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## Dipolar dynamics of low-molecular-weight organic materials in the glassy state

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**Abstract.** We have measured the dielectric relaxation of several low-molecular-weight glass-forming materials for temperatures ranging from 25 K to  $T \approx T_g$  and for values of the loss tangent down to  $\tan \delta \approx 10^{-7}$ . For the materials under study (salol, glycerol, N-methyl- $\epsilon$ -caprolactam, 2-methyltetrahydrofuran, 3-methylpentane, and *o*-terphenyl) a  $\beta$ -relaxation appearing in quenched samples can be suppressed effectively by annealing at  $T < T_g$ , thereby facilitating the study of the dipole dynamics in the absence of the secondary process. As a general behaviour of the remaining dielectric losses at  $f = 1$  kHz we find a variation of  $\log_{10}(\epsilon'') = a + bT$  ( $b \approx 0.015 \text{ K}^{-1}$ ) signalling the increasing constraint in the angular degree of freedom as the temperature is lowered and a further increase or peak of  $\epsilon''$  in the range  $25 \text{ K} < T < 50 \text{ K}$ . According to a comparison with the crystalline counterparts, the latter effects are characteristic features of the disordered solid state.

### 1. Introduction

Relative to liquids or supercooled liquids, the central feature of the glassy state of matter is the absence of larger-scale molecular motion in this non-ergodic solid state, while the positional and orientational disorder of the constituting molecules has been preserved [1–3]. The threshold for solidifying a supercooled liquid is expressed by the glass-transition temperature  $T_g$  which quantifies the temperature at which the structural relaxation time exceeds the time scale of observation, preset by the experimental conditions. Therefore, the material is no longer capable of restoring thermodynamic equilibrium within experimental times for  $T < T_g$ . On the other hand, the absence of structural relaxation on macroscopic length scales leaves sufficient room for local dynamic processes in disordered structures [4], which are commonly observed as secondary relaxations [5, 6], as excess heat capacity at cryogenic temperatures [7, 8], or as spectral diffusion of dye molecules in the sub-K regime [3, 9].

At temperatures moderately below the glass transition, many materials are notorious for exhibiting a so-called  $\beta$ -relaxation, which often obeys an Arrhenius type temperature dependence,

$$\log(\tau) = A + B/T \quad (1)$$

regarding a characteristic relaxation time  $\tau$  [5, 6]. In some cases the  $\beta$ -process can be unambiguously assigned to the motions of side groups of the molecule, while the segmental orientation of the molecular backbone contributes to the  $\alpha$ -process. Acrylic and methacrylic polymers are prominent examples for this situation [5, 10], where different and only partially coupled subunits of the molecule participate in the distinct relaxation processes. Although

phenomenologically similar, the Johari–Goldstein [6] types of  $\beta$ -processes are those where the molecule possesses no intramolecular degree of freedom which allows for side-group motion. Therefore, in a dielectric relaxation experiment on a material composed of rigid molecules, the  $\alpha$ - and  $\beta$ -relaxations are due to the same dipole and the  $\beta$ -process is often regarded as the precursor of the  $\alpha$ -process. Their relaxation times are well separated below the glass transition,  $T < T_g$ , but with the tendency to coincide at the so-called merging temperature  $T_\beta > T_g$  [11], above which only a single process is observed.

In the present work we investigate by dielectric relaxation techniques the dynamic behaviour of organic low-molecular-weight glasses with predominantly van der Waals interaction, which in part have been excessively studied above  $T_g$ : salol, glycerol, N-methyl- $\epsilon$ -caprolactam, 2-methyltetrahydrofuran, 3-methylpentane, and *o*-terphenyl. Although the systems are quite different as regards their chemical constitution and dipole moments, the dipolar dynamics appear to follow a common trend. Below  $T_g$ , the samples display a more or less pronounced  $\beta$ -relaxation after quenching the material, while annealing at  $T < T_g$  can lead to an effective suppression of the  $\beta$ -process. In the absence of this  $\beta$ -process the sub- $T_g$  dielectric behaviour is well approximated by the relation  $\log_{10}(\epsilon'') = a + bT$ , with the slope  $b$  varying only between  $1 \times 10^{-2} \text{ K}^{-1}$  and  $2 \times 10^{-2} \text{ K}^{-1}$ . Far below  $T_g$ , for  $T < 50 \text{ K}$ , many of the systems under study deviate from the  $\log_{10}(\epsilon'') \propto T$  trend by indicating an increase of  $\epsilon''$  and  $\tan \delta$  with decreasing temperature.

