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Energy landscape in molecular glasses probed by high-resolution dielectric experiments

Catalin Gainaru[*] and Roland Böhmer
Fakultät für Physik, Technische Universität Dortmund, 44221 Dortmund, Germany

Robert Kahlau and Ernst Rössler
Fakultät für Physik, Universität Bayreuth, 95540 Bayreuth, Germany

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Dielectric measurements between the glass transition temperature T_g and about 3 K are reported for a supercooled plastic crystal and several organic molecular glasses that exhibit a secondary loss peak (β process) close to T_g. Above about 10 K and up to $T_g/2$, the dynamics can be described as a thermally activated process taking place within an energy landscape characterized by a bimodal distribution of barrier heights. This energy landscape is revealed by subjecting the dielectric loss data to an appropriate scaling involving a single free parameter. At temperatures above about $T_g/2$, the scaling deteriorates for most glasses due to the emergence of the so-called excess wing.

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I. INTRODUCTION

The relaxational behavior of *organic* glass formers is well investigated near the glass transition temperature T_g (Refs. 1–3) and in the case of *inorganic* glasses also down to temperatures below a few kelvin.[4–6] At such low temperatures, the mechanical and electrical absorption coefficients of inorganic glasses are fairly insensitive to frequency and temperature, a behavior usually described within the standard tunneling model (STM).[4,7–9] At temperatures above 10 K, the frequency-dependent absorption coefficients often display maxima when plotted as a function of temperature,[10] and for a given frequency the positions of these maxima depend on the particular vitreous material.[4] Curiously, when plotting the same data isothermally as a function of frequency the absorption maxima are, however, *not* observed. In order to account for this peculiar behavior Gilroy and Phillips extended the STM to higher temperatures for which thermally activated transitions within asymmetric double-well potentials (ADWPs) are to be expected.[11,12]

In the low-temperature regime, $10\ \mathrm{K} < T \ll T_g$ dielectric information on organic glasses is relatively scarce.[13,14] In the recent past, research in this T range has focused on small-molecule systems for which a secondary relaxation peak is not immediately obvious from their dielectric loss spectra near T_g.[15,16] For such glasses a nearly constant loss with an exponential temperature dependence prevails below T_g down to a temperature of typically $\approx 0.35 T_g$.[16] Upon further cooling, deviations from this behavior occur as was first revealed via single-frequency, high-precision dielectric measurements by Hansen and Richert.[15] Recently, based on measurements using a multifrequency high-precision bridge, it was shown that ADWP dynamics dominates the dielectric loss of some molecular glasses at temperatures $T < 0.35 T_g$.[16]

This work extends the investigations on organic glasses to include systems that exhibit relatively strong high-frequency dielectric loss contributions close to T_g. In this temperature range, the Johari-Goldstein β process and the excess wing are the most prominent features.[17–19] Detailed analyses of the dielectric response of numerous organic glasses were carried out[17,19,20] and confirmed the notion that the β-relaxation process is a universal feature of molecular systems, although its relative strength can vary considerably from glass former to glass former. Furthermore, it was shown that the excess wing and the β process evolve independent of each other and that the frequency dependence of the dielectric loss associated with the excess wing follows a power law, $\varepsilon'' = A_{EW} \nu^{\gamma}$ with a negative exponent γ.[20] Here, A_{EW} is a temperature-dependent factor and the exponent γ was found to be close to -0.2, independent of material and of temperatures larger than about $T_g/2$.[20–22]

In the present paper, the following questions are addressed: can one find signatures for ADWP dynamics also for the systems exhibiting a large secondary relaxation peak below T_g? In other words, is the ADWP dynamics a universal feature of the glassy state? If so, can the ADWP dynamics and the β process, a relaxation feature commonly accepted to be genuine to the glassy state, be treated on the same footing? At first glance, the latter seems implausible: while the β relaxation is usually identified on the basis of symmetrically broadened susceptibility spectra, the ADWP dynamics does not lead to frequency-dependent maxima in the subterahertz regime. However, anticipating the main result of the present work we find that the β-relaxation peak in the glassy state and the ADWP dynamics, although historically often treated separately, derive from the same, common distribution $g(V)$ of energy barriers. For most systems studied in the present paper, it turns out that this distribution is bimodal so that thermally activated processes at low temperatures, mostly probing the low-barrier end of $g(V)$, give rise to ADWP characteristics, while excitation over larger barriers, requiring larger thermal energies, implicitly larger temperatures, are responsible for the β relaxation. To simplify the data analysis, we will nevertheless start by discussing β relaxation and ADWP dynamics separately.

