more detail, the annealing time dependence of the shape of the β -peak has been measured.

Fig. 3 shows that, if we subtract a suitable small frequency- and temperature-independent term from ϵ'' (equal to 0.045), the ratio of $\epsilon''(f)$ at 258 and 259 K is independent of frequency in equilibrium. Thus, the higher frequency region of ϵ'' at low temperatures may be separated into a constant term plus a time-temperature invariant term. Since at these temperatures $f_{p\alpha}$ is 9 orders of magnitude smaller than $f_{p\beta}$, interference effects may be neglected and the time-temperature invariant term identified with the β -peak. The non-equilibrium frequency-dependence seen at short annealing times of the ratio shown in Fig. 3, may be due to a time-dependent change in shape and/or a horizontal shift of the β -peak.

Two things can be said about Figs. 2 and 3: the loss peak frequency in the glassy state depends on cooling rate, and, in the equilibrium liquid state at lower temperatures, shape and loss peak frequency

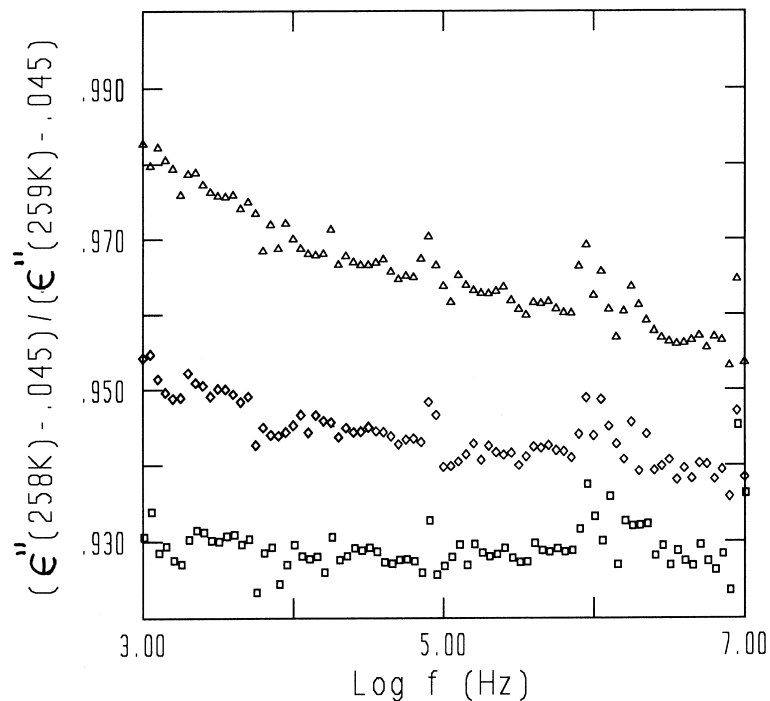


Fig. 3. The ratio between $\epsilon''(f) - 0.045$ at 258 K and the same quantity at 259 K after thermal equilibration for 32 h, shown for different annealing times at 258 K: 0.5 h (Δ), 10 h (\diamond) and 70 h (\square). The figure is consistent with our picture that, at low temperatures in equilibrium (and where the influence of α relaxation may be neglected), ϵ'' consist of two terms – a small frequency- and temperature-independent term (equal to 0.045) plus a frequency-dependent term, which is the β -relaxation. Contrary to what is seen in the glassy state, the horizontal shift is zero, i.e., β -relaxation is “time temperature invariant” in the equilibrium liquid state.

are both independent of temperature. If this holds also at higher temperatures, the vertical scaling may be calculated from the temperature-dependence of the high frequency tail of the β -peak as done in Fig. 4.

Fig. 4 shows the apparent “vertical activation temperature”, T_v , calculated from the temperature-dependence of ϵ'' (3 MHz) -0.045 (\diamond). Fig. 4 shows that, if we subtract the same constant term used in Fig. 3, T_v becomes independent of temperature above T_g . Applying the scaling principle discussed above, it is seen that the vertical shift of the β -peak follows an Arrhenius function of temperature with an activation temperature $T_v = 6000 \pm 200$ K. Below T_g , the apparent “horizontal activation temperature”, T_h , calculated from the temperature-dependence of $f_{p\beta}$ (\square) varies with temperature, even below temperatures where interference may be neglected. We find that $f_{p\beta}$ is still not fitted by an Arrhenius function down

to 225 K, far below T_g . Although, T_h seems to converge at lower temperatures towards $T_h = 7000 \pm 300$ K (in agreement with the value reported in Refs. [4,5]). This dependence indicates that, in contrast to the prevailing opinion, aging of the β -relaxation takes place at temperatures far below T_g .

