Low-temperature dielectric relaxation of molecular glasses: Crossover from the nearly constant loss to the tunneling regime

C. Gainaru,[1] A. Rivera,[1] S. Putselyk,[2] G. Eska,[2] and E. A. Rössler[1]

[1]*Experimentalphysik II, Universität Bayreuth, D 95440 Bayreuth, Germany*

[2]*Experimentalphysik V, Universität Bayreuth, D 95440 Bayreuth, Germany*

The dielectric loss of molecular glasses was investigated from the glass transition temperature T_g down to 2 K, for glycerol down to 0.1 K, in the frequency range 50 Hz–20 kHz. The systems studied here do not exhibit a β process. Three distinct relaxation regimes are identified, namely nearly constant loss (NCL), thermally activated dynamics in asymmetric double well potentials (ADWP), and tunneling. The NCL ($0.35 < T/T_g < 1$), described by $\varepsilon''(\nu) \propto \nu^{-\gamma}$ with $\gamma = 0.09 - 0.21$, exhibits the characteristic exponential temperature dependence. The ADWP dynamics ($0.05 < T/T_g < 0.35$) resembles that of silica. At lowest temperatures (2–6 K) the tunneling plateau is reached. This is associated with a power law spectrum revealing a universal positive exponent that agrees well with that reported for ionic, inorganic and polymeric glasses. The so-called "plateau strength" $C = (2/\pi) \cdot \tan \delta = P\mu^2/(3\varepsilon_0\varepsilon_r)$ is determined.

Glasses exhibit peculiar physical behavior (so-called "anomalies") at low temperatures.[1–4] For example, the acoustic attenuation below say 10 K displays a temperature-independent "plateau" from which the ratio of the phonon wavelength to the phonon mean-free path can be extracted, showing a quite similar value for all glasses.[5] Dielectric data show a similar relaxation pattern.[6,7] The low-temperature anomalies are well studied in inorganic glasses and in a few polymers,[5,8,9] but information on molecular glasses is sparse.[6,8] The widely accepted model to explain the low-temperature anomalies, the standard tunneling model (STM), assumes defects in the glass where groups of atoms are found in asymmetric double well potential (ADWP) configurations.[1–5,7,9] At lowest temperatures due to tunneling, two-level systems (TLS) are formed. Though a complete understanding of the anomalies of glasses is still missing, the STM provides a fair approximation.

Above 10 K the relaxation behavior of (inorganic) glasses is less universal and less understood.[3–5,8,9] Often a more or less pronounced peak appears when internal friction or dielectric loss is plotted as a function of temperature. In order to describe this, the STM was extended to higher temperatures, where thermally activated transitions over the barrier of the ADWPs are expected.[7,9–11] The distribution of barrier heights $g(V)$ characterizing the ADWPs can be extracted from frequency-dependent measurements, and, e.g., for silica an exponential or Gaussian distribution with barrier heights in the range 0–1500 K was extracted.[4,7,10,12] However, there are examples for which the relaxation data cannot be reproduced by this model,[13,14] even though the extension of the STM to high temperatures including thermally activated motion appears natural.

For molecular glasses the situation is even more puzzling since different secondary relaxation processes have been identified already in the supercooled liquid, i.e., above the glass transition temperature T_g, and they survive below T_g. Here, the Johari-Goldstein β process and the "excess wing" are discussed.[15–17] Both relaxation features may occur simul-

taneously rendering the relaxation pattern complex. There exist glass formers that do not exhibit the β-relaxation peak but rather only the excess wing. The latter systems may be called type A glassformers to discriminate them from type B glassformers, showing a discernible β-process peak.[16] Below T_g the excess wing contribution appears to degenerate to a nearly constant loss (NCL) behavior.[16,17] Given this, it is not at all clear how the crossover to the low-temperature regime with ADWP and tunneling dynamics takes place in molecular glasses.

