# Relaxational dynamics at the glass transition in orientational and canonical glasses investigated by dielectric spectroscopy

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# RELAXATIONAL DYNAMICS AT THE GLASS TRANSITION IN ORIENTATIONAL AND CANONICAL GLASSES INVESTIGATED BY DIELECTRIC SPECTROSCOPY

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Dedicated to Prof. G. Klages on the occasion of his 75th birthday.

## ABSTRACT

Measurements of the dielectric permittivity are reported for the canonical glass glycerol and for solid solutions of ferroelectric betaine phosphite and antiferroelectric betaine phosphate, which can be viewed as protype systems of orientational glasses. In this latter system long range dipolar order is suppressed by the competing ferroelectric and antiferroelectric interactions and the dipolar moments freeze-in devoid of long range order. In both systems the relaxation dynamics is studied for frequencies $10^{-3}Hz \leq \nu \leq 10^6 Hz$, close to the glass transition temperatures. The relaxation dynamics is characterized according to Angell's classification scheme of strong and fragile glass-formers.

## 1. INTRODUCTION

The recent interest in the phenonmenology of vitrification stems from the fact, that it is still an open question, whether the glass transition can be viewed as a purely kinetic phenomenon, or if it is characterized by an underlying (dynamic) phase transition. Canonical glasses, for example vitreous silica, are distinguished from orientational and spin glasses in that the glass transition is defined by a process in which an amorphous state is formed from the (undercooled) melt of the material. The glass formation usually is defined by solidifaction without any crystalization and depends strongly on time which is available for crystallization in the cooling process. The structural arrest is characterized by a divergence of the shear viscosity (or by the divergence of a microscopic mean relaxation time). However, the glass transition is not defined precisely and the existance of a true glass phase in these fluids remains ambiguous[1]. Close to the glass transition temperature the relaxation times become much longer than the experimentalist's time window. Hence, the existence of a true divergence at non-zero temperature can only be concluded from extrapolations, and can not be rigorously tested. From a fundamental point of view, it seems that there is always the possibility for activated motion to occur leading to relaxation, a fact that results from the absence of long range order. Most glass-forming liquids reveal an extraordinarily large temperature dependence of the viscosity $\eta$ which can be described by a Vogel[2]-Fulcher[3] law:

$$\eta \sim \exp(E_b/k_B(T - T_{VF})). \tag{1}$$

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Here, $E_a$ is the hindering barrier of the relaxation process, which separates two potential minima, $T_{VF}$ is the Vogel-Fulcher temperature where the viscosity diverges. In thermodynamic experiments, usually performed within a time window of 10s to 100s, the heat capacity reveals a rapid change $\Delta c_p$ near the glass transition $T_g \sim T_{VF}$. A severe problem in the interpretation of vitrification is to understand the origin of the observed anomaly in the heat capacity and to explain why it is more pronounced in some systems than in some others.

Recently, C.A. Angell[4] has classified glass-forming liquids along a scale of "strong" and "fragile" extremes. By rewriting the Vogel-Fulcher law in terms of a fragility parameter D,

$$\eta \sim \exp(D \cdot T_{VF}/k_B(T - T_{VF})), \tag{2}$$

he was able to distinguish between strong (D>20) and fragile (D<20) glass formers. According to Angell[4], strong (fragile) glasses are characterized by a low (high) density of configurational states in their potential energy surface. Hence, strong glasses exhibit a smeared-out heat capacity anomaly, while fragile glasses reveal a distinct anomaly.

The aim of the present work is to check these predictions in model systems, namely orientational glasses (OG), and to compare the results with what is found in canonical glasses. An orientational glass state appears when reorienting moments in solids freeze into random configurations[5]. The moments may be of dipolar or quadrupolar nature and belong to one of the constituents of a mixed-crystal solid. The interplay of site disorder and frustrated interactions is responsible for the freezing transition which bears similarities with the spin glass transition in dilute magnetic systems[6].