**Table 1.** Compilation of the series of low-molecular-weight organic glasses under study, together with their glass transition temperatures  $T_g$ , and the evaluated slopes of  $\log_{10}(\tan \delta)$  versus  $T$  and of  $\log_{10}(\epsilon'')$  versus  $\log_{10}(\omega \text{ (Hz)})$ . The values in the last column are for the temperatures given in parentheses, being representative for the temperature range  $T < T_g$ .

Material		$T_g$ (K)	$\frac{d \log_{10}(\tan \delta)}{dT}$ ( $\text{K}^{-1}$ )	$\frac{d \log_{10}(\epsilon'')}{d \log_{10}(\omega \text{ (Hz)})}$
Salol	SAL	220	0.0193	−0.24 (150 K)
Glycerol	GLY	190	0.0127	−0.065 (128 K)
N-methyl- $\epsilon$ -caprolactam	NMEC	172	0.0190	−0.069 (125 K)
2-methyltetrahydrofuran	MTHF	91	0.0150	$\approx 0$ (64 K)
3-methylpentane	3MP	77	—	—
<i>o</i> -terphenyl	OTP	246	0.0114	—

## 2. Experiments

The chemicals (Aldrich) that have been measured in this study are compiled in table 1 together with the abbreviations used in the following. SAL and GLY have been used as purchased, MTHF, NMEC and 3MP have been freshly distilled and passed through  $\text{Al}_2\text{O}_3$  filters prior to the measurement, OTP has been recrystallized.

The dielectric data at a fixed frequency of  $f = 1 \text{ kHz}$  have been acquired employing an ultraprecision bridge (AH-2500, Andeen–Hagerling) with a nominal resolution for  $\tan \delta$  of  $\approx 2 \times 10^{-8}$ . The sample cell consists of two brass electrodes of 12 mm diameter mounted on sapphire plates which are embedded in a massive brass block so that the electrode separation is  $\approx 200 \mu\text{m}$ . The data are measured relative to the geometric capacity  $C_{geo} \sim 5 \text{ pF}$  of the evacuated capacitor so that the precise value of  $C_{geo}$  is irrelevant for obtaining absolute  $\epsilon^*(\omega)$  values. The variation of  $C_{geo}$  with temperature has been experimentally confirmed not to exceed  $dC/dT \approx 180 \text{ aF K}^{-1}$  in the range 20 K to 300 K. The residual dielectric

loss of the evacuated sample capacitor has been checked to yield  $\tan \delta < 2 \times 10^{-6}$ . Due to this construction, no spacer material is necessary for defining the electrode separation. The vacuum tight sample cell is mounted on the final stage of a closed cycle helium refrigerator (Leybold RDK 10-320) equipped with silicon-diode sensors and temperature controlled to within  $\pm 30$  mK (Lake Shore model 330). This setup was used to acquire  $\varepsilon'(T)$  and  $\varepsilon''(T)$  at  $f = 1$  kHz and for temperatures ranging from 25 K to 300 K. Frequency dependent dielectric relaxation experiments were performed with the same cell and cryostat in the range  $1 \times 10^{-1}$  Hz to  $1 \times 10^6$  Hz. This system consists of a frequency response analyser (Solartron, SI-1260) equipped with a dielectric interface (Mestec, DM-1360) acting as transimpedance amplifier [12].

The cooling and heating rates,  $dT/dt$ , during the course of a measurement took values of  $|dT/dt| \approx 0.1$  K  $\text{min}^{-1}$  for the single-frequency scan at 1 kHz and  $|dT/dt| \approx 0.03$  K  $\text{min}^{-1}$  for the frequency dependent measurement of the entire loss spectra. Quenching was achieved by thermally isolating the cell from the cold stage by a 1 mm thick Teflon spacer and cooling the cell with a large amount of liquid  $\text{N}_2$ , leading to  $dT/dt \approx -10$  K  $\text{min}^{-1}$ .

