Axel Mellinger

Piezoelectric Resonances in the Dielectric Spectrum of Polymer Films

Piezoelectric polymer films have played an important role in sensor and actuator applications ever since high piezoelectric coefficients were reported in suitably prepared polyvinylidene fluoride (PVDF) in 1969 [1]. Subsequently, the same effect was found in odd-numbered polyimides, copolymers of vinylidene cyanide (VDCN) and aromatic and aliphatic polyurea. Even though these polymers exhibit piezoelectric coefficients that are at least one order of magnitude smaller than those found in inorganic materials, such as lead zirconate titanate (PZT), they are nevertheless attractive for transducer applications in an aqueous environment, since their acoustic impedance is comparable to that of water. In addition, they can be easily patterned to form complex shapes covering large areas. Moreover, piezoelectric coefficients of several hundred pC/N have recently been reported
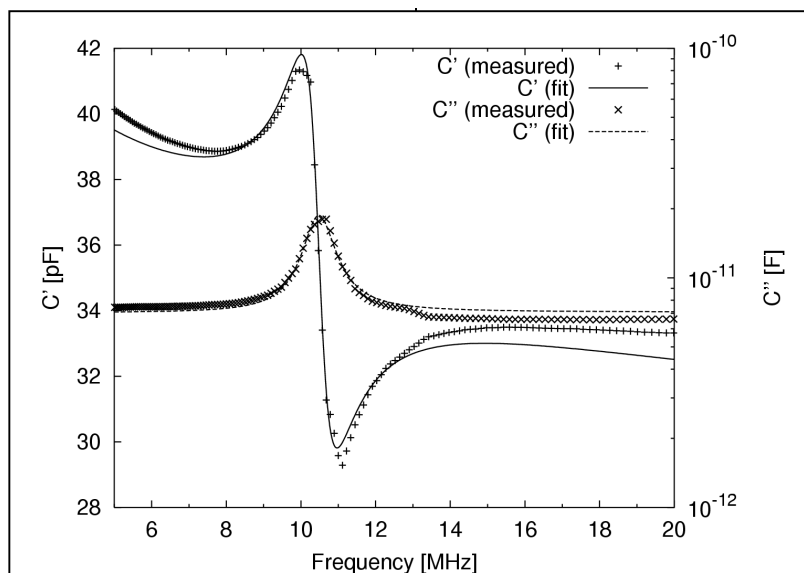

Fig. 1. Thickness-extension resonance of a 110 μm PVDF-TrFE film (Piezotech SA) at 40 °C. The solid and dashed lines were obtained by fitting Eq. (1) to the experimental data.

in cellular polypropylene [2] and in layer systems with porous polytetrafluoroethylene films [3,4].

Several techniques have been used to determine the piezoelectric d_{33} and d_{31} coefficients [5]. The direct piezoelectric effect (generation of an electrical signal upon a change in mechanical stress) can be measured in a quasi-static experiment [4]. Alternatively, the inverse piezoelectric effect can be measured by applying an electric field to the film and detecting the change in thickness by, e. g., optical interferometry [6] or acoustical techniques [7]. As a consequence of their thermodynamic definition [8], the piezoelectric coefficients of the direct and indirect effect must be equal.

Most of the above-mentioned methods are limited to frequencies between 0 and 100 kHz. In recent years, high-resolution dielectric spectroscopy has been successfully used to characterize piezoelectric polymers at much higher frequencies. Apart from the piezoelectric coefficient, this technique also yields the elastic moduli and electromechanical coupling coefficients. In its basic form, the admittance $Y(\omega)$ of a sample forming a thin parallel-plate capacitor is recorded as a function of frequency. Near the thickness-extension (TE) mode anti-resonance frequency, the complex capacitance $\tilde{C}(\omega) = Y(\omega)/(i\omega) = C'(\omega) - iC''(\omega)$ is given by [9,10]
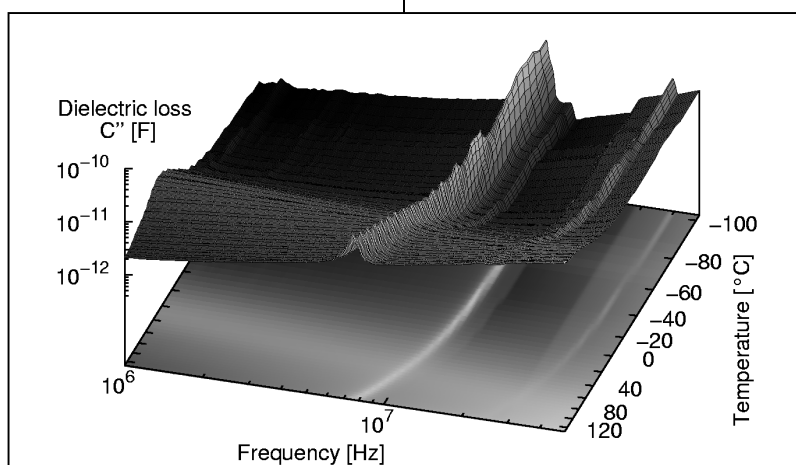