II. MATERIALS AND METHODS

The frequency dependence of the dielectric loss for organic glasses with obvious secondary relaxation peaks was not systematically studied down to 4 K, so far. In order to fill this gap, in the present paper the loss spectra of m-fluoroaniline (m-FAN, $T_g=172$ K), toluene ($T_g=116$ K), 1,4-polybutadiene with a molecular weight $M_n=335$ g/mol (PB330, $T_g=141$ K), and the plastic crystalline phase of cyano cyclohexane (CCH, $T_g=134$ K) were investigated down to cryogenic temperatures. All these systems reveal clear secondary peaks close to their respective glass transition temperature, as indicated by previous broadband dielectric studies.[18,23–28] Typically, these measurements were limited to dielectric loss amplitudes $\varepsilon'' > 10^{-2}-10^{-3}$ but with the 2700A Andeen-Hagerling ultraprecision bridge employed in the present work the resolution could be extended down to $\varepsilon'' \approx 10^{-5}$ in the frequency range between 50 Hz and 20 kHz. Additional technical details can be found elsewhere.[16,27]

For comparison we included in our study glycerol [$T_g=189$ K (Ref. 29)] and polydimethylsiloxane with a molecular weight $M_n=311$ g/mol [PDMS311, $T_g=126$ K (Ref. 28)]. For these two systems a secondary relaxation peak cannot be directly identified in their loss spectra. For PDMS311 the dielectric signal was strong enough to be investigated with a broadband Alpha analyzer from Novocontrol down to 2 K. All chemicals were used without further purification.

III. THEORETICAL BACKGROUND

The double-well potentials relevant in the present context can be characterized by a certain asymmetry Δ, and a barrier height, V. The Gilroy-Phillips model[11] assumes that deep in the glass the dynamics is activated only for those ADWPs with asymmetries (in temperature units) $\Delta \leq 2T$. Under this assumption the dielectric loss is obtained by integrating over a practically constant distribution of asymmetries $f(\Delta) \approx f_0$,

$$\varepsilon'' = A_0 \int_0^\infty \frac{2\pi\nu\tau}{\sqrt{1+(2\pi\nu\tau)^2}} \frac{g(V)}{1+\sqrt{1+(2\pi\nu\tau)^2}} dV. \qquad (1)$$

Here A_0 is a dielectric strength proportional to f_0 and τ obeys an Arrhenius temperature dependence $\tau=\tau_0 \exp(V/T)$. Regarding the distribution of barriers $g(V)$, for a large number of studies an exponential function

$$g(V) = \frac{1}{V_0} \exp\left(-\frac{V}{V_0}\right) \qquad (2)$$

with no low-energy cutoff and a mean activation barrier V_0 (in temperature units) of a few hundreds of kelvin was found suitable to describe the low-temperature data of inorganic glasses.[11,30–35]

Employing such an exponential $g(V)$ distribution, the Gilroy-Phillips model predicts loss spectra with a temperature-independent intensity A_0, a ν^{-1} Debye-type limit for $2\pi\nu > 1/\tau_0$, and low-frequency power laws with exponents $\alpha=T/V_0$ that are proportional to temperature. As shown in Ref. 11, for $2\pi\nu\tau_0 \ll 1$ the dielectric loss obtained via Eqs. (1) and (2) can be well approximated by

$$\varepsilon'' \approx A_0 \alpha (2\pi\nu\tau_0)^\alpha. \qquad (3)$$

For a thermally activated process based on a distribution of activation barriers $g(V)$, the latter can be extracted directly from dielectric loss measurements in a model independent way. This is because the dielectric loss

$$\varepsilon''(\nu,T) = \Delta\varepsilon(T) \int g(V) dV \frac{2\pi\nu\tau(V,T)}{1+[2\pi\nu\tau(V,T)]^2} \qquad (4)$$

can be approximated simply by

$$\varepsilon''(\nu,T) \approx \frac{\pi}{2} \Delta\varepsilon T g(V), \qquad (5)$$

if $g(V)$ is broad enough with respect to the Lorentzian term $2\pi\nu\tau/[1+(2\pi\nu\tau)^2]$. If this assumption works then the distribution $g(V)$ can be revealed by plotting

$$g(V) = \frac{2}{\pi} \frac{\varepsilon''}{\Delta\varepsilon T} \qquad (6)$$

versus $V=T \ln \nu_0/\nu$. Under these conditions, the spectra $\varepsilon''(\nu)$ are expected to collapse onto a curve proportional to $g(V)$ and the free parameters necessary for this scaling are $\Delta\varepsilon$ and the attempt frequency $\nu_0=(2\pi\tau_0)^{-1}$ which should have a reasonable value in the range of $10^{13}-10^{14}$ Hz.

As mentioned above, in the model by Gilroy and Phillips the temperature-dependent cutoff of the flat distribution of asymmetries, occurring at about $\Delta \approx 2T$, leads to a temperature-*independent* relaxation strength $\Delta\varepsilon \equiv A_0$ for the ADWP dynamics.[11] Thus, for a given system only a single free scaling variable, ν_0, is required to determine the distribution $g(V) \propto \varepsilon''/T$ if this model applies.

IV. RESULTS AND DISCUSSION

A. Dielectric results

In Fig. 1, we show previously published dielectric loss spectra for several organic glass formers (open circles) to which the high-resolution, low-temperature data from the present work are added (crosses). Although the main focus is here on systems with clearly discernible secondary relaxation peaks, for reference purposes Fig. 1(a) also contains data for glycerol. For this glass only single-frequency $\varepsilon''(T)$ data recorded at 1 kHz and a spectrum at 4 K were available, so far.[15,16,20] At high temperatures, the $\varepsilon''(\nu)$ spectra of glycerol are dominated by the α process, and close to T_g an excess power law shows up on the high-frequency flank of the α peak, which is commonly referred to as the excess wing. Similar observations can be made also for the PDMS311 data shown in Fig. 2(a).