### 3. Results

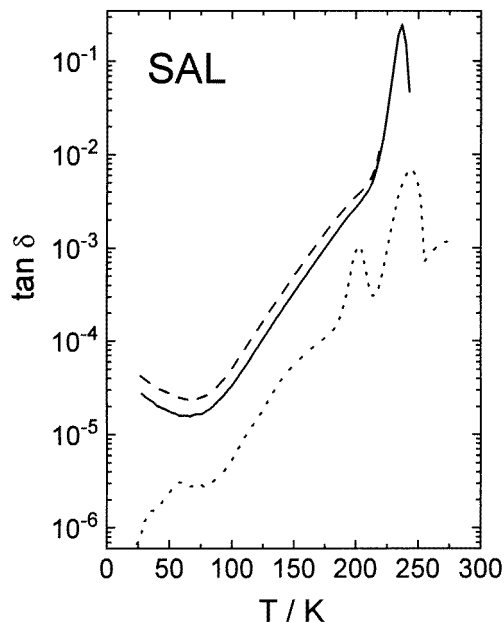
Some general remarks on measuring dielectric properties at low temperatures appear in order. Glass-forming materials with values of  $T_g$  well above room temperature, like many inorganic network glasses and polymers, can themselves define the electrode distance at the preparation temperature near 300 K. The present series of organic liquids are associated with  $T_g$  values near or below 300 K, so that we are confronted with low-viscosity liquids in course of the sample preparation. For this reason, a capacitor is necessary whose electrode separation is defined already in the absence of the sample material and preferably without the use of spacer materials between the electrodes. The sample cell described above meets these requirements and is subject to only minor changes in its geometry over a large temperature range. Measuring an equilibrium liquid or supercooled liquid in such a manner results in a situation under constant-pressure conditions. This condition is no longer warranted after cooling in order to enter the glassy state, where macroscopic flow of the material is arrested. Therefore, the situation for glasses is likely to also have aspects of a constant-volume measurement.

Large temperature alterations for a solid state material between rigidly supported electrodes usually results in the formation of cracks inside the material or in the separation from one of the electrode surfaces [6]. The signature of this release of mechanical stresses in a dielectric measurement is sudden jumps in  $\varepsilon'$  and  $\varepsilon''$ . To a first approximation, however, the value of

$$\tan \delta = \varepsilon''/\varepsilon' \quad (2)$$

is insensitive to cracks or air-gaps. We note here that such effects have been observed in the course of the present series of measurements, where the concomitant jumps  $\Delta\varepsilon'$  can amount to a change in  $\varepsilon'$  of several per cent. Note that tremendous alterations in the pressure would be required to invoke equivalent changes in the density.

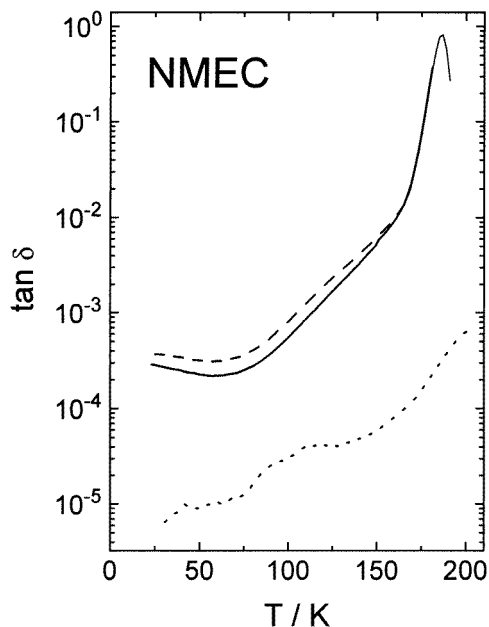
Figures 1–4 show the dielectric results in terms of  $\tan \delta$  versus  $T$  measured at  $f = 1$  kHz for some of the organic low-molecular-weight glasses listed in table 1, in some cases including the results obtained for the corresponding polycrystalline sample. The peak at the highest temperatures reflects the main structural or  $\alpha$ -process in all cases. The change in slope,  $d \log_{10}(\tan \delta)/dT$ , just below this peak marks the glass transition for the present experimental time window set by the 1 kHz test frequency. Below the glass transition



**Figure 1.** Experimental dielectric data for salol (SAL) plotted as  $\tan \delta$  measured at  $f = 1$  kHz as a function of temperature  $T$ . The solid curve is obtained by measuring slowly from high to low temperatures, the dashed curve is for the quenched sample. The dotted line refers to the same material but after crystallization.

we observe either a more or less pronounced curvature with  $d^2 \log_{10}(\tan \delta)/dT^2 < 0$  or a linear relation of  $\log(\tan \delta)$  versus  $T$ , depending on the thermal history. The rule for the dependence on thermal history is that quenched samples display non-linear curves, while annealed samples are associated with a practically linear increase of  $\log(\tan \delta)$  with temperature. The resulting slope values for  $d \log_{10}(\tan \delta)/dT$  ( $50 \text{ K} < T < T_g$ ) for the annealed cases, i.e. when the slope is constant over a significantly large range of temperatures, are compiled in table 1.

