

Anomalies in the Scaling of the Dielectric α -Relaxation

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By measuring the complex dielectric function over 15 decades in frequency we evaluate the scaling of the α -relaxation for several glass-forming liquids including propylene carbonate. The temperature dependence of the mean relaxation time and of the relaxation strength of the relaxation function displays two dynamical regions being separated by a crossover temperature. The observed findings are essentially not in accordance with predictions of the mode-coupling theory and light scattering results for propylene carbonate [M. Elmroth *et al.*, Phys. Rev. Lett. **68**, 79 (1992)].

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The glass transition is an old, central problem of condensed matter physics [1] and up to now no microscopic theory exists. Also the dynamic behavior related to the glass transition, the α -relaxation, is quite complex and not well understood. Among others the rapid increase of the viscosity or characteristic relaxation time τ with decreasing temperature and the non-Debye behavior of the relaxation function [1-7] are the most important features of this relaxation process. It is well established that τ increases dramatically near the glass transition temperature T_g according to the Vogel-Fulcher-Tamann (VFT) equation [8], i.e., $\log_{10}\tau = \log_{10}\tau_\infty + A/(T - T_0)$, where τ_∞ is a characteristic time constant in the order of magnitude of 10^{-13} s, A is a constant, and T_0 is the Vogel temperature, 30-50 K below T_g . Thus the VFT equation suggests that T_0 is a significant temperature for the dynamics of the glass transition.

Recently the discussion concerning the microscopic origin of the glass transition has been stimulated by the application of the mode-coupling formalism (MCT) [9]. This theory predicts a dynamical phase transition from an ergodic to a nonergodic behavior at a critical temperature T_c , 30-50 K above T_g . In some cases detailed relations have been deduced. For instance, the viscosity or relaxation time should follow a power law $\tau \sim (T - T_c)^{-\gamma}$ for $T > T_c$ [10]. In a high temperature region ($T > 1.2T_g$) the viscosity can be fitted by a power law [11] and γ is found in the range of 2-3 for simple glass-forming liquids [12,13]. Also the predicted anomalies of the Debye-Waller factor at T_c [10,11] found with neutron and Brillouin scattering [13-15] and a change in diffusion behavior [16] support this concept. But it is a serious difficulty of this theory that the critical temperature where the α -relaxation should freeze in is far above T_g . The remaining mobility below T_c is explained by activated hopping processes [9]. However, it is not clear and no answer is given by the MCT how the universal VFT scaling could be deduced. Recent broadband dielectric measurements [5-7] show no indication for a critical behavior although a wide temperature range including the expected T_c was

covered. This fact was also discussed by Kim and Mazenko [17] concluding that the MCT has to be reinterpreted. Also a detailed scaling analysis of the α - and β -relaxation in polymers according to the MCT delivers only partial agreement with the predicted behavior [18].

To analyze the scaling of the α -relaxation we carried out broadband dielectric experiments on three low molecular glass-forming liquids. To compare directly dielectric with scattering results propylene carbonate was chosen for which a mode-coupling analysis has been presented [13]. In addition, propylene glycol and glycerol as typical glass-forming liquids were selected. It should be noted that the samples include van der Waals liquids like propylene carbonate as well as hydrogen bonded networks like glycerol. All liquids show only one dielectric active relaxation process, the α -relaxation [5-7]. To broaden the experimental basis we include data for salol taken from Ref. [6] for which a MCT analysis has been presented as well [19].

Figure 1 shows dielectric function $\epsilon^*(f) = \epsilon'(f) - i\epsilon''(f)$ for glycerol in the available frequency range from 10^{-5} to 10^{10} Hz, measured with the equipment described elsewhere [7]. As is well known the peak frequency f_p of ϵ'' decreases and the half-width broadens when the temperature is lowered.