The purpose of this contribution is to study the dielectric loss of molecular glasses starting at T_g down to very low temperatures. We concentrate on type A glassformers to avoid interference with the β relaxation. At $T < T_g$, most molecular glasses exhibit a weak dielectric loss. Thus, high precision measurements are needed, and in a few cases, data at a single frequency were reported.[8,18] We applied the rather new Andeen Hagerling high precision bridge AH 2700A that allows us to cover the frequency range 50 Hz $< \nu <$ 20 kHz and a loss angle $\tan \delta > 10^{-6}$. By this we were able to probe the relaxation behavior down to 2 K. The following questions are addressed: (i) How universal is the NCL behavior in molecular glasses? (ii) At what temperatures occurs the crossover to the low-temperature relaxation features discussed extensively for inorganic glasses? (iii) Does one find contributions from thermally activated ADWP dynamics? (iv) What is the frequency dependence of the tunneling plateau? In the STM the tunneling plateau is expected to be frequency independent, however, there are indications that a weak dependence prevails,[5,6,9,13,19–21] leading to further extensions of the model.[22,23]

The dielectric relaxation spectra of the molecular glasses glycerol, propylene carbonate (PC), propylene glycol (PG), 2-picoline, 4-tert butyl pyridine (4-TBP) and salol were investigated by inserting the dielectric cell in a dynamic Oxford CF1200 cryostat. The capacitance of the empty cell is 14 pF and varies within 0.05% (4–300 K); the cell design was inspired by Wagner and Richert.[24] The setup shows a
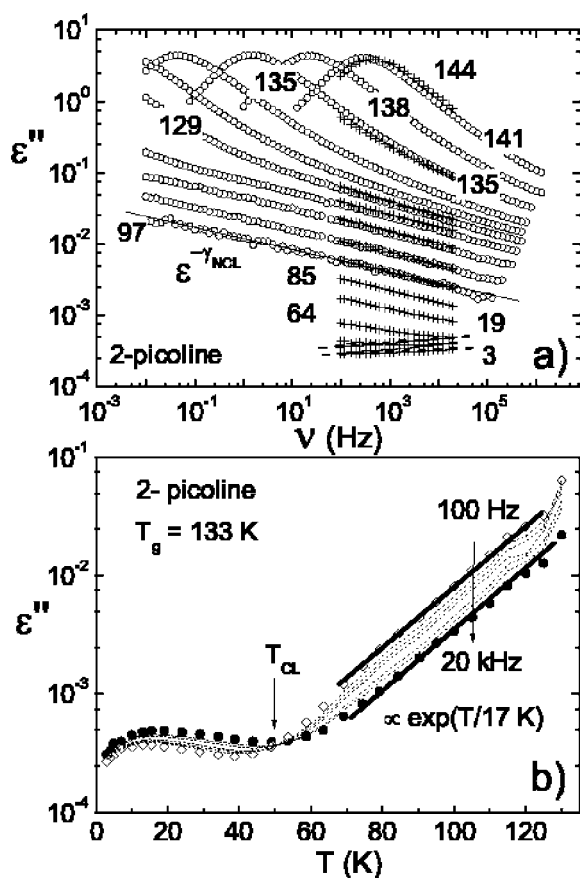
FIG. 1. (a) Frequency dependence of the imaginary part of the dielectric permittivity ε'' for 2-picoline obtained by broadband spectrometer (open circles) and by the high precision bridge (crosses); at low temperatures the dashed lines indicate the power law spectrum. (b) Temperature dependence of ε'' below T_g for several frequencies; the extreme frequencies are highlighted. The solid lines represent fits to an exponential temperature dependence [cf. Eq. (1)]. Numbers indicate temperature.

resolution limit of tan $\delta \cong 10^{-6}$ for all the frequencies, as assured by measuring the empty cell at room temperature. Temperatures between 4 and 2 K were obtained by the pumping procedure of liquid helium in the Oxford cryostat. For lowest temperatures a homebuilt cryostat was used.[25]

Figure 1 presents the frequency and temperature dependence of the imaginary part of the dielectric permittivity ε'' of the glassformer 2-picoline obtained by applying our broadband spectrometer[16] together with the high precision bridge. The latter allows ε'' to be monitored for more than two decades in frequency down to a minimum level of 5×10^{-4}. Both datasets (broadband and high precision) agree well in the common temperature range, and no indication of a secondary relaxation peak is observed as typical for type A glassformers. Clearly, the new bridge significantly extends the previous resolution limit (also well seen in Fig. 2 for the other systems), and, most important, accesses the frequency dependence of the permittivity.