For the more polar materials, SAL, GLY, NMEC, and MTHF, we have also measured the frequency dependence of  $\varepsilon^*(\omega)$  in the range  $0.1 \text{ Hz} \leq f \leq 1 \text{ MHz}$ . For 3MP and OTP the signals below  $T_g$  are no longer resolved with the frequency domain setup. The observation is again systematic in the sense that the annealed samples displaying a constant slope  $d \log_{10}(\tan \delta)/dT$  in the range  $50 \text{ K} \lesssim T < T_g$  can be characterized by a frequency invariant slope of  $d \log_{10}(\varepsilon'')/d \log_{10}(\omega \text{ (Hz)})$  in the entire experimental frequency range, as long as the high-frequency components of the  $\alpha$ -process have shifted to below 0.1 Hz. The results obtained for these slopes are included in table 1, indicating that  $\varepsilon''$  decreases by a factor of  $2 \times 10^{-2}$  or less upon increasing  $\omega$  by one decade. In figure 5 we show for glycerol the temperature dependence of  $\tan \delta$  for three different frequencies, 1 Hz, 100 Hz, and 10 kHz, which are equally spaced on the  $\log(f)$  scale. This plot demonstrates that the observed value of  $d \log_{10}(\tan \delta)/dT$  is insensitive to the selected frequency and that the frequency dependence of the dielectric loss,  $\varepsilon''(\omega)$ , is practically identical over a wide range of temperatures. Note that  $\varepsilon''$  and  $\tan \delta = \varepsilon''/\varepsilon'$  differ practically only by a constant factor, since the value of  $\varepsilon'$  (around 2–3) is only slightly temperature dependent.

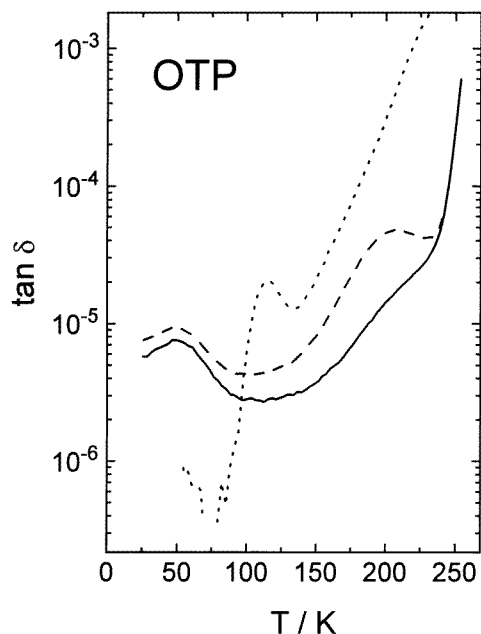


**Figure 2.** Experimental dielectric data for N-methyl- $\epsilon$ -caprolactam (NMEC) plotted as  $\tan \delta$  measured at  $f = 1$  kHz as a function of temperature  $T$ . The solid curve is obtained by measuring slowly from high to low temperatures, the dashed curve is for the quenched sample. The dotted line refers to the same material but after crystallization.

#### 4. Discussion

The molecular dynamics of disordered solids have been frequently addressed, including temperatures well below 1 K [13], where transitions within double-well potentials are assumed to dominate the behaviour [3, 9, 13]. Such low-temperature studies have also been conducted using high-resolution dielectric techniques, but applied mainly to inorganic network type glasses, e.g.  $\text{SiO}_2$  [14] or  $\text{B}_2\text{O}_3$  [15], and to various polymers [16]. A very different type of glass-forming material is the so-called van der Waals systems, where the short-ranged and relatively weak dipole-induced dipole forces dominate in the intermolecular interactions, i.e. covalent, ionic and hydrogen bonds are absent. Although such low-molecular-weight organic compounds have been subjected to intensive dielectric studies in the supercooled liquid and liquid state, i.e. above  $T_g$ , little is known about their dielectric behaviour in the glassy state, i.e. for  $T \ll T_g$ .

