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Dielectric β relaxation in a pyridine-toluene solution is studied close to the glass transition. Loss peak frequency and maximum loss both exhibit thermal hysteresis. An annealing-state-independent parameter involving loss and loss peak frequency is identified. This parameter has a simple Arrhenius temperature dependence. The same behavior is found for four other viscous liquids, indicating that the phenomenon is possibly general.

PACS number(s): 64.70.Pf, 77.22.Gm

Viscous liquids are characterized by relaxation times that increase strongly upon cooling toward the glass transition [1–4]. The relaxation time of molecular rotation is monitored by dielectric relaxation experiments probing the linear response to a periodic external electric field [5–11]. The dominant relaxation process is referred to as the α-process. For most viscous liquids, upon cooling the α-peak bifurcates just before the glass transition and an additional loss peak appears at higher frequencies [12–15]. This additional relaxation process is traditionally referred to as β relaxation [5,16–19] (now sometimes termed Johari-Goldstein β relaxation to distinguish it from the mode-coupling theory's "cage rattling" at much higher frequencies). β relaxation has also been observed in mechanical [20,21] and thermal [22] relaxation experiments. Here, we limit ourselves to dielectric β relaxation. We show that the conventional view that the β relaxation loss peak frequency is unaffected by the glass transition does not hold for nonpolymeric liquids. We have not studied β relaxation in polymers, but believe based on the literature that β relaxation in polymers is probably *not* similarly affected by the glass transition.

β relaxation was first seen in polymers, where it was attributed to side-chain motion [5]. In 1970 Johari and Goldstein found β relaxation in a number of viscous liquids of rigid molecules and conjectured that β relaxation should be considered "a characteristic property of the liquid in or near the glassy state" [23,24]. However, for some glass-forming liquids (e.g., glycerol) no β relaxation was observed. Today, viscous liquids are sometimes classified according to whether or not they exhibit β relaxation [19], although there are recent speculations that β relaxation indeed *is* universal with the β peak sometimes hiding under the α peak [25,26].

There is no general agreement about the cause of β relaxation [19,26,27]. It is unknown whether every molecule contributes to the relaxation [28,29] or only those within "islands of mobility" [16,30]. Similarly, it is not known whether small angle jumps [31] or large angle jumps [32] are responsible for β relaxation. Of course, a possible explanation of these disagreements is that β relaxation is nonuniversal [33,34].

As traditionally reported in the literature (see, e.g., [16]), β 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 β 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 β relaxation strength *is* affected [35] (in the glassy state the β relaxation strength decreases during annealing [36,37], in some cases to below the resolution limit [29]). Actually, few detailed investigations of β relaxation in the equilibrium liquid phase of nonpolymeric liquids have been carried out. This may be because studying β relaxation above the glass transition temperature T_g is difficult since there is only a tiny temperature window if any where α and β relaxations are well separated (this problem arises only because human life is too short).

Motivated by the above reasoning, one of us recently investigated β relaxation in sorbitol and found that the temperature-dependence of both loss peak frequency and relaxation strength in the equilibrium liquid state is indeed different from what is found in the glassy state [26]. This result was obtained on a system which—like most others— has a β relaxation that in the equilibrium liquid phase is not well separated from the α relaxation. Below, we present data for β relaxation in a liquid with a strong β peak that is well separated from the α peak in a range of temperatures above T_g. The liquid is a 71%/29% mixture of pyridine and toluene, a system first studied by Johari [37]. 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 [38]. The dielectric data for the pyridine-toluene mixture are analyzed in detail below, but we also briefly discuss similar results on four other viscous liquids, indicating that our findings may be general.