In Fig. 1(a) one recognizes that besides the shift of the main relaxation peak (α process) the excess wing emerges close to T_g. The latter is discernible as a distinct power law on the high-frequency side of the main relaxation peak and
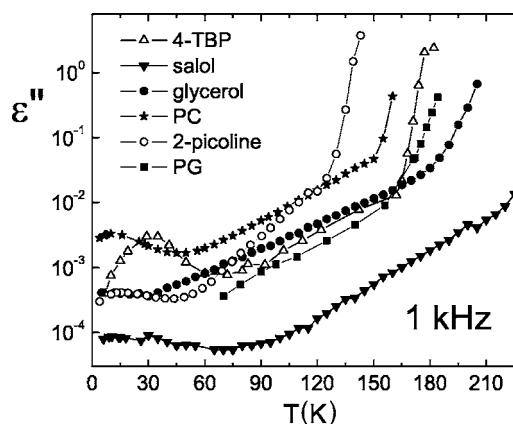

FIG. 2. Temperature dependence of ε'' at 1 kHz.

may be described by $\varepsilon''(\nu) \propto \nu^{-\gamma}$, with γ decreasing above T_g while cooling. Concerning the spectral shape of the excess wing it was recently shown for some type A systems that it develops into a shoulder when the system is aged for weeks.[26] However, for any cooling rate producing the glassy state on a realistic time scale, this effect can be safely ignored and a power law fits well the spectra that extend in some cases over seven decades.

Below T_g, the α peak has moved out of the frequency window, and the exponent γ stays constant at a quite low value $\gamma = 0.17$ in the case of 2-picoline, i.e., below T_g the excess wing degenerates to a NCL that extends over several decades in frequency. As indicated by Fig. 1(b), the corresponding temperature dependence is exponential for all frequencies, which appears to be typical of the NCL contribution.[16,18,27] Below 60 K the value γ crosses over to a small but negative value (cf. also Fig. 3 for quantitative values), i.e., the slope of the spectra in Fig. 1 becomes positive. Thus, a further relaxation phenomenon appears. This is also seen in the temperature dependence of ε'' [Figs. 1(b) and 2], where a shallow minimum and at lowest temperatures again a maximum is observed. The crossover between the different relaxation regimes may be characterized by the temperature where the $\varepsilon''(T)$ curves for the different frequencies all intersect at a common temperature T_{CL}. Here, a true constant loss
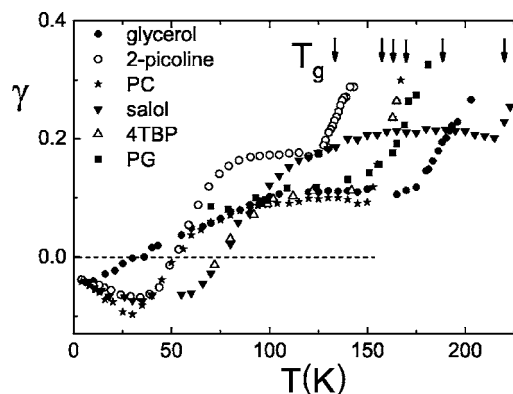

FIG. 3. Power law exponent of the loss spectra $\gamma [\varepsilon''(\nu) \propto \nu^{-\gamma}]$ at temperatures around and below T_g (indicated by an arrow for every system).

TABLE I. Parameters of the different relaxation regimes, namely nearly constant loss [NCL, Eq. (1)], thermally activated ADWP dynamics [Eq. (3)], and the tunneling regime [Eq. (2)]. For details, see the text. Data on other types of glasses are included for comparison.