By contrast, for all other materials represented in Figs. 1(b)–1(e) a (very) broad secondary relaxation peak becomes obvious near the glass transition temperature, T_g. The secondary relaxation peak remains detectable and constitutes the main contribution to the loss spectra if one does not cool too deep into the glassy state. At temperatures on the order of $T_g/2$, the phase resolution limit of typical broadband dielectric spectrometers is reached. But as the present high-resolution data (crosses) in Fig. 1 show, frequency-dependent losses, $\varepsilon''(\nu)$, can be measured down to liquid helium temperature.

The general trends evident from these measurements are very much alike for the systems shown in Figs. 1(b)–1(e) and also similar to the ones reported for molecular glasses devoid of an obvious secondary relaxation peak.[16] At sufficiently

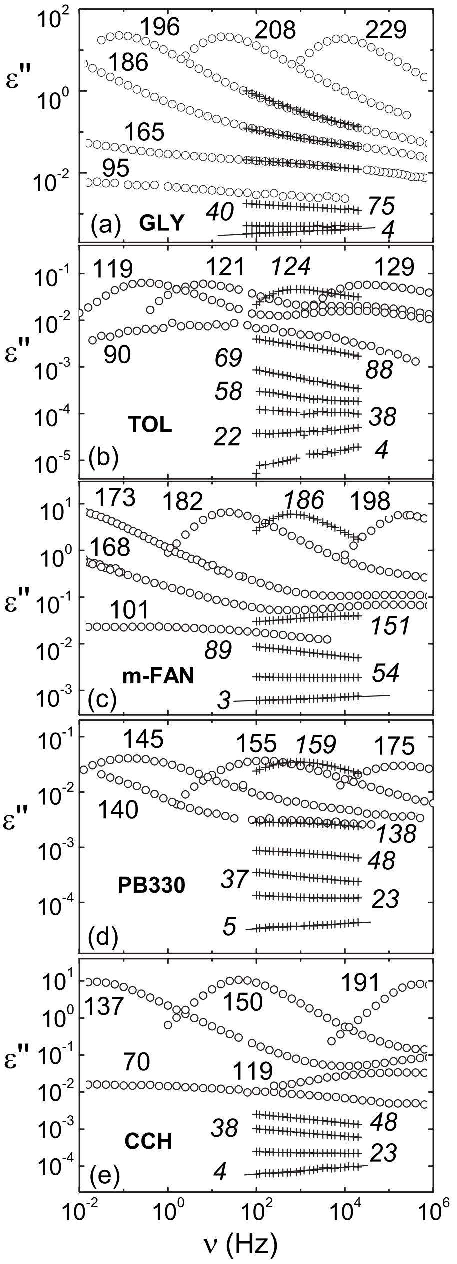

FIG. 1. Frequency dependence of the imaginary part of the dielectric permittivity ε'' for (a) glycerol (GLY), (b) toluene (TOL), (c) m-fluoroaniline, (d) 1,4-polybutadiene ($M_n=335$ g/mol), and (e) the plastically crystalline phase of cyano cyclohexane. Results from broadband spectroscopy (open circles) are compared with those from high-precision dielectometry (crosses). At low temperatures, the dashed lines indicate a power law $\varepsilon'' \propto \nu^{\gamma}$ with an exponent $\gamma=0.04$. The numbers indicate temperatures in Kelvin, the italic ones corresponding to the high-precision measurements.

low temperatures, the $\varepsilon''(\nu)$ spectra start to flatten and at a given temperature (40 K for glycerol, 54 K for m-FAN, 22 K for toluene, 23 K for PB330, and 23 K for CCH) the loss becomes frequency independent. At even lower temperatures, the slope $\gamma \equiv d \log \varepsilon''(\nu)/d \log \nu$ turns positive and continuously increases upon further cooling. At the lowest temperatures, the spectra of all systems except toluene can be described by a power law with an exponent γ close to 0.04.