In this paper we present dielectric spectroscopy results obtained in the canonical glass glycerol and in solid solutions of antiferroelectric betaine phosphate (BP) and ferroelectric betaine phosphite (BPI) which are good candidates for dipolar glasses[7],[8]. Dielectric and other measurements have been performed on glycerol since the initial studies by, Danforth[9],Morgan[10], and Davidson and Cole[11]. One result of the study by Davidson and Cole was the conclusion that dielectric relaxation in glycerol is well described by what has since become known as the Davidson-Cole formula[11]. The literature on dielectric measurements in glycerol is abundant[12] and thus glycerol provides one with a well-studied glass with which comparison to other glasses is possible. Glycerol is a simple glass-forming liquid which has recently been shown to obey a scaling relation obeyed by many other supercooled fluids[1]. According to Angell's classification scheme it is a fragile glass: $T_{VF}$=134K and $E_a$=1465K yielding a fragility parameter D=11. Accordingly, a well-defined jump of $C_p$ at the glass transition temperature can be observed[13]. BP and BPI are molecular crystals of the amino acid betaine and the phosphoric or the phosphorous acids, respectively. In both compounds the inorganic components ($PO_4$ or $PO_3$ groups) are linked by hydrogen bonds to quasi-one-dimensional chains[14]. BP reveals antiferroelectric order at $T_c$=86K[14]. At the ordering temperature it is believed that the O-H$\cdots$O bonds order along the one dimensional chains and the chains are linked antiferroelectrically. BPI reveals ferroelectric order below $T_c$=216K[14]. It has been shown that at intermediate concentrations long range electric order is suppressed and the mixed crystals transform into an orientational glass state[8]. Specifically, we are interested in a comparison of the dipolar relaxation dynamics in glycerol and in BP:BPI solid solutions and to classify them according to Angell's scheme[4].

## 2. EXPERIMENTAL

Nominally pure (Selectipure$^R$) water-free (<0.7%) glycerol was purchased from

Merck. It has been distilled additionally since it is known that water contamination produces changes in the relaxation time and other properties of glycerol[15]. The glycerol was transferred into the sample capacitor under nitrogen atmosphere. BP:BPI single crystals were supplied by J. Albers (Fachbereich Physik, Universität des Saarlandes, FRG). They were grown by controlled evaporation from aqueous solution. For the dielectric spectroscopy thin slices of the single crystalline material were gold plated. The samples were oriented along the monoclinic b-axis.

To cover a broad range of frequencies two different experimental set-ups were used: a frequency response analyzer (Solartron-Schlumberger 1260 impedance analyzer) supplemented with a high-impedance preamplifier (Chelsea Dielectric Interface) allowed measurements from $10^{-2}$Hz to approximately $10^{4}$Hz. In the audio frequency range ($10^{2}$Hz - $10^{6}$Hz) automated low-frequency bridges (HP 4192A impedance analyzer and HP 4274A LCR meter) were used. These experiments were performed in a home manufactured variable flow He$^{4}$ cryostat (2K$\leq$T$\leq$300K).

## 3. RESULTS AND DISCUSSION

Using the above mentioned dielectric spectroscopy techniques, the dielectric permittivity in glycerol and in solid solutions of betaine phosphate and betaine phosphite BP$_x$BP$_{1-x}$ [BP:BPI(x·100)] has been measured for frequencies $10^{-2} \leq \nu \leq 10^{6}$ and temperatures between 2K and 300K. The frequency dependence of $\epsilon'$ and $\epsilon''$ were fitted using the Fourier transform $\mathcal{F}$ of the time-honoured Kohlrausch[16]-Williams-Watts[17] (KWW) function. This function describes stretched exponential behaviour in the time domain:

$$\Phi(t) = \exp{-(t/\tau_{KWW})^{\beta_{KWW}}} h(t).$$ (3)

Here, $\tau$ is a characteristic relaxation time, $\beta_{KWW}$ is a fractional exponent. The Heviside step function is defined by $h(t)$ which is 0 for $t <0$ and 1 otherwise. The relationship between the KWW function and $\epsilon(\omega,T)$ can be expressed as

$$\epsilon^*(\omega,T) = \epsilon'(\omega) - i\epsilon''(\omega) = \epsilon_S - i\omega(\epsilon_S - \epsilon_\infty) \int_0^\infty \exp[-(i\omega t)] \exp[-(t/\tau_{KWW})^{\beta_{KWW}}]dt,$$ (4)

where $\epsilon_\infty = \epsilon(\omega=\infty)$ and $\omega$ is the angular frequency $\omega=2\pi\nu$.