Fig. 2. Dielectric loss C" of a 110 μm PVDF-TrFE film (Piezotech SA) versus frequency and inverse temperature. The maxima correspond to the fundamental and the third harmonic of the thickness-extension mode.

$$\widetilde{C}(\omega) = \frac{\varepsilon_r^S \varepsilon_0 A}{h} \frac{1}{1 - k_{33}^2 \frac{\tan(\omega/4f_p)}{(\omega/4f_p)}} - iC_{\text{loss}}$$

(1)

where ε_r^S is the relative permittivity of the sample under constant strain, A and h are the electroded sample area and thickness, respectively, k_{33} is the complex electromechanical coupling factor, and f_p is the complex anti-resonance frequency of the TE mode. For a free-standing film, f_p is related to the complex elastic stiffness c_{33}^D under constant electric displacement and the sample density ρ via

$$f_p = \frac{1}{2h} \sqrt{\frac{c_{33}^D}{\rho}} \; , \quad (2)$$

and the electromechanical coupling factor k_{33} is given by

$$k_{33}^2 = e_{33}^2 / (\varepsilon_r^S \varepsilon_0 c_{33}^D) \; , \quad (3)$$

where the piezeoelectric stress coefficient e is related to the piezoelectric strain coefficient d via $e/d=c$ [11]. The $-iC_{\text{loss}}$ term in Eq. (1) accomodates the inherent dielectric loss of the sample. From the experimental data, the sample parameters k_{33} and f_p are determined via a non-linear least squares fit. Other methods of analysis have been suggested [12], but appear to be more likely to generate artefacts. c_{33}^D and d_{33} can then be calculated with Eqs. (2) and (3), respectively. To accommodate mechanical losses, f_p and k_{33} must be treated as complex quantities. Piezoelectric polymer films investigated via the dielectric resonance method include PVDF [13] and vinylidene-trifluoroethylene copolymers (P(VDF-TrFE)) [14]. Figure 1 shows the complex capacitance of a commercial 110 μm P(VDF-TrFE) sample (Piezotech SA). The spectrum was acquired with a Novocontrol Concept80 dielectric spectrometer. Unlike molecular relaxations, where the full width at half maximum (FWHM) is 1.14 decades, resonance peaks are much narrower, thus requiring a high frequency resolution. When the resonance spectrum is acquired over a wide range of frequencies, it may be necessary to include the contribution from dipole relaxation in the form of, e. g., a Havriliak-
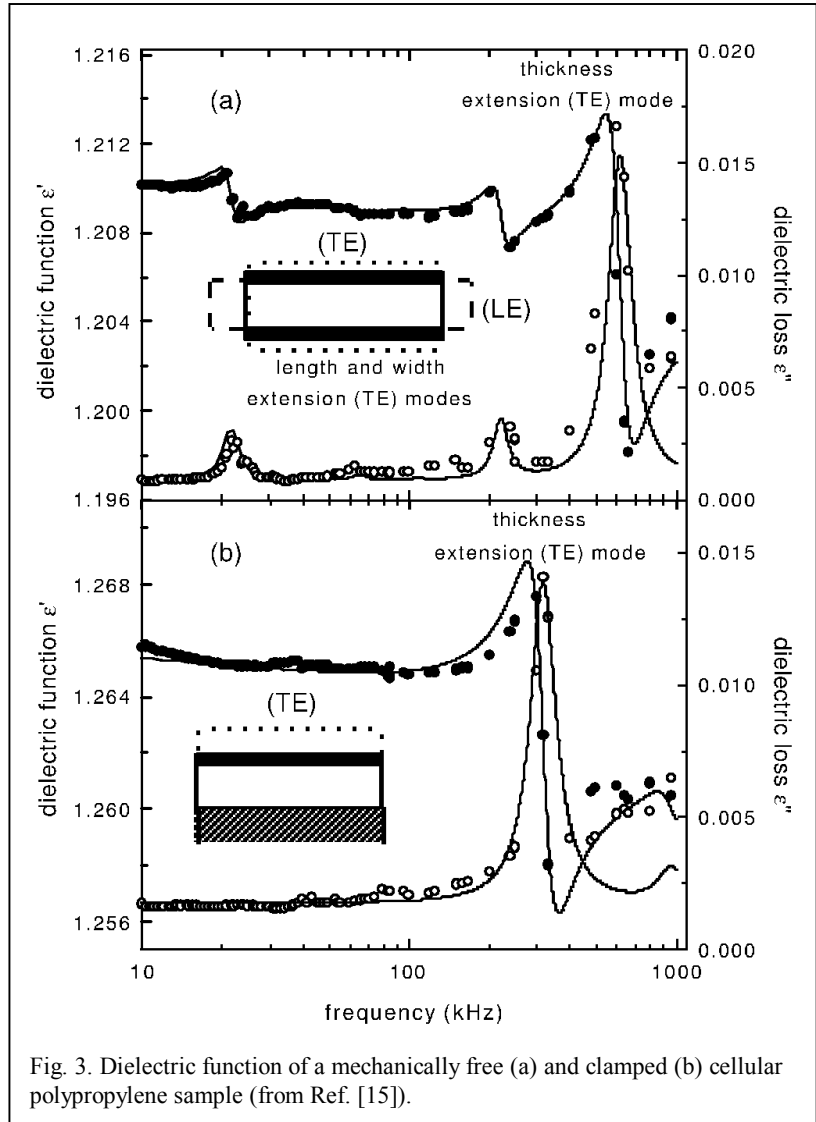

Fig. 3. Dielectric function of a mechanically free (a) and clamped (b) cellular polypropylene sample (from Ref. [15]).