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 nine 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 wave form generator was used. The dielectric loss was determined with 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.
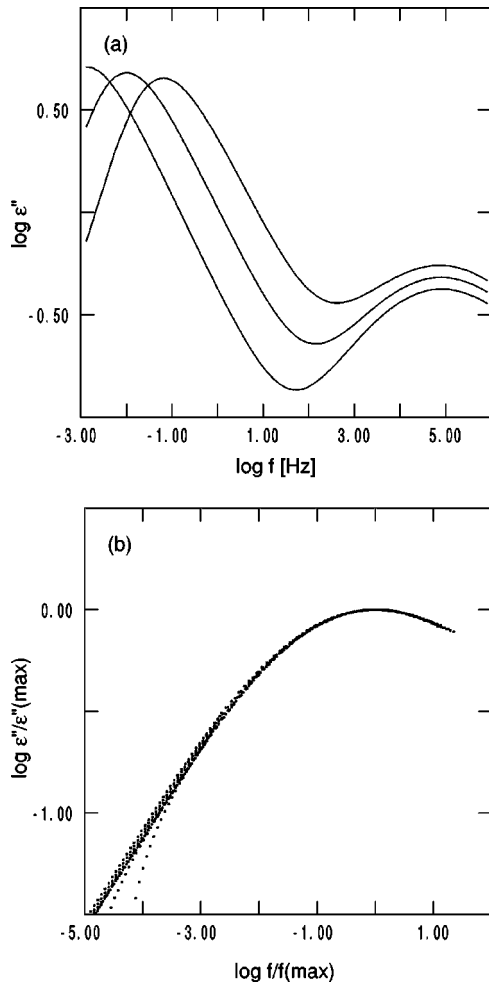
FIG. 1. (a) Log-log plot (base 10) of dielectric loss as a function of frequency for a 71%-29% mixture of pyridine and toluene at 125.0, 126.0, and 127.0 K (16 measured points per decade, no smoothing applied). The large low-frequency peak is the α relaxation process, the small high-frequency peak is β relaxation. The fact that the entire α 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 this system is characterized by a clearly visible β peak in the equilibrium liquid. The α relaxation is characterized by a power-law tail, proportional to $f^{-0.47}$. (b) Log-log plot (base 10) of the normalized β peak in the pyridine-toluene solution at eight temperatures ($T = 119.0$–126.0 K) after subtraction of the high-frequency α tail $\propto f^{-0.47}$. The magnitude of the subtraction was determined uniquely from requiring that the β peak follow 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 α and β relaxation, (2) α tail given by a power-law decay with a temperature-independent exponent, and (3) β relaxation at low frequencies following a power law. Deviations are found at low frequencies for the highest temperatures (where the α peak is so close to the β peak that the power-law α tail subtraction overestimates the α contribution).

Figure 1(a) shows the dielectric loss at 125.0, 126.0, and 127.0 K. The α and β peaks are quite well separated. Despite this a procedure is needed to eliminate the α tail influence on the β peak. From Fig. 1(a) we find that the α peak follows a high-frequency power-law decay with exponent

-0.47. *In order to arrive at the true β peak this α tail was subtracted by applying the following procedure. At each temperature the magnitude of the subtraction was uniquely determined by requiring that the β peak follow a low-frequency power law. We used a power-law fit* [10,11] *because a Gaussian, as sometimes used to fit β peaks* [39,40], *cannot fit our data. This way to eliminate the α contribution involves the following assumptions*: (1) *The dielectric spectrum is a simple sum of α and β relaxations*; (2) *in the relatively narrow temperature interval under study the α tail's power-law decay has an exponent that is temperature independent. Figure 1(b) shows eight normalized β peaks* (119.0–126.0 K) *after subtraction of α tails. The figure shows that the subtraction procedure is consistent: The corrected β peaks do follow a low-frequency power law to a good approximation.*

Figure 2(a) shows β loss peak frequency f_{max} ($\square$) and maximum loss ϵ''_{max} ($\diamond$) as functions 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 min 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 [41] while the maximum loss decreases sharply during the cooling [42]. At low temperatures—in the glassy state—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 2(b) shows β loss peak frequency f_{max} and maximum loss ϵ''_{max} as functions 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 min at each temperature [as in Fig. 2(a)]. The cooling continued until 119 K was reached. The sample was then heated in steps of 1.0 K every 30 min. The figure shows hysteresis of both relaxation strength and loss peak frequency, just like the hysteresis found for all other quantities changing temperature dependence at the glass transition. While β relaxation strength hysteresis is well known [36,37], to the best of our knowledge β loss peak frequency hysteresis is a new observation. For both quantities the relative change due to hysteresis (e.g., at $1000/T = 8.1$) is more than ten times larger than the correction [Fig. 2(a)] arising from the subtraction of the α peak.