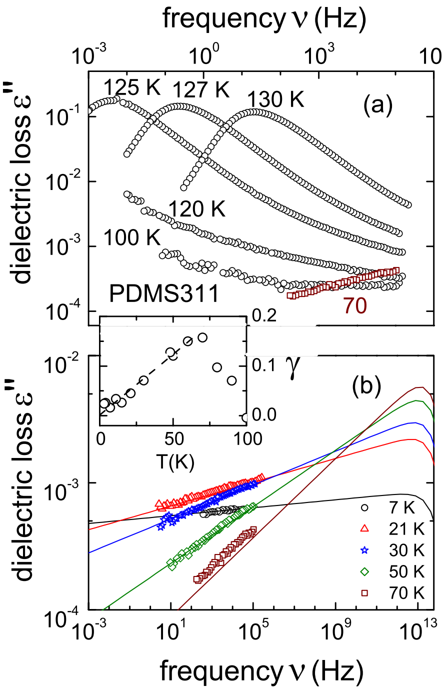

FIG. 2. (Color online) Frequency dependence of the imaginary part of the dielectric loss ε'' for PDMS311 (a) for 130 K$\geq T \geq$70 K and (b) for 70 K$\geq T \geq$7 K. For clarity the spectra below 70 K are represented using different colors. Frame (b) includes calculations based on the Gilroy-Phillips model using Eqs. (1) and (2) with $\tau_0=10^{-13}$ s, $A_0=0.036$, and $V_0=450$ K at the given temperatures. In the range $2\pi\nu\tau_0 \ll 1$, the approximation by a power law, Eq. (3) with an exponent $\alpha=T/V_0$ is excellent. The deviation at the highest temperature may indicate the presence of an additional (secondary) process. The inset shows the frequency exponent $\gamma(T)$ describing the PDMS311 data with the solid line highlighting the linear temperature dependence predicted by the ADWP model. Above 70 K, the T dependence of γ indicates again the emergence of an additional process.

This low-temperature exponent universally appears in many investigations of network, ionic, and organic glasses.[14,16,36–39] According to previous work, a γ value of about 0.04 indicates that the tunneling regime is reached.[16,37]

B. Energy barrier scaling

In Fig. 2, we plot $\varepsilon''(\nu)$ of PDMS311 for selected temperatures down to 7 K. For the sake of clarity data for temperatures above 70 K are shown in frame (a) and for $T \leq 70$ K in frame (b). The spectra in frame (a) are similar to those discussed for glycerol: below T_g the α process shifts out of the accessible frequency window and the remaining spectral contribution continuously flattens down to $T \approx 100$ K. At lower temperatures, the loss starts to increase on the high-frequency side signaling the emergence of a new feature. As obvious from Fig. 2(b), below 70 K the evolution of $\varepsilon''(\nu)$ is in harmony with the Gilroy-Phillips model: the spectra can be well described using Eq. (3) with a temperature-independent relaxation strength $A_0=0.036$ and a power-law exponent γ (that here may be identified with $\alpha = T/V_0$). According to the inset of Fig. 2, this exponent is

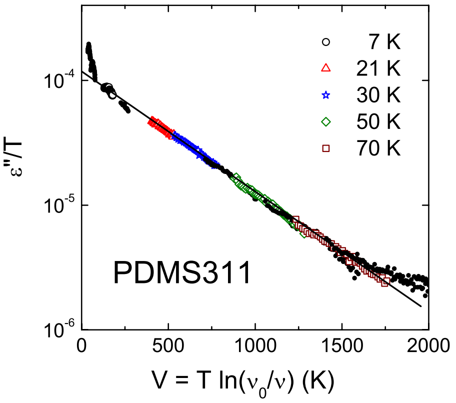

FIG. 3. (Color online) The barrier distribution $g(V)$ obtained from the PDMS311 data via the scaling procedure prescribed by Eq. (6). The open symbols represent the data plotted in Fig. 2(b) while the dots symbolize data at additional temperatures. The solid line represents an exponential function $g(V) \propto \exp(-V/450\ \mathrm{K})$.

proportional to temperature for $T \leq 70$ K and the proportionality constant yields $V_0 = (450 \pm 5)$ K.

In order to extract the underlying distribution of barriers $g(V)$, we applied the scaling procedure based on Eq. (6) and plotted the results in Fig. 3. One recognizes that this procedure collapses all spectra measured below 70 K onto a single-exponential curve $g(V) \propto \exp(-V/V_0)$ with $V_0 = 450$ K, confirming the estimate just given. Only *one* parameter, $\nu_0 = 10^{13}$ Hz, was adjusted and used to scale the spectra for all temperatures.

We are not aware of another organic glass for which the Gilroy-Phillips model describes the low-temperature dielectric data so well. An exponential distribution $g(V)$ is revealed here in a particularly broad V range, complementing previous mechanical and light scattering investigations mostly performed on inorganic materials.[11,30–35]

At the lowest and at the highest V values plotted in Fig. 3 deviations from the general exponential behavior of $g(V)$ appear. While at the low barriers, probed at temperatures $T < 7$ K, tunneling effects may play a role,[40] in the high V range of several thousand kelvin further processes are expected to gain significance, as discussed next.

It is commonly accepted that the β process in the glassy state is a thermally activated phenomenon and that its relaxation strength does not change much with temperature. In this sense, this process shares a number of similarities with the ADWP dynamics described by the Gilroy-Phillips model. It is therefore tempting to test whether the scaling procedure performed for PDMS311 can also be applied for systems with sub-T_g spectra that are clearly dominated by contributions originating from a β peak.