The temperature dependence of f_p in all studied samples shows two regimes [9,11,20]. At low temperatures f_p obeys the VFT equation which becomes obvious in a plot of $\log_{10}f_p$ vs $1/(T - T_0)$ [21] (Fig. 2). At temperatures which are sufficiently high the motion of molecules is determined principally by the energy required for a rotation and dependence of f_p upon temperature should be governed by an Arrhenius equation $\ln f_p = \ln f_\infty - E_a/kT$. Indeed in the high temperature range f_p can be fitted for all liquids studied by this equation where f_∞ is a relaxation rate in the order of magnitude of 10^{13} to 10^{16} Hz and E_a is an activation energy, with reasonable values between 20 and 40 kJ/mol (see Fig. 2). A crossover temperature T_A can be defined by the intersection of the Arrhenius with the VFT law as indicated in Fig. 2 by an ar-

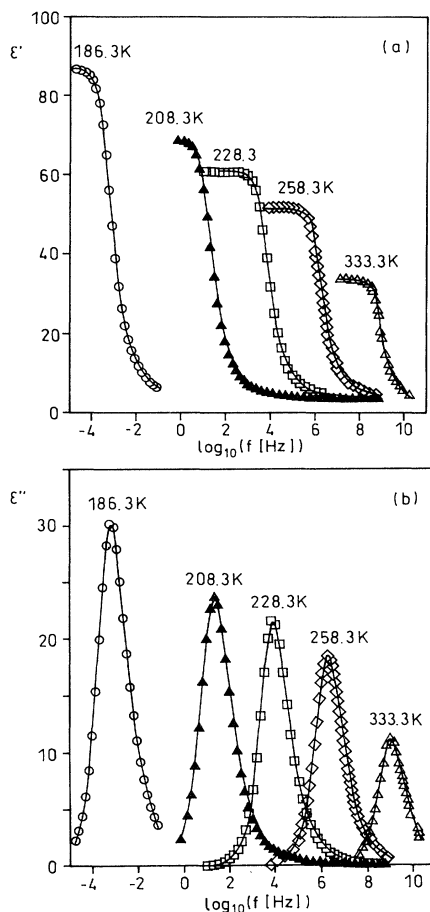


FIG. 1. (a) ϵ' and (b) ϵ'' of glycerol at the labeled temperatures. Each curve represents an example for the measuring system used. For $T=186.33$ K the time-domain spectrometer is used and the Fourier transformation of the measured data is given. (Because with this method only $\Delta\epsilon$ and not the absolute value of ϵ' can be measured, an extrapolated value of 3.8 for ϵ_∞ is added.)

row. It should be noted that the crossover from the VFT to the Arrhenius behavior is more pronounced for the van der Waals liquids propylene carbonate and salol.

The temperature dependence of f_p in the neighborhood of T_A and above also can be fitted by the power law proposed by the MCT, $f_p \sim (T - T_g)^\gamma$ (Fig. 3) where the estimated T_c and γ values are collected in Table I. Using this ansatz one finds for propylene carbonate $T_c = 186.6$ K which compares well with $T_c = 196$ K determined from viscosity measurements and of 180 K from neutron scattering results [13]. Hence the scaling of the α -relaxation is characterized by two characteristic temperatures: the Vogel temperature T_0 and the crossover temperature T_A or the critical temperature T_c at high temperatures. Clearly T_A differs from T_c because different fit functions for the determination are used. Figure 4, where $1/\log_{10}(f_\infty/f_p)$ vs T is plotted, shows the relation-

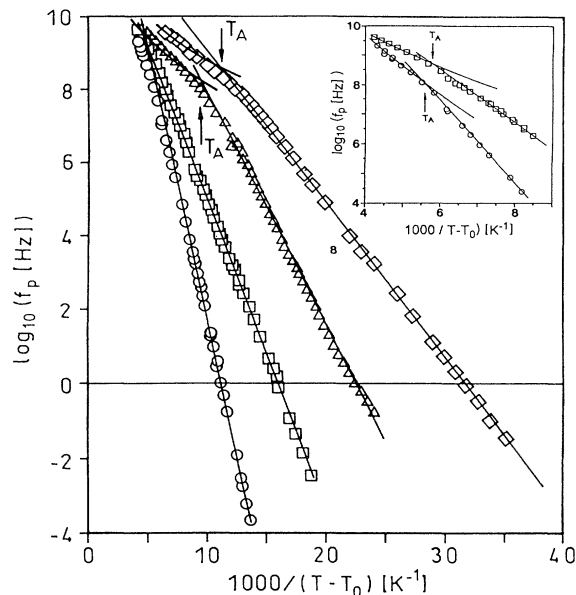


FIG. 2. $\log_{10} f_p$ vs $1/(T - T_0)$: \circ , glycerol; \square , propylene glycol; \diamond , propylene carbonate; \triangle , salol, data taken from Ref. [6]. The crossover temperatures T_A are indicated by arrows and for the T_0 values see Table I.

ship between T_A , T_c , and T_0 for propylene carbonate.