System	T_g (K)	T_{NCL}	γ_{NCL}	T_{CL}	T_{CL}/T_g	V_0/k (K)	C
2-picoline	133	17	0.17	51	0.38	360	8.5×10^{-5} (1 kHz)
PC	158	28	0.09	59	0.37	350	6.1×10^{-4} (1 kHz)
4-TBP	163	31	0.11	75	0.46	—	—
Glycerol	189	34	0.11	35	0.19	—	7.5×10^{-5} (1 kHz)
PG	170	28	0.12	—	—	—	—
Salol	220	23	0.21	79	0.36	300	2.4×10^{-5} (1 kHz)
Silica (<1.5 ppm OH)	—	—	—	—	—	570 [7]	10^{-5} (2.2 kHz) (Ref. 30)
$GeO_2 + 0.1\% Na_2O$	—	—	—	—	—	—	6×10^{-5} (1 kHz) (Ref. 30)
BK7	—	—	—	—	—	—	3×10^{-4} (1 kHz) (Ref. 6)
PMMA	—	—	—	—	—	—	3.4×10^{-5} (10 kHz) (Ref. 6)
CKN	—	—	—	—	—	—	3×10^{-5} (10 kHz) (Ref. 6)
$LiCl \cdot 5H_2O$	—	—	—	—	—	—	3×10^{-4} (50 kHz) (Ref. 20)

behavior is observed as the frequency dependence of ε'' disappears [Figs. 1(b) and 3].

Figure 2 compiles the temperature dependence $\varepsilon''(T)$ at 1 kHz of the molecular glasses investigated and Fig. 3 the behavior of the exponent $\gamma(T)$. Similar relaxation features are found for all the systems: at high temperatures close to but below T_g the NCL dominates the relaxation. The exponent γ varies in a small interval $0.09 < \gamma_{NCL} < 0.21$, and, with the exception of 2-picoline, the exponential temperature dependence is quite similar. Thus, for the regime of the NCL we write

$$\varepsilon''_{NCL}(\nu, T) \propto \nu^{-\gamma_{NCL}} e^{T/T_{NCL}}. \qquad (1)$$

The values T_{NCL}, γ_{NCL}, and T_{CL} are listed in Table I. Salol was also measured at a single frequency by Hansen and Richert,[18] and a good agreement is observed (cf. the line in Fig. 5). At temperatures below the NCL regime, a minimum is found for $\varepsilon''(T)$ (except for glycerol) and at lowest temperatures a weak maximum appears that is better seen when the data are plotted linearly (cf. Fig. 7).

In a recent analysis of the dielectric spectra of several glassformers above T_g, Blochowicz et al.[28] found that the excess wing exhibits a similar evolution upon cooling that is revealed when the exponent γ is plotted as a function of the time constant of the α process. Thus, one expects γ to be similar for all systems at T_g. In order to demonstrate this we have displayed γ as a function of T/T_g in Fig. 4. Indeed, γ at $T/T_g = 1$ is very similar for all the systems. Moreover, for the three glasses PC, 2-picoline and salol the NCL behavior with a temperature-independent γ ends around $T/T_g \cong 0.6$, and $\gamma = 0$ is reached at $T_{CL}/T_g \cong 0.35$. However, glycerol and 4-TBP behave differently: while for 4-TBP the crossover at T_{CL}/T_g occurs at higher temperatures, it happens for glycerol at lower temperatures, and neither a minimum nor a maximum is recognized in $\varepsilon''(T)$ below T_g. Further inspection of Figs. 3 and 4 reveals a remarkable fact. Independent of the individual details of the curve $\gamma(T)$ it appears that a system-independent exponent γ is reached at the lowest temperature.

Here, all spectra exhibit a negative γ, which means in our terminology a power law behavior with a positive exponent, we find $|\gamma| \cong 0.04 \pm 0.003$ (2–6 K).

In all (inorganic) glasses studied so far at temperatures below say 10 K (and in the kHz regime) the tunneling plateau is reached, i.e., the dielectric loss becomes independent of temperature.[1–5] Only at much lower temperatures a decrease is observed upon further cooling. In order to check whether we have reached the tunneling regime we extended the temperature range from the liquid helium temperature down to 2 K for all systems except PG and 4-TBP, and for glycerol down to 0.1 K. The data are displayed in Fig. 5, the saturation of loss indicates that the tunneling plateau is reached for all the systems investigated at such low temperatures. For glycerol the plateau extends for more than one decade in temperature. As mentioned, the plateau regime is characterized by a common very low exponent γ. Actually, in the frame of the STM the plateau value is expected to exhibit no temperature and frequency dependence. In Fig. 6 we compare the frequency dependence of the plateau for the systems studied here with the ones from the literature. For
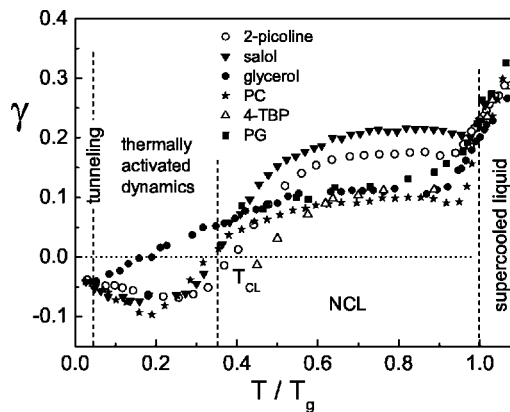