Fig. 5 shows aging just below the glass transition. Johari has suggested [2] that the magnitude of the β -peak decreases with aging time but with no shift of $f_{p\beta}$. For sorbitol, however, Fig. 5 shows that $f_{p\beta}$ does change during annealing. Furthermore, Fig. 5 demonstrates a correlation between the change of magnitude and the loss peak frequency during annealing. Fig. 5 shows three different temperature scans: (1) decreasing temperatures in 1 K steps starting at 263 K, each temperature kept constant for 20 min (\square), resp. 30 min (\diamond); (2) as above but now with variable equilibration time, changing from 3 h at 263 K, to 70 h at 258

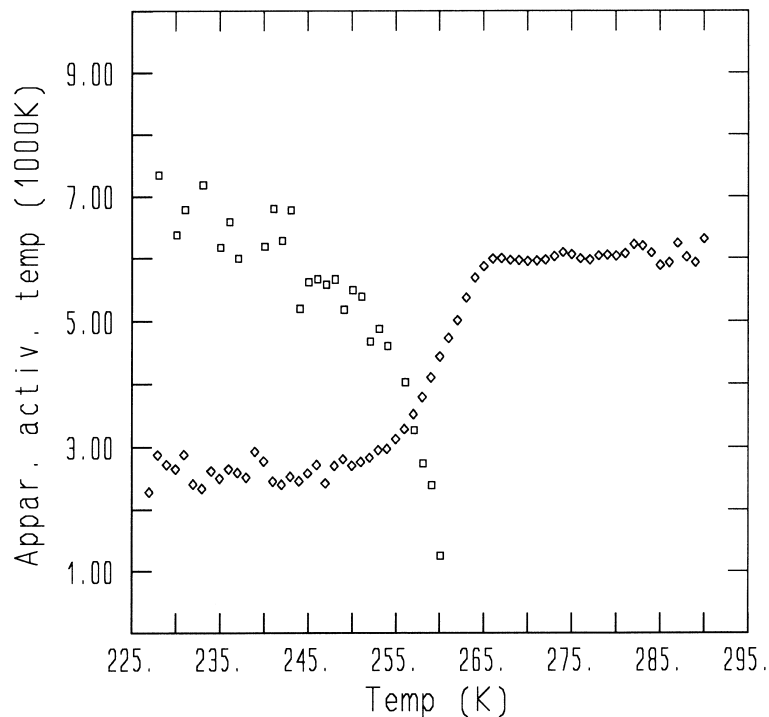


Fig. 4. The horizontal and vertical apparent activation temperatures, T_h and T_v , calculated from the temperature dependence of $f_{p\beta}$ (\square), resp. from the temperature-dependence of ϵ'' (3 MHz) -0.045 (\diamond). Below the glass transition, T_h changes with temperature. Above the glass transition, T_v becomes constant.

K (at each temperature spectra are obtained every 30 min (Δ)); (3) points obtained at 260 K each 30 min after a 2 K step from 258 K (70 h) (∇). The solid line shows the extrapolated equilibrium curve.

4. Discussion

In the temperature interval where T_v is independent of temperature, the magnitude of the β -peak increases almost one order of magnitude, while the static dielectric constant ϵ_s is nearly constant. Due to dc-conductivity and electrode effects ϵ_s can only be measured directly for temperatures above 275 K. At this temperature $\epsilon_s = 44 \pm 2$ with

a relative variation with temperature equal to $0.46\% \text{ K}^{-1}$, which is 20 times smaller than that of the β -peak. Thus, if we assume that the normalized loss-peak magnitude $\epsilon''(f_{\beta\beta})/[\epsilon_s - \epsilon'(\infty)]$ is proportional to the relative amount or the density of loosely bounded β -molecules, as proposed by Johari [2], this quantity follows a Boltzmann population law. Fig. 5 shows that, independent of thermal prehistory, the isotherms fall on straight lines with a temperature-independent slope (equal to -0.84 ± 0.02). Thus, at a given temperature loss peak-magnitude and frequency are always related through a power law with exponent -0.84 which does not depend on temperature. If we again interpret the loss peak-magnitude as a measure of the density of loosely