If the dipole fluctuations couple to density fluctuations treated by the MCT [9], one would expect a similar behavior for the product $T\Delta\epsilon$, where $\Delta\epsilon$ is the relaxation strength, as predicted for the Debye-Waller factor. To determine $\Delta\epsilon$ we apply an evaluation method [7] based on the model function of Havriliak and Negami (HN function) [22] given by $\epsilon^*(f) - \epsilon_\infty = \Delta\epsilon [1 + (if \times 2\pi\tau)^\alpha]^{-\beta}$, where α and β are shape parameters, τ is a

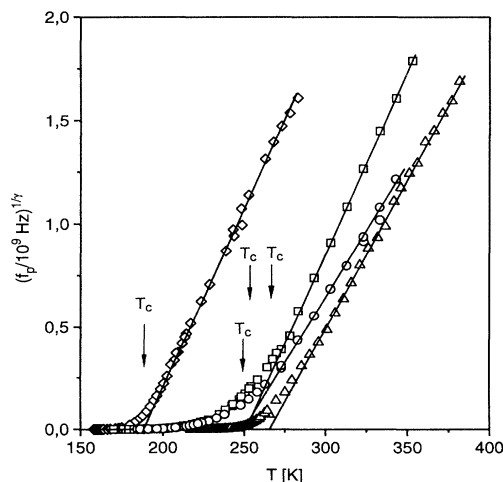


FIG. 3. $(f_p/\text{GHz})^{1/\gamma}$ vs T : \circ , glycerol; \square , propylene glycol; \diamond , propylene carbonate; \triangle , salol, data taken from Ref. [6]. The critical temperatures are indicated by arrows.

TABLE I. Characteristic temperatures for the scaling of the α -relaxation. T_c was determined from Fig. 3. For the determination of T_0 see Ref. [21].

Samples	T_0 (K)	T_A (K)	T_c (K)	γ
Propylene carbonate	130	216.6	186.6	2.45
Glycerol	111.2	288.0	248.8	3.65
Propylene glycol	117	291.6	251.3	2.42
Salol ^a	182.5	279.7	267.7	2.25

^aThe T_0 value is 40 K greater than the value reported in Ref. [6] although the same data are used. The reason may be the unrealistic prefactor $\tau_\infty \approx 10^{-24}$ s given in Ref. [6].

relaxation time, and $\epsilon_\infty = \epsilon'(f)$ for $f \gg \tau^{-1}$. In Fig. 5 $(T\Delta\epsilon)^2$ vs T is shown. This plot does not show the functional form expected from the MCT, i.e., $T\Delta\epsilon \sim (T_c - T)^{1/2}$ for $T < T_c$ and $T\Delta\epsilon \approx \text{const}$ for $T > T_c$ [23]. But, in the same temperature region where f_p deviates from the VFT behavior $T\Delta\epsilon$ also shows a change in its temperature dependence as indicated by T_c in Fig. 5. Again the changes are more pronounced for the van der Waals liquids.

Fitting the HN function to the experimental data delivers also the shape parameters β and α . For all samples $\alpha = 1$ independent of temperature is found. In Fig. 6 the shape parameter β is plotted versus temperature yielding the conclusion that β is temperature dependent for all samples studied. This is in contradiction in detail to light scattering results on propylene carbonate where a temperature independent β is found [13] and to the MCT, in general, where a temperature independent behavior above T_c is predicted [4]. There is no change in

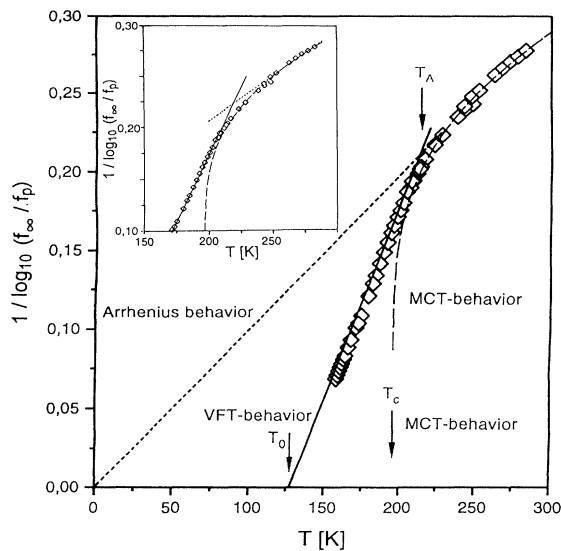


FIG. 4. $1/\log_{10}(f_\infty/f_p)$ vs temperature for propylene carbonate ($\log_{10}f_\infty = 13.11$). The crossover between the Arrhenius or MCT behavior and the VFT law is demonstrated more clearly in the inset. T_A , T_c , and T_0 are indicated by arrows.