FIG. 4. Power law exponent γ of the loss spectra versus reduced temperature T/T_g for the systems measured; relaxation regimes are indicated.
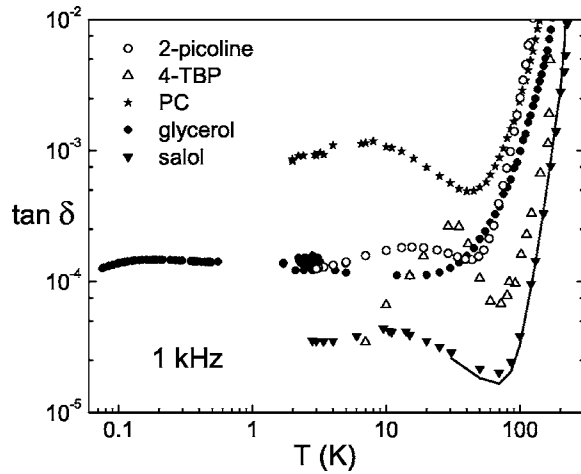
FIG. 5. tan $\delta(\varepsilon''/\varepsilon')$ at 1 kHz as a function of temperature (logarithmic scale) for the molecular glasses. For comparison the data from Ref. 18 for salol are included as a solid line.

obtaining comparable data we normalized the spectra by the plateau value at $\nu=12$ kHz. A very similar frequency dependence is found for all the glasses, including polymers (PMMA[6]), ionic glasses [CKN (Ref. 6) and LiCl·5H$_2$O (Refs. 19 and 20)], and inorganic network glasses [BK7 (Refs. 6 and 19)], as well as the molecular glasses studied here. The literature data were obtained at somewhat lower temperatures (1.2–1.5 K).

In the STM the value of the dielectric tunneling plateau is related to the density P of tunneling systems and to the effective dipole moment μ of the TLS and, as said, does not exhibit a frequency dependence, explicitly[29]

$$\tan \delta = \pi/2 \ C, \quad \text{with } C = 1/3 \ P\mu^2/(\varepsilon_0 \varepsilon_r), \qquad (2)$$

where ε_0 is the electric field constant and ε_r is the static permittivity. Equation (2) assumes that the TLS dipole moments are randomly oriented. The expression may need corrections for including the effects of the local field. We
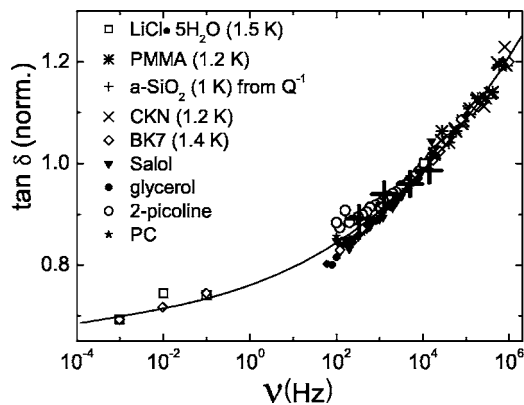