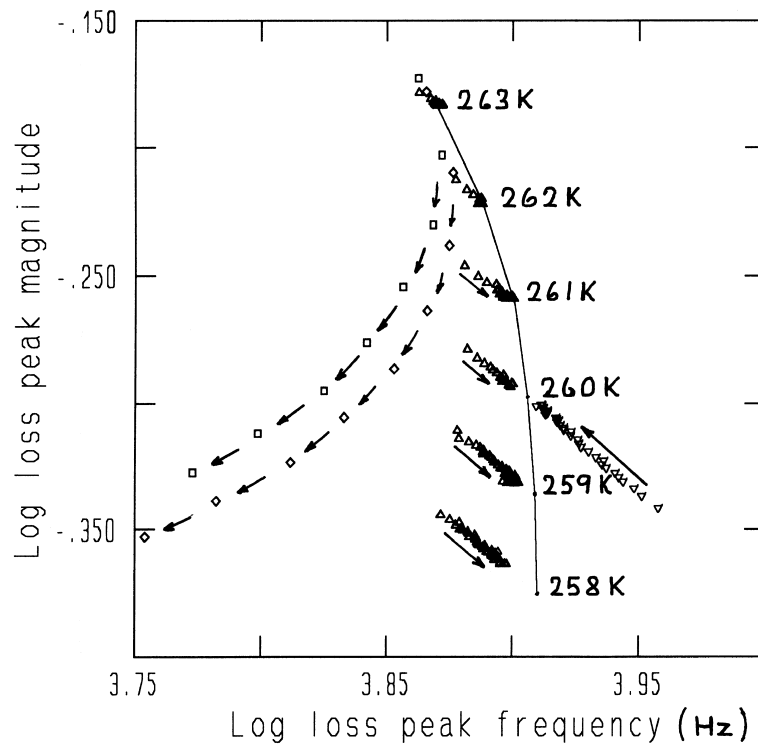


Fig. 5. Mapping of annealing behavior of β -relaxation in a loss peak frequency versus loss peak magnitude plot: The points to the left were obtained by decreasing the temperature in 1 K steps (same data as in Fig. 2), while keeping each temperature constant for 20 min (\square), resp. 30 min (\diamond). The remaining points were partially obtained as above but with variable equilibration time, changing from 3 h at 263 K, to 70 h at 258 K; at each temperature spectra were obtained every 30 min (Δ), and finally points obtained at 260 K each 30 min after a 2 K step from 258 K (70 h) (∇). The solid line shows the estimated equilibrium liquid state points. The figure shows that isotherms near equilibrium fall on different straight lines with the same slope. In the equilibrium liquid state the loss peak frequency becomes independent of temperature at low temperatures (where interference between α - and β -relaxation may be neglected).

bound molecules, we could think of aging as a structural process which adjusts this density to its equilibrium value, with a loss peak frequency unambiguously depending on this density. In this picture, a spontaneous temperature jump from equilibrium changes the loss peak frequency corresponding to a horizontal shift in Fig. 5. After equilibration the density is adjusted in such a way that the loss peak frequency is unchanged. This picture is consistent with the results shown in Fig. 4: The horizontal shift in Fig. 5 corresponds to an apparent activation temperature $T_h = 6900 \pm 200$ K, in good agreement with that seen in Fig. 4 deep into the glassy state. In the same way, the vertical shift of Fig. 5 corresponds to an apparent activation temperature $T_v = 5900 \pm 200$ K which agrees with the high temperature value of T_v seen in Fig. 4. At higher temperatures (top of Fig. 5) the equilibrium curve (solid) bends over towards lower frequencies due to the onset of merging between α - and β -relaxation. Only at low temperatures does $f_{p\beta}$ become independent of temperature.

In sorbitol the β -loss peak frequency in the equilibrium liquid state is 10 kHz, and a separation of the α - and β -peak is possible within a reasonable frequency scale. For other liquids the loss peak frequency could be anywhere on the frequency scale even in the mHz region. Thus, it is possible that the high frequency “wing” in liquids like glycerol and salol reflects an underlying β -peak with a merging temperature below or near the glass transition temperature. The reason that this picture has not been proposed already could be that horizontal and vertical shifts are indistinguishable if only a high frequency power law tail is observable. This interpretation shows that the existence of the β -peak could be even more general than generally accepted.

5. Conclusions

The dielectric loss of sorbitol has been measured near the glass transition. It has been shown that both loss peak frequency and magnitude for the β -peak depend on annealing time not too far from equilibrium. In equilibrium at temperatures where the α - and β -peaks are well separated, the β -loss peak frequency does not depend on temperature and the β -loss peak magnitude follows an Arrhenius function of temperature. In this temperature region a simple non-equilibrium isothermal correlation between loss peak frequency and magnitude was found (a correlation which is independent of thermal prehistory). This correlation is given by a power law with an exponent (-0.84), independent of temperature and numerically equal to the ratio between the “vertical activation temperature” T_v in the equilibrium liquid state and the “horizontal activation temperature” T_h deep in the glassy state.

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