In Fig. 4(a), we replot the ε'' data from Fig. 1(b) for toluene as a function of temperature for different frequencies down to 60 K. Applying the scaling procedure prescribed by Eq. (6), the master curve shown in Fig. 4(b) was obtained using $\nu_0 = 10^{14}$ Hz as the only adjustable parameter. Again, no vertical shift, which would correspond to a temperature dependence of $\Delta\varepsilon$, was required. The maximum position of the resulting distribution $g(V)$ agrees well with the mean activation energy previously reported for the β process of toluene.[18,41] Furthermore, the shape of the distribution is compatible with a Gaussian function

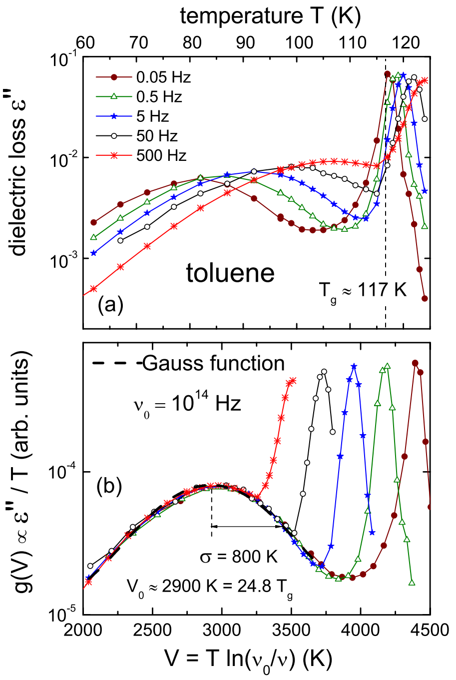

FIG. 4. (Color online) Dielectric loss of toluene as a function of temperature for the frequencies indicated in the figure. (b) The distribution $g(V)$ obtained by scaling the data presented in frame (a).

$$g_\beta(V) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(V - V_\beta)^2}{2\sigma^2}\right] \qquad (7)$$

in the entire temperature range covered by the present study. Here V_β and σ are the mean value and the variance, respectively, of the distribution. Let us reiterate that the scaling for the β process of toluene works with a temperature-independent relaxation strength. It is important to point out that toluene exhibits a secondary peak with a comparatively high intensity. In particular, no indications for an excess wing are obvious at temperatures above T_g, see also Fig. 1(b). A glance at Fig. 1 shows that this is different for the other glass formers, as we will discuss in the following.

m-FAN is a glass former exhibiting a secondary peak *and* an excess wing.[41,42] In Fig. 5(a), we present the results of the scaling procedure for this system. A parameter ν_0 with a physically reasonable value of 10^{13} Hz was used to collapse the spectra for more than 15 temperatures. The success of the scaling at the lowest temperatures is expected if the ADWP model is valid.[11] Starting from low barriers $g(V)$ strongly decreases with increasing V until, at energies of the order of 1000 K, the distribution reaches a broad minimum. This minimum, indicated by the arrow in Fig. 5(a), corresponds to ε'' data measured close to the temperature at which the spectrum is flat $(\gamma \approx 0)$.

Although not immediately anticipated by the ADWP model, the quality of the scaling remains excellent also for higher temperatures, which are up to about three times larger than those corresponding to the susceptibility minimum, see

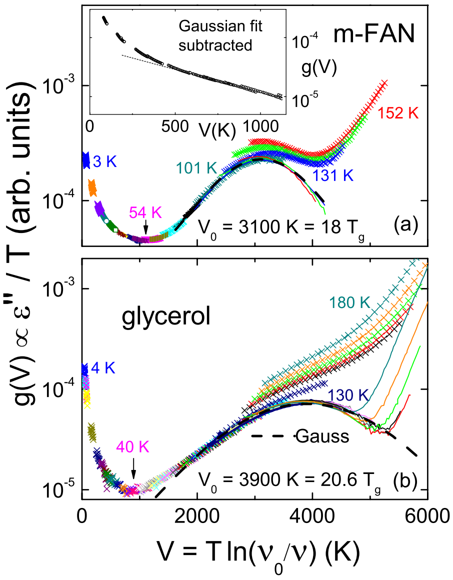

FIG. 5. (Color online) The distribution of barriers $g(V)$ extracted from the $\varepsilon''(\nu)$ spectra of (a) m-FAN and (b) glycerol below their respective T_g. Different colors represent different temperatures which are indicated for a few spectra. For temperatures above 101 K in frame (a) and above 130 K in frame (b) the symbols are obtained by scaling the raw data while the lines represent the scaling of the same data subsequent to the subtraction of a power-law contribution $A\nu^{-0.2}$. The thick dashed lines represent Gaussian functions. Inset (a): the barrier distribution of m-FAN obtained after subtracting a Gaussian contribution from the total $g(V)$. The dotted line represents an exponential barrier distribution with $V_0=570$ K. Significant deviations from an exponential $g(V)$ dependence show up for $V<350$ K, corresponding to measuring temperatures $T<18$ K.

Fig. 5(a). Here the β process should come into play and is expected to give the main contribution to the dielectric loss when further increasing the temperature. As revealed by Fig. 5(a) the scaled loss data yield a peaked distribution function: $g(V)$ reaches a maximum for $V\approx 3000$ K, which results from scaling the dielectric loss spectrum recorded at 101 K, i.e., deep in the glass. Comparison with Fig. 1(c) confirms that the β process is in fact probed at this temperature. Furthermore, the energy at which $g(V)$ is maximum agrees very well with the mean activation energy reported for the β process of m-FAN.[18]

Figure 5(a) demonstrates that for m-FAN the scaling works at least up to 101 K but at higher temperatures it fails and the spectra do no longer superimpose. As one may infer from Fig. 5(a) the resulting apparent increase in $g(V)$ cannot be rectified by allowing for a change in the free parameter ν_0 or for an increase in $\Delta\varepsilon$ with increasing temperature. In other words, a horizontal or a vertical rescaling of the data is not sufficient to recollapse them to a Gaussian profile. This suggests that additional dielectric loss contributions affect the spectra in this temperature range.