The dielectric dispersion for glycerol is shown in Fig. 1. Here the real (upper frame: Fig. 1a) and the imaginary part (lower frame:Fig. 1b) part of the dielectric constant, $\epsilon'$ and $\epsilon''$ respectively, are plotted vs. the logarithm of the measurement frequency $\log_{10}(\nu)$ for different temperatures between 189K and 236K. The dispersion step and the loss peak indicate the polydispersive nature of the relaxation process, $\epsilon''$ is slightly asymmetric and broader that the 1.14 decades as expected for a monodispersive Debye relaxator. Both, the width and the asymmetry stay almost constant over the range of temperatures of this investigation.

The frequency dependence of the real (upper frame: Fig. 2a) and the imaginary part (lower frame: Fig. 2b) part of $\epsilon^*$ in BP:BPI(40) shows strikingly different behaviour from glycerol. Fig. 2 provides clear evidence of a strong asymmetry and an enormous width, both of which are strongly temperature dependent. Fits to Eq. (4) are indicated by solid lines in both figures. The rather different temperature dependence of width and asymmetry of the canonical glass glycerol and of the dipolar glass BP:BPI(40) becomes even more evident in a plot of scaled data.
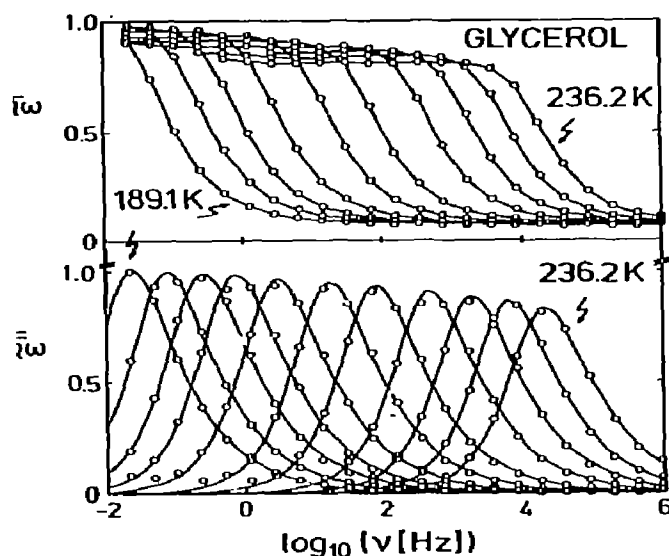
Figure 1a.    The normalized real part of the dielectric constant of glycerol as a function of $\log_{10}(\nu)$. Successive curves are separated by 5K. Fits to Eq. (4) are indicated by solid lines.

Figure 1.

Figure 1b.    The normalized imaginary part of the dielectric constant of glycerol as a function of $\log_{10}(\nu)$. Successive curves are separated by 5K. Fits to Eq. (4) are indicated by solid lines.

Figure 2a.    The real part of the dielectric constant of BP:BPI(40) as a function of $\log_{10}(\nu)$. Successive temperatures are indicated. Fits to Eq. (4) are indicated by solid lines.

Figure 2.