Figure 2(b) also shows ($\triangle$) the temperature dependence during both cooling and subsequent reheating of the quantity

$$X = f_{max}(\epsilon''_{max})^{\gamma}. \tag{1}$$

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 is Arrhenius temperature dependent.

These findings are not specific to the pyridine-toluene mixture. Thus, Fig. 2(c) shows similar data for β relaxation in tripropylene-glycol. Again, there is hysteresis of both loss peak frequency and relaxation strength and the variable X ($\gamma = 2.25$) is Arrhenius temperature dependent and unaf-
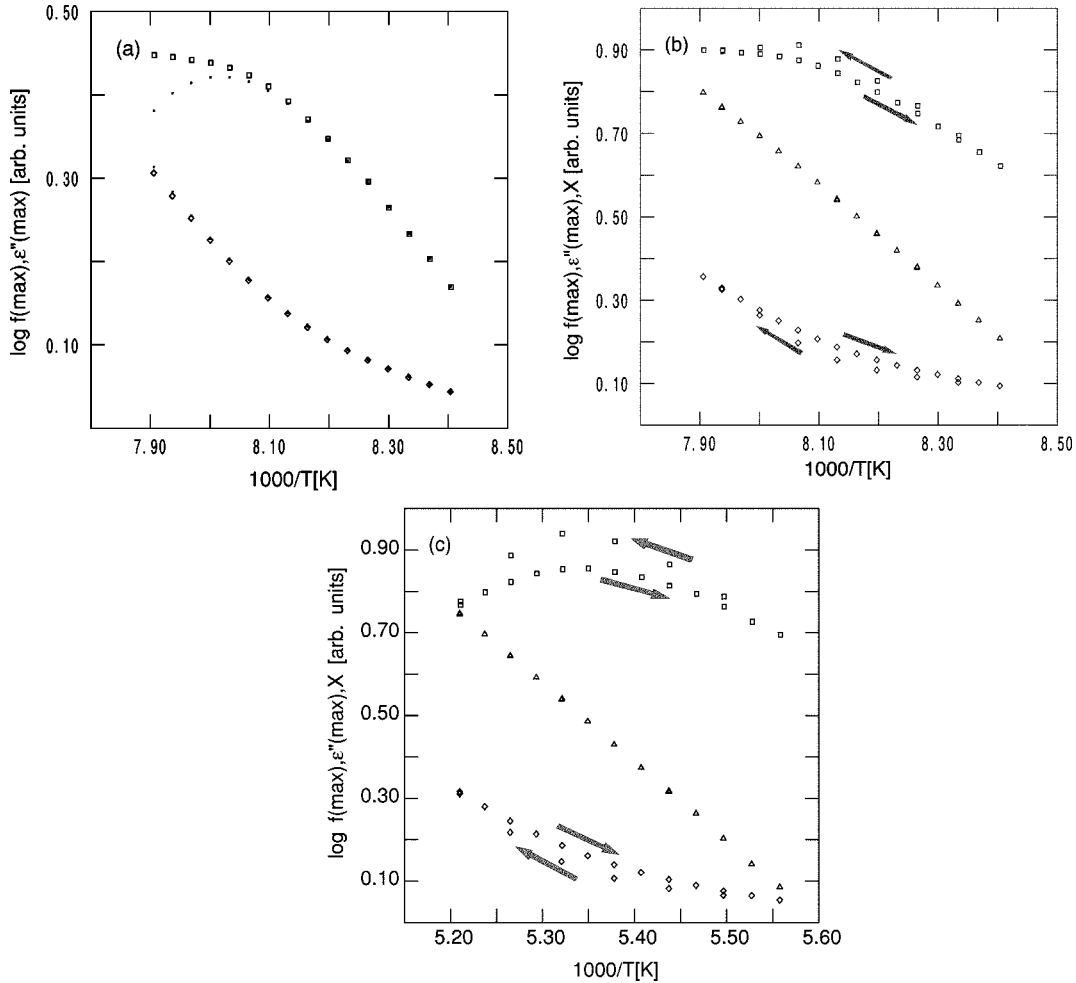
FIG. 2. (a) Logarithm (base 10) of β loss peak frequency ($\square$) and maximum loss ($\diamond$) in the pyridine-toluene solution as function of inverse temperature for a cooling from 126.5 K to 119.0 K (raw data before subtraction of α tail marked by dots). The system was cooled in steps of 0.5 K with dielectric measurements carried out after annealing for 30 min at each temperature immediately before decreasing temperature 0.5 K. The figure shows a clear change of behavior at the glass transition, which takes place around $x=8.1$, corresponding to $T_g \cong 123.5$ K. Above T_g (in the equilibrium liquid) the loss peak frequency is almost temperature independent while the maximum loss shows Arrhenius temperature dependence; below T_g the opposite is the case. (b) Logarithm (base 10) of β loss peak frequency ($\square$) and maximum loss ($\diamond$) for cooling of the pyridine-toluene solution from 126.5 K to 119.0 K at 1 K/h as in (a) and reheating at double the rate. Both quantities exhibit hysteresis as expected for quantities that change their temperature dependence at the glass transition. The symbol $\triangle$ marks the quantity $X = f_{max}(\epsilon''_{max})^{1.19}$ for both cooling and subsequent reheating. X exhibits no hysteresis, is insensitive to the glass transition, and is Arrhenius temperature dependent. (c) Logarithm (base 10) of β loss peak frequency ($\square$) and maximum loss ($\diamond$) for cooling of tripropylene-glycol from 192.0 K to 180.0 K at 1 K/h and reheating at double the rate. The β loss peak frequency in the liquid phase is around 20 kHz. The symbol $\triangle$ marks the quantity $X = f_{max}(\epsilon''_{max})^{2.25}$ for both cooling and subsequent reheating. Just as for the pyridine-toluene solution (b) X exhibits no hysteresis, is insensitive to the glass transition, and is Arrhenius temperature dependent.