In view of the spectral analysis presented elsewhere,[20] it appears plausible to attribute these deviations to the loss contributions that originate from the excess wing. Its frequency dependence is typically described by a power law of the form $A_{EW}\nu^{\gamma}$ with $\gamma\approx -0.2$.[21,43,44] With the constraint to obtain a symmetric distribution $g_{\beta}(V)$ for the secondary relaxation of m-FAN also above 101 K, we subtracted such a power law from the original spectra [shown in Fig. 1(c)]. The implicit assumption that excess wing and β process are additive loss contributions returns a value for the γ exponent of -0.23 ± 0.01 for all temperatures up to T_g. As shown in Fig. 6, the prefactor A_{EW} resulting from the corresponding fits varies exponentially with temperature.

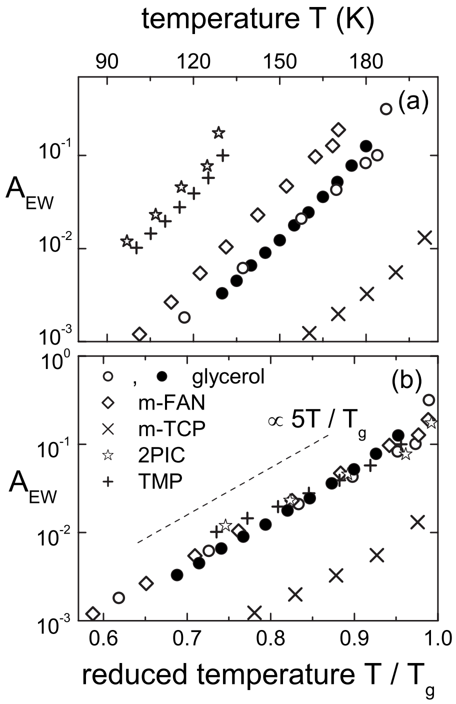

FIG. 6. (a) The prefactor A_{EW} characterizing the amplitude of the excess wing in m-FAN and glycerol glasses are shown as a function (a) of temperature and (b) of reduced temperature. The prefactors $A_{EW}=\varepsilon''(\nu=1\text{ Hz})$ for 2-picoline, m-TCP, and TMP are added for comparison. For glycerol the closed circles are from the present analysis while the open symbols are taken from Ref. 22.

C. Excess wing and nearly constant loss

Turning to glycerol, a system for which no secondary peak is obvious from the spectra shown in Fig. 1(a), the $g(V)$ scaling again works for low temperatures, see Fig. 5(b). The ADWP scaling fails, however, as temperatures close to $T_g/2$ are approached. Thus, from the scaling procedure a maximum in $g(V)$ cannot be identified. Nevertheless, when applying the excess wing subtraction, just demonstrated for m-FAN, a Gaussian shape emerges also for $g(V)$ of glycerol (the power-law exponent turned out to be $\gamma=-0.21\pm 0.01$). To arrive at this result, we again imposed the condition that $g(V)$ should be a symmetric function. This result agrees well with that previously obtained from aging experiments on glycerol from which not only an excess wing but also a weak β process was identified.[20,22]

The prefactor A_{EW} resulting from the present scaling analysis of glycerol exhibits an exponential temperature dependence up to T_g, see Fig. 6. This figure also contains the

A_{EW} parameters obtained from our previous line-shape analysis of glycerol.[22] The results from the various analyses show perfect agreement, indicating that the failure of the low-temperature ADWP scaling is to be attributed to the emergence of an excess wing at temperatures close to 100 K. In Fig. 6, we added the temperature dependence of $\varepsilon''(\nu=1\ \mathrm{Hz})$ for m-tricresylphosphate (m-TCP), trimethyl phosphate (TMP), and 2-picoline (2PIC).[16,27,45] For these three systems, a β process is not discernible and thus does not affect the dielectric loss in the temperature range just below T_g.[20] In the absence of a secondary relaxation peak, $\varepsilon''(\nu=1\ \mathrm{Hz})$ may be identified with the prefactor A_{EW}.[46] For all glass data included in Fig. 6(b), the parameter A_{EW} shows the same phenomenological variation,

$$A_{\mathrm{EW}} \propto \exp(5T/T_g). \tag{8}$$

Indications for a frequency-dependent relaxational feature characterized by a power law with a small, negative, temperature-independent exponent close to 0.2, and an amplitude with an exponential temperature dependence were also reported on the basis of light scattering studies: for numerous glasses the ADWP model describes the fast dynamics for temperatures considerably below T_g quite well,[47] however, this model fails to account for the data at higher temperatures close to T_g. This failure was connected with the appearance of a "nearly constant loss" in the spectra. According to Ref. 47, this feature "has a rather strong temperature dependence proportional to $\exp(T/T_1)$" with T_1 denoting a material-dependent temperature. A similar temperature dependence was also reported by some dielectric studies of molecular glasses.[48,49] Since we observe the same frequency and temperature dependence [cf. Eq. (8)] for the excess wing in the glass, we interpret the nearly constant loss as being the same phenomenon.