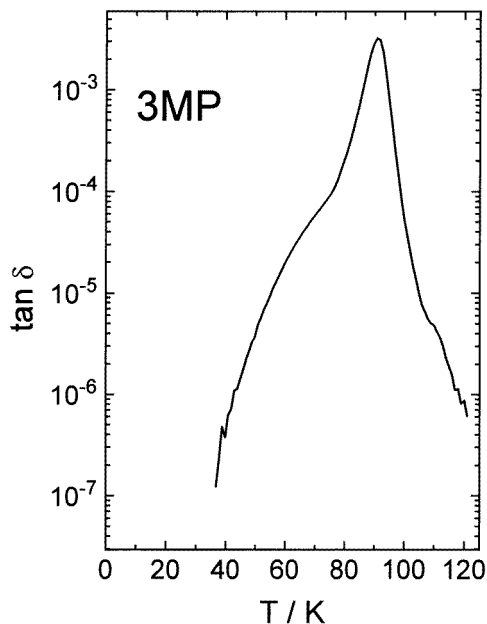
For the sake of having comparable materials, the present study has been confined to only those molecules which have no significant intramolecular degree of freedom. That also these rigid molecules display secondary relaxation was initially observed in detail by Johari and Goldstein (JG) [6], e.g. for OTP, noting also that the intensity of this JG type  $\beta$ -relaxation shows some sensitivity to the thermal history involved in the cooling process. The picture developed later [17] suggests that glass formation leads to a dynamically heterogeneous material where the  $\beta$ -relaxation is located within certain 'islands of mobility'. The particular questions addressed in the following are which dielectrically active dynamics can be found apart from the  $\beta$ -process in disordered solids and how are they related to the structural relaxation in the melt. For an unambiguous discrimination between JG type and other



**Figure 3.** Experimental dielectric data for *o*-terphenyl (OTP) plotted as  $\tan \delta$  measured at  $f = 1$  kHz as a function of temperature  $T$ . The solid curve below  $T_g$  is obtained after annealing the sample for 24 h at  $T \approx T_g - 10$  K, the portion above  $T_g$  is recorded afterwards. The dashed curve is for the quenched sample, the dotted line refers to the same material but after crystallization.

dynamical features we exploit the observed dependence of the JG process intensity on the thermal history.

In our study, the materials SAL, GLY, NMEC, 3MP, and OTP indicate a JG type  $\beta$ -relaxation for the rapidly cooled samples in terms of the dashed lines in figures 1–4, with only MTHF being the exception to this rule. That the signature of the  $\beta$ -relaxation in  $\tan \delta$  ( $f = 1$  kHz) data is paralleled by a peak in  $\varepsilon''(\omega)$  has been shown for OTP [6, 18]. For the more polar systems, SAL, GLY, and NMEC, the curvature (dashed lines) in the  $\tan \delta$  versus  $T$  plots below  $T_g$  is associated with a slight shoulder in the frequency dependent dielectric loss,  $\varepsilon''(\omega)$ , at the corresponding temperatures. As indicated by a comparison between SAL and OTP, the relative intensity of the  $\beta$ -relaxation can vary strongly. In the cases of only a subtle indication of such a secondary process (SAL, GLY, NMEC), successively measuring from higher ( $T \geq T_g$ ) towards lower temperatures implies a sufficiently slow cooling rate ( $dT/dt \approx -0.1$  K  $\text{min}^{-1}$ ) which already suppresses the  $\beta$ -relaxation to below the resolution limit. We suspect that for this reason the JG type secondary process has remained unresolved for some materials, where rapid quenching is required to invoke even small  $\beta$ -features. Whether the  $\beta$ -relaxation is universally observable in the case of extremely fast cooling rates could be judged by investigating the counterpart structures prepared by vapour deposition. For the more pronounced effect in OTP a much longer annealing process, 24 h at  $T = T_g - 10$  K, is necessary in order to suppress the  $\beta$ -relaxation significantly. Therefore, it appears that there exists a correlation between the intensity of the  $\beta$ -relaxation and the extent of sample annealing required to eliminate this process almost entirely. With this annealing effect we can now selectively look at the dynamics of the glassy state in the



**Figure 4.** Experimental dielectric data for 3-methylpentane (3MP) plotted as  $\tan \delta$  measured at  $f = 1$  kHz as a function of temperature  $T$ .

absence of this secondary relaxation.

For the systems where the thermal history has been observed to influence the dynamics in the glassy state (SAL, GLY, NMEC, OTP), we observe as a general rule that the annealed samples always display a  $\log_{10}(\tan \delta)$  behaviour which is linear in  $T$  over a substantial range of temperatures below  $T_g$ , i.e.