Figure 2b. The imaginary part of the dielectric constant of BP:BPI(40) as a function of $\log_{10}(\nu)$. Successive temperatures are indicated. Fits to Eq. (4) are indicated by solid lines.
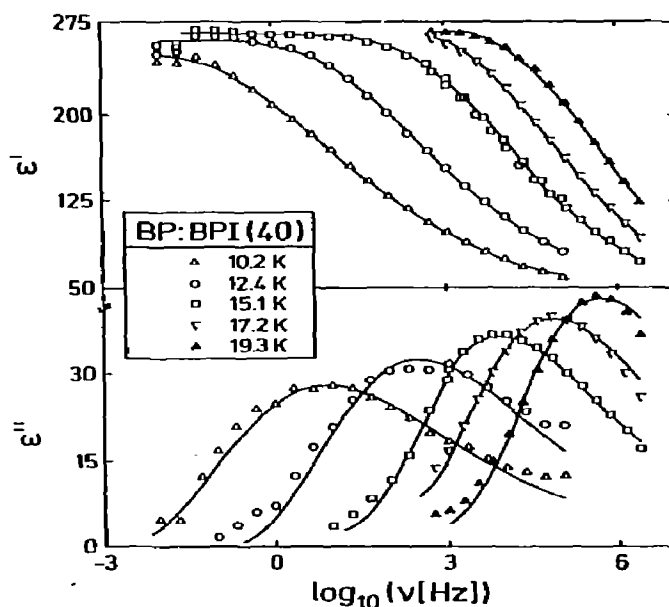
Fig. 3 shows the scaled data for glycerol (lower frame: Fig. 3b) and BP:BPI(40) (upper frame: Fig. 3a). The data collapse onto a single scaling curve for glycerol. However, no meaningful master plot can be achieved for BP:BPI(40), due to the strong temperature dependence of width and asymmetry. Here we focus on the temperature dependence of $\tau_{KWW}$ and $\beta_{KWW}$. Fig. 4 shows the temperature dependence of the fractional exponent (upper frame) and of the characteristic relaxation time (lower frame) for glycerol and BP:BPI(40). Both sets of data are shown vs. a normalized inverse temperature $T_g/T$. The glass transition temperature $T_g$ is defined as the temperature where the relaxation time $\tau_{KWW}=100s$ (Glycerol:$T_g=183K$: BP:BPI(40): $T_g=7K$). As indicated already by a master plot of the data, for glycerol, $\beta_{KWW}$ is only weakly temperature dependent. The plot or $\tau_{KWW}$ shows strong deviations from an Arrhenius behaviour. The solid line is the result of a Vogel-Fulcher fit with $E_a=1465K$ and $T_{VF}=134K$. These values are in reasonable agreement with the results of previous investigations[11]. In BP:BPI(40), $\beta_{KWW}$ is below 0.3 and strongly temperature dependent. The characteristic relaxation time follows a pure Arrhenius behaviour with $E_a/k_B=252K$. An estimate of a lower limit of a Vogel-Fulcher temperature yields values well below 1K; hence the fragility parameter D >100.

The lower frame of Fig. 4 reveals that glycerol is a fragile glass-former with D=11, while BP:BPI(40) exhibits the characteristics of a strong glass. Accordingly, the jump in the specific heat at the glass transition is significant in glycerol[13], but negligible in BP:BPI.[18] In the coupling model of Ngai and colleagues[19] the magnitude of the deviations from exponentiality in the KWW-law (quantified by $n=1-\beta_{KWW}$ in their model) signals the level of disorder in the environment of the "primitive" species. It has been suggested that for strong liquids the exponent $\beta_{KWW}$ lies in the range of 0.8-1 and is weakly temperature dependent. Fragile liquids exhibit nearly single-exponential relaxation ($\beta_{KWW} \sim 1$) at high temperatures, and show non-Arrhenius behaviour close to the glass transition temperature.[20] This correlation of $\beta_{KWW}$ with the other system parameters seems to be at odds with the present investigation. Within the framework of the coupling model the small values of the fractional exponent may be explained by combining coupling and site disorder[21].

# 4. CONCLUSIONS

In conclusion, we have presented dielectric results in solid solutions of ferroelectric BPI and antiferroelecric BP which undergo a transition into an orientational glass state and compare the results to the dielectric permittivity obtained in the canonical glass glycerol. The relaxation dynamics at the glass transition was studied in detail. For both glasses the dispersion of $\epsilon^*$ is well described with the Fourier transform of a stretched exponential time behaviour (Kohlrausch-Williams-Watts function). However, the fractional exponent behaves very different in the two glass-formers investigated. It is 0.8 and almost temperature independent for glycerol, while in BP:BPI(40), $\beta_{KWW}$ decreases from 0.3 to 0.2 with decreasing temperatures. The mean relaxation times follow a Vogel-Fulcher law for glycerol and can be described by a pure Arrhenius behaviour in the orientational glass. Within the classification scheme proposed by Angell, glycerol is a fragile liquid with a fragility parameter D=11; BP:BPI(40) is a strong glass-former with D exceeding 100. This signature of a strong and fragile glass is consistent with the predictions concerning the specific heat anomaly at the glass transition: it is well known that glycerol exhibits a well-defined anomaly[13]. The heat capacity in the orientational glass BP:BPI is absolutely smooth at the glass transitions temperature[18].