FIG. 6. Frequency dependence of tan δ at the lowest temperatures (2–6 K, tunneling plateau) for the molecular glasses studied here and for several other glasses reported in the literature (Refs. 6, 19, and 20). For a comparison, internal friction (Q^{-1}) for a-SiO$_2$ estimated from Ref. 4 (crosses) is included. Data are normalized at 12 kHz and the solid line is a guide for the eye.
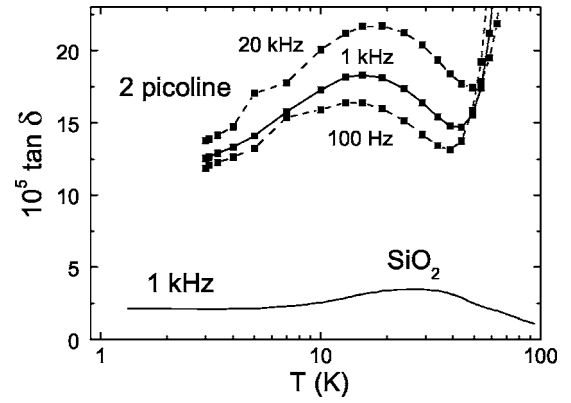

FIG. 7. Tangent of the loss angle of 2-picoline and silica [20 ppm OH content (Ref. 33), digitized from Ref. 7] on a linear scale.

listed the values of the plateau strength C in Table I. Neglecting the weak frequency dependence displayed in Fig. 6, among the molecular glasses the constant C varies by about a factor of 50. Comparing our results for C with those reported in the literature (Table I), we notice that the plateau strength varies within that factor for all glasses. Moreover, the extent of variation is also close to what was reported for the acoustic attenuation data.[5]

Next, we discuss the origin of the relaxation behavior in the temperature range in between the tunneling and the NCL regime, say at 0.05 T/T_g–0.35 T/T_g (cf. Fig. 4). Here, while heating $\varepsilon''(T)$ exhibits a maximum and then a minimum, and $\gamma(T)$ shows a shallow minimum. The behavior of $\varepsilon''(T)$ is similar to that found in silica (amorphous SiO$_2$) although the maxima of the molecular glasses occur at somewhat lower temperatures (cf. Fig. 7). In silica and other inorganic glasses, these maxima are attributed to thermally activated transitions in ADWPs.[7,9–12] In several cases a broad distribution of barrier heights $g(V)$ modeled by an exponential or Gaussian distribution with no low-energy cutoff was discussed.[7,10,31] When a low energy cutoff is missing in $g(V)$, a peak is expected in $\varepsilon''(T)$ but not in the spectra $\varepsilon''(\nu)$. Indeed this is the behavior observed in silica[7,10,12]—and as we see from Figs. 1–3 also for the molecular glasses PC, salol, and 2-picoline. For 4-TBP the relaxation peak is observed in both $\varepsilon''(\nu)$ and $\varepsilon''(T)$ and for glycerol no peak at all is discernible, behavior found also for other glasses.[13] In Fig. 7 we plotted tan $\delta(T)$ for 2-picoline at three frequencies (100 Hz, 1 kHz, 20 kHz). Clearly, the maximum shifts to higher temperatures with increasing frequency and the maximum's value increases with the temperature of the maximum; both features are expected for thermally activated ADWP dynamics.[10] From the shift, assuming an exponential barrier height distribution

$$g(V) = 1/V_0 \exp(- V/V_0), \qquad (3)$$

the mean activation energy V_0 can be obtained.[7] The results for picoline, PC, and salol are indicated in Table I. The values V_0 are similar among each other and not much different from that of silica. We note that the result for V_0 extracted from the data depends somewhat on whether indeed the $g(V)$

is exponential. Also, we neglected in the analysis that some influence from the tunneling contribution may be still present up to 30 K.

In conclusion, restricting our study on type A molecular glasses at $T < T_g$, we observed three well-distinct relaxation regimes, namely NCL, thermally activated ADWP dynamics, and tunneling. The weak frequency dependence observed at the lowest temperature appears to be universal, as it is observed in very different types of glasses, however, it is at variance with the STM. This frequency dependence may be reproduced by a version of the soft potential model.[19,32] In Fig. 6 we included the frequency dependence of the tunneling plateau for silica, as obtained by acoustic attenuation

data. Clearly, the behavior is very similar to that of the dielectric relaxation. Generalizing our results, it may be possible that the extent of similarity of the relaxation pattern in molecular glasses, with their dominating van der Waals interaction, is high as compared to that in inorganic or polymeric glasses, where at $T > 10$ K a large variety of relaxation processes can be identified.

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