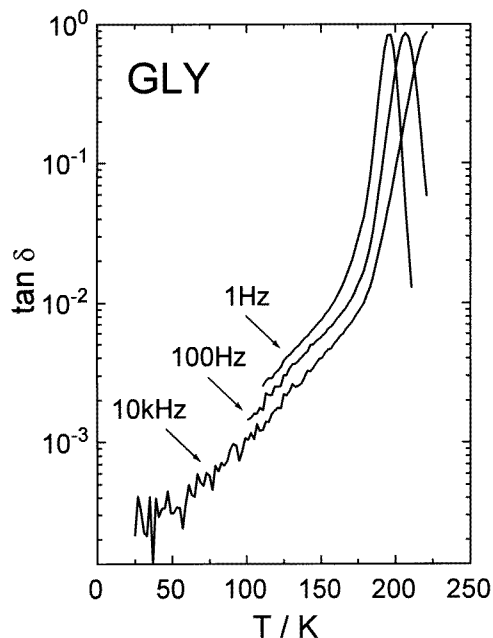
$$\log_{10}(\varepsilon'') = a + bT \quad \text{at } f = 1 \text{ kHz.} \quad (3)$$

The observed linearity of  $\log(\tan \delta)$  or  $\log(\varepsilon'')$  versus  $T$  is superior over that found on a  $\log(\varepsilon'')$  versus  $1/T$  scale for all materials studied here. In particular, the values of these slopes as compiled in table 1,  $d\log_{10}(\tan \delta)/dT$ , cover only the limited range of  $1\text{--}2 \times 10^{-2} \text{ K}^{-1}$ . For other than van der Waals type glasses, an equivalent ‘universality’ is not obvious [13–16]. To rationalize a constant slope, i.e. the dependence  $\log_{10}(\tan \delta) \propto T$ , two limiting possibilities can be proposed, one based on a temperature dependent shift of a characteristic frequency, the other one assuming that only the dielectric strength is lowered as the temperature is decreased. In the first case, one would view the slightly frequency dependent loss  $\varepsilon''(\omega)$  in the glassy state as the high-frequency component of the  $\alpha$ -relaxation, whose main contribution has shifted to well below 0.1 Hz for  $T < T_g$ . The problem here is that the temperature dependence of the  $\alpha$ -relaxation time scale is no longer experimentally accessible at these low temperatures and an extrapolation of equilibrium relaxation times to well below  $T_g$  is not appropriate, even if applied only to the high-frequency wing of the  $\alpha$ -relaxation. The quantity of interest for such an interpretation is the slope

$$\kappa = d\log_{10}(\varepsilon'')/d\log_{10}(\omega \text{ (Hz)}) \quad (4)$$

as compiled in table 1. Independent of how the characteristic time scale varies in the glassy state, it should be expected in this case that the very different values of  $\kappa$  lead to a





**Figure 5.** Experimental dielectric data for glycerol (GLY) plotted as  $\tan \delta$  as a function of temperature  $T$ . The curves are for different frequencies  $f = 1$  Hz,  $f = 100$  Hz, and  $f = 10$  kHz, from top to bottom near 150 K.

corresponding variation of  $d \log_{10}(\tan \delta)/dT$ , in contrast to the experimental findings seen in table 1.

For an alternative explanation regarding  $\tan \delta(T)$  one can assume that lowering the temperature within the glassy state reduces solely the dielectric strength  $\Delta \epsilon$  of the dipolar activity, independent of the loss spectrum  $\epsilon''(\omega)$ . Changes in  $\Delta \epsilon$  can either be attributed to changes in the number of dipoles still participating in the relaxation processes or to changes in their angular degree of freedom. The latter effect can be thought of as a restriction of the librational motion of molecules which becomes more severe as the material is further densified by cooling. Anticipating similar coefficients of thermal expansion for this type of glass, the picture of a temperature dependent restriction in the angular degree of freedom is likely to result in somewhat similar values for  $d \log_{10}(\tan \delta)/dT$ , as observed.

We now turn to the temperature regime below the linear trend of  $\log(\tan \delta)$  versus  $T$ , i.e. where  $T \approx 80$  K or below. In figures 1–3 it is seen for SAL, NMEC, and OTP that the dielectric loss increases again while the temperature is decreased further below  $\approx 80$  K. The resulting minima as regards  $\tan \delta$  are found to be  $\tan \delta = 1.6 \times 10^{-5}$  at 67 K for SAL,  $\tan \delta = 2.2 \times 10^{-4}$  at 61 K for NMEC, and  $\tan \delta = 7.7 \times 10^{-6}$  at 113 K for OTP, i.e. values clearly indicating dipolar motion in the entire experimental temperature range. Obviously, the extent of increase in  $\tan \delta$  at  $f = 1$  kHz by a factor of  $\approx 2$  at 25 K relative to the minimum value is not correlated with the polarity or dipole moment of the material ( $\mu \approx 0.1$  D for OTP and  $\mu \approx 2$  D for SAL). Secondly, quenching the sample leads to a more pronounced loss at the low temperatures by a constant factor of  $\approx 1.5$  if compared to the annealed cases. 3MP, having practically no dipole moment according to the peak amplitude of  $\epsilon''(f = 1$  kHz) [19], displays no such enhancement in the low-temperature

loss. For all materials for which we have compared the effects of quenched versus annealed cases, the thermal history near  $T_g$  in the course of sample preparation has an impact on the dynamics around  $T = 25$  K. The quenching of a liquid is known to form a glass with lower density compared to slowly cooling the material near  $T_g$ , which can be understood as having arrested the system in a state of higher free volume. This state again leaves more room for librational motions of the dipoles, irrespective of the absolute level of  $\tan \delta$ , as has been argued for the dynamics just below  $T_g$ .