D. Bimodal distribution of activation energies $g(V)$

Figure 7 summarizes $g(V)$ versus V/T_g for all presently investigated molecular systems additionally including data for 2PIC, salol, and propylene carbonate (PC).[16] For the lowest energies, $g(V)$ decreases strongly with increasing V. Then, as a consequence of the appearance of frequency-independent spectra at $T \approx 0.35T_g$, for $g(V)$ of all samples a broad minimum is reached at $V/T_g \approx 5\ldots8$. At higher barriers, $g(V)$ increases and for some glasses a maximum is observed for $V \approx (20\ldots25)T_g$. These values correspond to the typical mean activation energies of the β process in molecular glasses.[18,20]

To put the dielectric results into a broader perspective, Fig. 7 also includes light scattering data for the inorganic glass $\mathrm{Ca_{0.4}K_{0.6}(NO_3)_{1.4}}$ (CKN, $T_g=333$ K) and for amorphous polystyrene (PS, $T_g=370$ K).[32,34] For these two, as well as for many inorganic systems[11,30,31,33–35] not included in Fig. 7, at relatively small energies $g(V)$ exhibits an exponential V dependence as predicted by the initial Gilroy-Phillips model.[11]

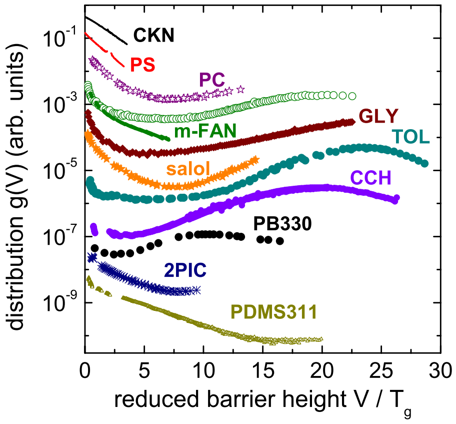

FIG. 7. (Color online) The distributions $g(V)$ for the molecular glasses investigated in this work are represented by symbols. The previously measured dielectric data for 2PIC, PC, and salol (Ref. 16) are also included. For comparison we added $g(V)$ as extracted using the ADWP model from the light scattering data (represented as lines) of an inorganic glass (CKN) (Ref. 32) and a polymer (PS) (Ref. 34) recorded from 70 to 300 K and from 100 to 300 K, respectively. For each system $g(V \rightarrow 0)$ was chosen arbitrarily, i.e., the data sets were shifted vertically for clarity.

As compared with CKN and PS, the V dependence in the low-energy limit of $g(V)$ for the small-molecule systems is much stronger, see also Fig. 3 and the inset of Fig. 5(a). This seeming discrepancy between the dielectric vs the light scattering results is simple to rationalize: On the one hand, the light scattering data (shown in Fig. 7) refer to temperatures ($T > 70$ K) much above those at which tunneling excitations should be relevant. On the other hand, the dielectric measurements, which indicate a stronger decrease in $g(V)$, were performed at temperatures (e.g., $T < 18$ K for m-FAN and $T < 7$ K for PDMS311) for which tunneling contributions might play an important role,[40] then distorting the effective shape of $g(V)$.

To obtain a more complete picture for the frequency-dependent susceptibility, in addition to the ADWP dynamics [see, e.g., Eq. (3)] one needs to include the plethora of the typically observed primary response, other secondary processes, as well as those arising from the tunneling excitations within two-level systems.[4–8] In fact, from our scaling analysis as summarized in Fig. 7 one may conclude that for molecular glasses the ADWP dynamics and the β process have the same physical origin, both arising from thermally activated jumps in an energy landscape characterized by a *bimodal* distribution of activation barriers. Along this line of thought, the two processes are not to be distinguished, but merely arise from an "overall" distribution,

$$g_N(V) = \frac{1}{V_0 + B\sigma\sqrt{2\pi}} \left\{ \exp\left(-\frac{V}{V_0}\right) + B \exp\left[-\frac{(V-V_\beta)^2}{2\sigma^2}\right] \right\}. \tag{9}$$

Here the index N indicates that $g_N(V)$ is normalized and B designates the relative area of the Gaussian with respect to the exponential contribution.

In general, the overlap of this process with other relaxational features and the limited experimentally accessible dynamic range can make it difficult to extract the relaxation strength of the thermally activated dynamics unambiguously.

To circumvent this difficulty one can employ Eq. (5) in the limit $V \to 0$. Under this condition Eq. (9) reduces to $g_N(V\to 0) = \{1+B\exp[-V_\beta^2/(2\sigma^2)]\}/(V_0+B\sigma\sqrt{2\pi}) \cong 1/(V_0+B\sigma\sqrt{2\pi})$ since V_β/σ is typically much larger than unity.[41,50] Inserting $g_N(V\to 0)$ into Eq. (5), one obtains

$$\Delta\varepsilon \approx (2/\pi)(V_0+B\sigma\sqrt{2\pi})(\varepsilon''/T)_{V\to 0}. \tag{10}$$

All parameters appearing in this expression can be obtained by fitting the scaled ε''/T curve.