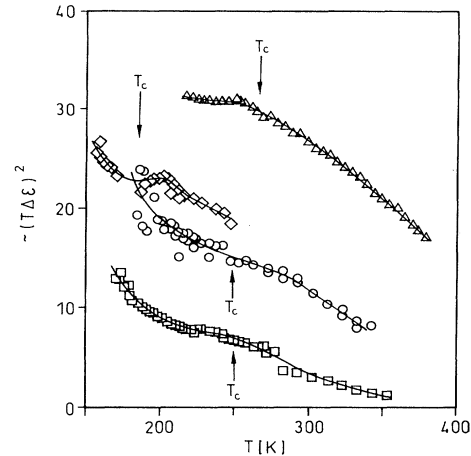


FIG. 5. $(T\Delta\epsilon)^2$ vs T : \circ , glycerol; \square , propylene glycol; \diamond , propylene carbonate; \triangle , salol, data taken from Ref. [6]. T_c as extracted from Fig. 3 are indicated by arrows. Lines are guides for the eye.

the temperature dependence of β at T_c . Moreover, at least for propylene carbonate we can prove without any experimental uncertainty that β approaches unity (Debye process) at the high temperature site.

To discuss the scaling of the α -relaxation it seems necessary to treat the α -relaxation as a cooperative process characterized by a correlation length [16,24–26] where the decrease of f_p with decreasing temperature is explained by a strong temperature dependence $\xi(T)$ setting in at T_A and going to infinity as T approaches T_0 [25,26]. This model is supported by observations that above T_A the scaling is given by an Arrhenius law with reasonable activation energies and a Debye-like relaxation function. Below T_A the dipoles within the correlation volume $V_a = \xi(T)^3$ are dynamical coupled and hence

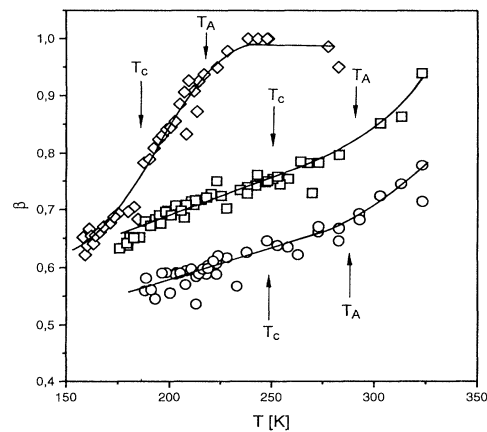


FIG. 6. Shape parameter β vs T . \circ , glycerol; \square , propylene glycol; \diamond , propylene carbonate. Lines are guides for the eyes. T_A and T_c as extracted from Figs. 2 and 3 are indicated by arrows.

it is not surprising that the cooperative movement of dipoles leads to a more complicated temperature dependence not only for f_p but also for the relaxation strength and the shape of the relaxation time distribution. Furthermore, the observation that the transition between the two dynamical regions is less pronounced for the H-bonded liquids (see Figs. 2 and 5), because the interaction between the molecules is increased, supports this concept. It should be emphasized that in this consideration T_A is not a critical temperature in the sense of a phase transition but a crossover temperature separating local and cooperative motional processes. A similar transition was assumed in the coupling model developed by Ngai *et al.* [27].

In conclusion, we have shown by means of broadband dielectric relaxation spectroscopy that the α -relaxation shows two different dynamical regions separated by a crossover temperature T_A , or T_c . In the temperature region where the peak frequency f_p deviates from the VFT behavior we show, for the first time, that also the temperature dependence of the intensity $\Delta\epsilon$ of the dielectric relaxation function changes. Above T_A the temperature dependence of f_p can be described by the power law behavior predicted by the MCT with exponents between 2 and 4 or by an Arrhenius law with reasonable parameters. The temperature dependence of the shape of the relaxation function and of its dielectric strength is in contrast to predictions of the MCT. Instead it is suggested that the α -relaxation at temperatures below the crossover temperature T_A cannot be comprehended without taking into consideration its cooperative nature.

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