As shown by figures 1–3, the low-temperature increase in  $\tan \delta$  for the glassy states (solid and dashed lines) is not paralleled by the polycrystalline counterparts (dotted lines). We conclude that the low-temperature dielectric loss in the glassy state is due to excess modes not present in the crystalline structures and thereby intimately linked to the disordered nature of the glassy state of matter. At all temperatures  $T < T_g$ , SAL and NMEC both display loss values for the disordered state which are throughout larger than those observed after crystallization. However, new peaks appear for crystalline SAL and for OTP the signals for the crystalline sample are larger than those of glassy OTP. It should be noted that crystallization in the capacitor leads to rather small crystallite structures with a large density of grain boundaries where the molecular packing is unknown. The large  $\tan \delta$  values for crystalline OTP (and possibly also the unexpected peaks for SAL) are most likely due to the effects of conductivity along the grain boundary instead of dipolar orientational polarizability, which cannot exceed the values observed for the equilibrium liquid. In these materials dc conductivity stems from ionic impurities [20, 21] which upon crystallization may tend to concentrate at the crystallite boundaries, thus giving rise to high apparent values for  $\tan \delta$  unless frozen in at sufficiently low temperatures. This structure dependent effect appears to be pronounced only for OTP, but may also be contributing to a lower extent to the crystalline data for SAL and NMEC. Furthermore, some residual amount of amorphous material might still be present after crystallization, but according to the data near 25 K the fraction of glassy structures is well below the 10% level for all three materials. Therefore, the dotted lines in figures 1–3 should be regarded as the upper bounds for dipolar contributions to  $\tan \delta$  in the polycrystalline samples.

For many disordered materials at temperatures between  $\approx 0.1$  K and  $\approx 10$  K it has been shown by various techniques that a wealth of dynamical features can be observed. Among the classical low-temperature techniques are heat-capacity measurements which result in values in excess of the Debye type  $c_p(T)$  expected for crystals [22], dielectric absorption and ultrasonic attenuation applied to inorganic network type glasses [14] and polymers [16], and the time resolved effects of spectral diffusion observed by hole-burning [23, 24] or photon-echo techniques [25, 26]. In the temperature range below  $\approx 10$  K, mainly the transitions within two-level systems (TLS) are made responsible for the dynamics, noting that thermal activation is insufficient for a state to explore a larger portion of the entire potential hypersurface. Especially from heat capacity and spectral diffusion data it has been inferred that the distribution of tunnelling parameters which outline the TLS transition probabilities must be practically flat and spanning a very large range of relaxation times [7, 9]. With the present experimental limitation of  $T \geq 25$  K we can only speculate that the low-temperature losses observed here are the dielectric signatures of the highly local sub-10 K molecular mobility which seem to be a universal feature of the otherwise rigid disordered state of matter.

In summarizing the experimental evidence, low-molecular-weight organic glasses display dielectrically active molecular dynamics at temperatures between 25 K and  $T_g$ , which gives rise to dielectric losses over a broad range of frequencies. As a consequence, the dielectric constant of glassy materials is not only a matter of the electronic polarizability, but

also reflects subtle orientational effects of permanent dipoles even in the absence of distinct secondary relaxations. The depression of these remaining molecular motions towards lower temperatures is consistent with further confining the angular degrees of freedom of the dipoles while the density is increased. The observed slopes of  $\tan \delta(T)$  just below  $T_g$  are not simply rationalized by assuming that the high-frequency portion of the  $\alpha$ -relaxation shifts further towards lower frequencies as in the equilibrium melt. Contrasting the comparatively small effects in polymers [27, 28], the intensity of the  $\beta$ -relaxation in the present materials is strongly dependent on the thermal history of glass formation, suggesting that the absence of directional interactions in van der Waals liquids facilitates a dense and homogeneous molecular packing even at moderate cooling rates, such that ‘islands of mobility’ are no longer observable.