In the absence of a significant Gaussian contribution ($B \approx 0$), as is the case for PDMS311, Eq. (9) reduces to Eq. (2) and Eq. (10) becomes $\Delta\varepsilon \approx (2/\pi)V_0\varepsilon''/T$. Using $V_0 = 450$ K and $(\varepsilon''/T)_{V\to 0} = 1.16\times 10^{-4}$ K^{-1} as obtained from Fig. 3 one can estimate that $\Delta\varepsilon \approx 0.033$ for PDMS311. This value is very close to A_0(=0.036) obtained by fitting Eq. (3) the spectra plotted in Fig. 2(b). Also, for $B \approx 0$ the frequency exponent γ for PDMS311 can be identified with the parameter $\alpha = T/V_0$ appearing in Eq. (3) and the expected linear temperature dependence of the exponent γ is nicely borne out in this case, see the inset of Fig. 2. For all the other systems the contribution of the Gaussian term is not negligible (see Fig. 7) and the relaxation strength for the overall thermally activated process becomes more difficult to estimate.

The complex interplay of the mean barrier heights V_0 and V_β with the B parameter can also impede the observation of temperature-dependent loss peak maxima originating from thermally activated jumps over the small barriers. As pointed out by Gilroy and Phillips[11] for a given frequency such maxima should appear at temperatures $T_m = V_0/\ln(2\pi\nu\tau_0)$. Calculations of the overall dielectric loss $\varepsilon''(T)$ taking into account ADWP and β dynamics for various V_β/V_0 ratios and B factors reveal that a relatively low V_β combined with a relatively large amplitude B can easily hamper the observation of these peaks (not shown). Conversely, for systems with negligible β contributions (small B) such as, e.g., 2PIC, salol, PC, or PDMS311 the "ADWP characteristics" are revealed most clear-cut: the shapes of their barrier distributions $g(V)$ are close to exponential for low V (see Fig. 7) and the corresponding temperature dependent dielectric losses $\varepsilon''(T)$, as measured in the kilohertz range, reveal pronounced maxima at temperatures below about 50 K.[16]

Most researchers in the field conceive the β relaxation of glass formers as a feature leading to a *symmetrically* broadened loss spectrum. However, a different appearance can result if this relaxation shows up in a range in which the contributions of the ADWP dynamics are significant and thus provide an asymmetric "background" for the β relaxation. For example, DGEBA and PMMA show such asymmetric "β peaks."[42,51] In the framework of the present discussion, their experimental observation requires that coefficient B is not too large.

V. CONCLUSIONS

The Gilroy-Phillips model was used to describe low-temperature dielectric data of a large number of molecular glasses including systems that reveal secondary relaxation peaks in their spectra close to T_g. A simple scaling based on a single free parameter allowed us to extract the system-dependent distribution of energy barriers $g(V)$ in a broad V range.

For the presently investigated molecular glasses, the applicability of the Gilroy-Phillips model was thus extended up to the glass transition temperature and used to fully describe the thermally activated glassy dynamics. It appears that the overall $g(V)$ distribution for the molecular glasses generally includes two contributions: On the one hand (disregarding the tunneling regime), there exists a more or less exponential component at lowest energies with a mean barrier of a few hundred kelvin, as was analogously reported previously for inorganic glasses. On the other hand, at higher energy $g(V)$ exhibits a Gaussian shape and is typically centered around $20\ldots 25T_g$. In the framework of our scaling analyses, PDMS311 could be discussed to exhibit the typical ADWP characteristics in a particularly clear fashion likewise toluene was presented as a system for which the β relaxation is dominant. However, such a separation of phenomena, albeit convenient and historically justified, is artificial in the sense that the two relaxational aspects refer to thermal excitation of the *same* degrees of freedom in the *same* energy landscape: β relaxation and ADWP dynamics refer to probing their common (usually bimodal) distribution at different energy or temperature scales. The two ingredients of $g(V)$ will appear with different relative weight as parameterized here via the coefficient B in Eq. (9).

The initial Gilroy-Phillips model predicts the static susceptibility of the ADWP excitations to be temperature independent. Treating β process and ADWP dynamics on the same footing, a temperature-independent static susceptibility is thus also expected for the former and is indeed found, e.g., for toluene. In terms of the present framework, deviations from the expected constancy of $\Delta\varepsilon$ should, however, show up if additional relaxational features emerge such as, e.g., the so-called excess wing. Thus, for glasses like m-FAN for which significant excess wing contributions exist, the static susceptibility becomes temperature dependent at temperatures as low as $T_g/2$. For larger temperatures the Gaussian contribution to $g(V)$ is consequently revealed only after subtraction of the excess wing. In the glassy state this phenomenon is also referred to as nearly constant loss.

*catalin.gainaru@uni-dortmund.de

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