fected by the glass transition. Furthermore, the already published sorbitol data [37] when replotted as in Figs. 2(b) and 2(c) show the same Arrhenius behavior of X ($\gamma = 1.19$). We have also found this behavior in polypropylene-glycol-425 ($\gamma = 1.90$) and in the commercial catalyst 4,7,10-trioxadecane-1,13-diamine ($\gamma = 2.45$). We have no measurements contradicting the conjecture that this behavior is general.

Our findings contradict the conventional view that the β loss peak frequency is unaffected by the glass transition. How should one model these findings, in particular the puzzling fact that the variable X is Arrhenius-temperature dependent and annealing-state independent? We do not at present have a satisfactory model. One possibility [43] is to use the model of Ref. [26], according to which the size of islands of

mobility determines both β loss strength and loss peak frequency. The particular case $\gamma = 1$ may alternatively be modeled by an asymmetric two-level system: If the large barrier is temperature independent X is Arrhenius temperature dependent [44]. However, in order to explain the findings of Fig. 2, a rather peculiar temperature dependence of the higher of the two energy minima must be assumed [44].

In conclusion, we have shown that both loss peak frequency and relaxation strength of β relaxation in a pyridine-toluene solution are strongly affected by the glass transition. Furthermore, it has been shown that the quantity X of Eq. (1) exhibits no thermal hysteresis around T_g and that X is Arrhenius temperature dependent. It has been shown that these findings are not specific to the particular system studied, leaving open the possibility that they are general to β

relaxation in viscous liquids close to the glass transition.

Our results show the need for further experimental as well as theoretical work in this field. The recent findings by Wagner and Richert that liquids like o-terphenyl and salol, previously believed to have no β relaxation, exhibit β relaxation deep in the glassy state after fast quenchings [34,45] emphasize the potential for further work in this exciting field.

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[44] In an asymmetric two-level system, where all three energy differences (of the two 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 relaxation strength is Arrhenius temperature-dependent 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 relaxation strength is Arrhenius temperature-dependent, 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 assumptions may seem, they do make sense in one respect: The prefactor of the Arrhenius maximum loss above T_g [Fig. 2(a)] is 10^7, but in the model this prefactor is the product of an 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. We finally note that the model reduces the prefactor of the loss peak frequency in the glassy phase from $10^{13.6}$ Hz to $10^{12.6}$ Hz.

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