## 5. Conclusions

By measuring the dielectric properties of low-molecular-weight van der Waals type glass-formers in the glassy state for temperatures  $25 \text{ K} \leq T \leq T_g$ , we generally observe a regime just below  $T_g$  where  $\log_{10}(\tan \delta)$  varies linearly with  $T$  at rates around  $0.015 \text{ K}^{-1}$  over a substantial range of temperatures and where  $d \log(\epsilon'')/d \log(\omega \text{ (Hz)})$  attains small and frequency invariant values. Therefore, even without the appearance of a distinct secondary process, subtle reorientations of dipoles occur over a broad spectrum of frequencies in the otherwise frozen material. Towards lower temperatures this behaviour is followed by an increase of the dielectric loss, or by a pronounced peak at  $T = 48 \text{ K}$  in the case of OTP. A comparison with the crystalline counterparts renders the above effects as characteristic features of the disordered structure. The quenched materials display more or less pronounced JG type  $\beta$ -processes while annealing the sample suppresses this secondary relaxation, yet without strongly acting on the remaining dielectric losses. We conclude that the dielectric contribution leading to the linear variation of  $\log_{10}(\tan \delta)$  with  $T$  and to the low-temperature peak is not associated with ‘islands of mobility’ believed to be responsible for the  $\beta$ -process but rather reflects a bulk property of the glassy state of matter.

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## References

- [1] Jäckle J 1986 *Rep. Prog. Phys.* **49** 171
- [2] Brawer S 1985 *Relaxation in Viscous Liquids and Glasses* (Columbus, OH: American Ceramic Society)
- [3] Richert R and Blumen A (eds) 1994 *Disorder Effects on Relaxational Processes* (Berlin: Springer)
- [4] Dissado L A 1984 *Chem. Phys.* **91** 183
- [5] Donth E 1992 *Relaxation and Thermodynamics in Polymers* (Berlin: Akademie)
- [6] Johari G P and Goldstein M 1970 *J. Chem. Phys.* **53** 2372
- [7] Pohl R O 1981 *Amorphous Solids—Low Temperature Properties (Topics in Current Physics 24)* ed W A Phillips (Berlin: Springer) p 27
- [8] Sokolov A P, Rössler E, Kisluk A and Quitmann D 1993 *Phys. Rev. Lett.* **71** 2062
- [9] Friedrich J and Haarer D 1986 *Optical Spectroscopy of Glasses* ed I Zschokke (Dordrecht: Reidel) p 149
- [10] Ishida Y and Yamafuji K 1961 *Kolloid-Z.* **177** 97
- [11] Hansen C, Stickel F, Berger T, Richert R and Fischer E W 1997 *J. Chem. Phys.* **107** 1086
- [12] Richert R 1996 *Rev. Sci. Instrum.* **67** 3217

- [13] Phillips W A (ed) 1981 *Amorphous Solids—Low Temperature Properties (Topics in Current Physics 24)* (Berlin: Springer)
- [14] Hunklinger S and von Schickfus M 1981 *Amorphous Solids—Low Temperature Properties (Topics in Current Physics 24)* ed W A Phillips (Berlin: Springer)
- [15] Höhler R, Münzel J, Kasper G and Hunklinger S 1991 *Phys. Rev. B* **43** 9220
- [16] Jonscher A K 1996 *Universal Relaxation Law* (London: Chelsea Dielectric)
- [17] Cavaille J Y, Perez J and Johari G P 1989 *Phys. Rev. B* **39** 2411
- [18] Wu L and Nagel S R 1992 *Phys. Rev. B* **46** 11 198
- [19] Johari G P and Goldstein M 1971 *J. Chem. Phys.* **55** 4245
- [20] Stickel F, Fischer E W and Richert R 1995 *J. Chem. Phys.* **102** 6251
- [21] Stickel F, Fischer E W and Richert R 1996 *J. Chem. Phys.* **104** 2043
- [22] Debye P 1912 *Ann. Phys. Lpz.* **39** 788
- [23] Wannemacher R, Koedijk J M A and Völker S 1993 *Chem. Phys. Lett.* **206** 1
- [24] Schmidt Th, Baak J, van de Straat D A, Brom H B and Völker S 1993 *Phys. Rev. Lett.* **71** 3031
- [25] Huber D L, Broer M M and Golding B 1984 *Phys. Rev. Lett.* **52** 2281
- [26] Pack D W, Narasimhan L R and Fayer M D 1990 *J. Chem. Phys.* **92** 4125
- [27] Arbe A, Richter D, Colmenero J and Farago B 1996 *Phys. Rev. E* **54** 3853
- [28] Hansen C and Richert R 1997 *Acta Polymer* **48** at press