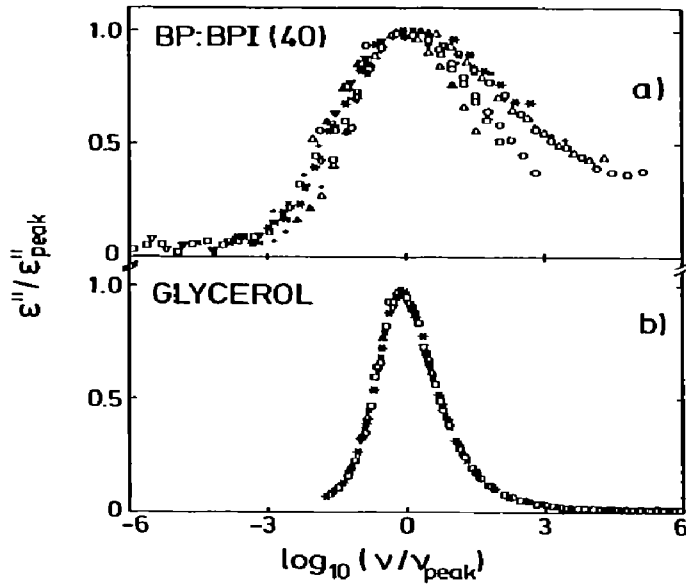Figure 3a. A master plot of the dielectric loss in BP:BPI(40) as a function of $\log_{10}(\nu)$ shifted by $\nu_{peak}$ and scaled by $\epsilon_{max}$. Temperature range is the same as in Figure 2.

Figure 3.

Figure 3b. A master plot of the dielectric loss in glycerol as a function of $\log_{10}(\nu)$ shifted by $\nu_{peak}$ and scaled by $\epsilon_{max}$. Temperature range is the same as in Figure 1.

Figure 4a. The variation of $\beta_{KWW}$ resulting from fits of Eq.(4) to the data in Figures 1 and 2 as a function of normalized inverse temperature $T_g/T$. For Glycerol, $T_g=183K$ whereas for BP:BPI(40) $T_g=7K$. Broken lines are to guide the eye.

Figure 4.

Figure 4b. Variation of $\log_{10}$ of relaxation times resulting from fits of Eq.(4) to the data in Figures 1 and 2 as a function of normalized inverse temperature $T_g/T$. For Glycerol, $T_g=183K$ whereas for BP:BPI(40) $T_g=7K$. Solid lines result from fits to Eq.(2).
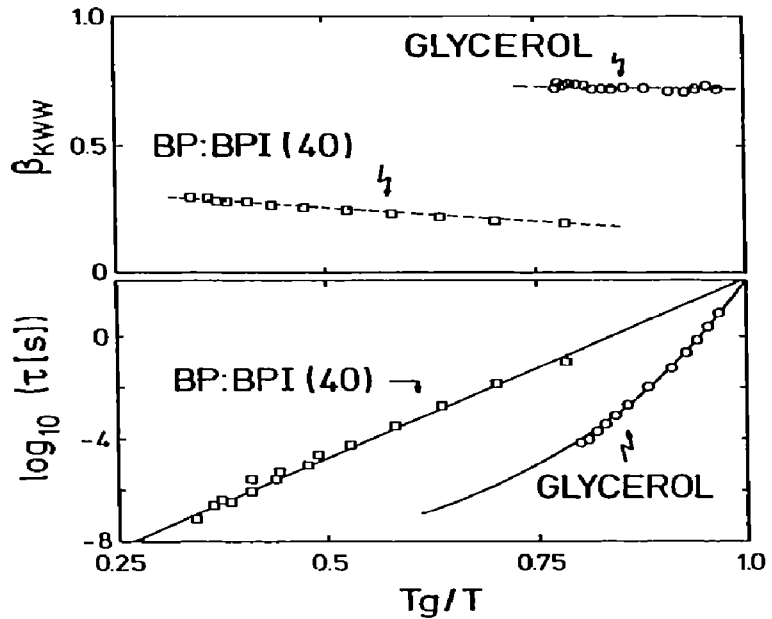
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