Negami term, leading to a frequency-dependent ε_r^S.

By acquiring the dielectric spectrum at different temperatures, the temperature dependence of c_{33}^D, k_{33} and d_{33} can be measured. Figure 2 shows the dielectric loss of the same film as mentioned in Fig. 1. The data were acquired as a function of frequency under nearly isothermal conditions ($\Delta T_{\text{max}}=0.25$ K) in 10 K intervals. The softening of the sample at higher temperatures results in a decrease of the anti-resonance frequency. Analyzing the dielectric spectra potentially requires a large number of least squares fits (one for each temperature). This task is best performed using high-level scripting languages such as Matlab® or Gnuplot.

A recent study of corona-charged cellular polypropylene (PP) films showed dynamic piezoelectric coefficients of 140 pC/N at 600 kHz [15]. The large piezoelectric effect is caused by charges trapped at the surfaces of flat internal voids with lateral dimensions of approximately 100 μm and vertical dimensions of several μm which act as oriented macroscopic dipoles. The dielectric spectrum in Fig. 3 reveals TE as well as length (LE) and width-extension (WE) resonances. Due to their lower elastic modulus in the 3 (z) direction, the thickness-extension resonance frequency of porous polymers is typically one order of magnitude lower that that of their non-porous counterparts.

A different boundary condition can be imposed on the piezoelectric resonator by gluing the film onto a glass substrate with a thin layer of epoxy. In this case, the factor 2 in the denominator of Eq. (2) must be replaced by 4, thus lowering the TE

anti-resonance frequency by a factor of 2.

One drawback of the cellular PP films is their limited thermal stability. Very recently, corona-charged Teflon® AF amorphous fluoropolymer sandwich films were shown to exhibit strong piezoelectricity with coefficients of up to 600 pC/N [16]. From Figures 4 and 5 it is evident that the samples show only a small decrease in d_{33} up to 120 °C.

In summary, dielectric spectroscopy is a convenient tool to investigate not only the electrical, but also the mechanical and electromechanical properties of polymer films, and will continue to play an important part in the search for new transducer materials.

Fig. 4. Frequency-temperature map of the dielectric loss (C″) of a 55 μm porousTeflon® AF 2400/non-porous Teflon® AF 1600 sandwich film.

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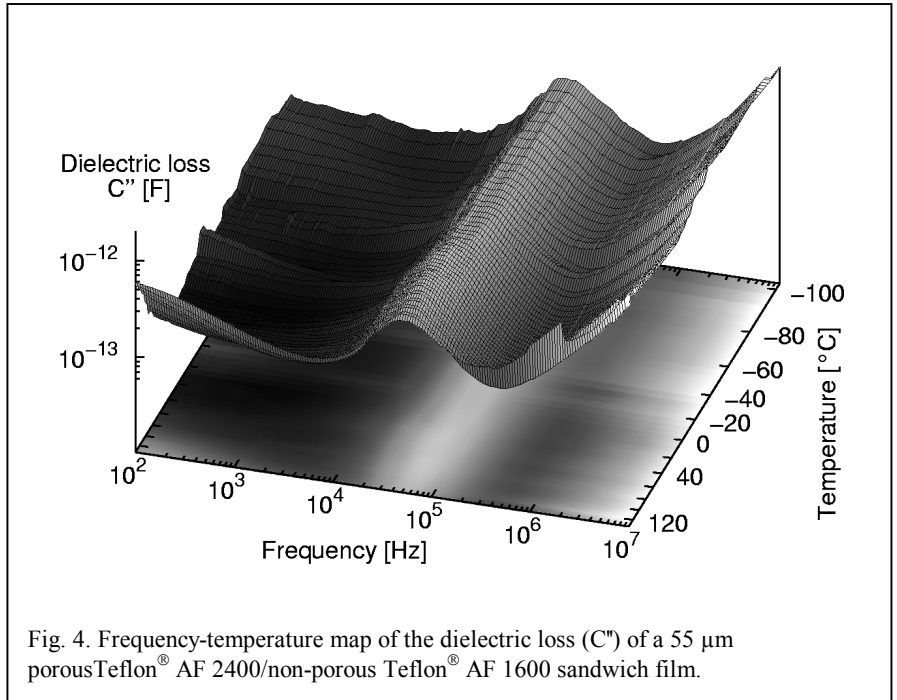
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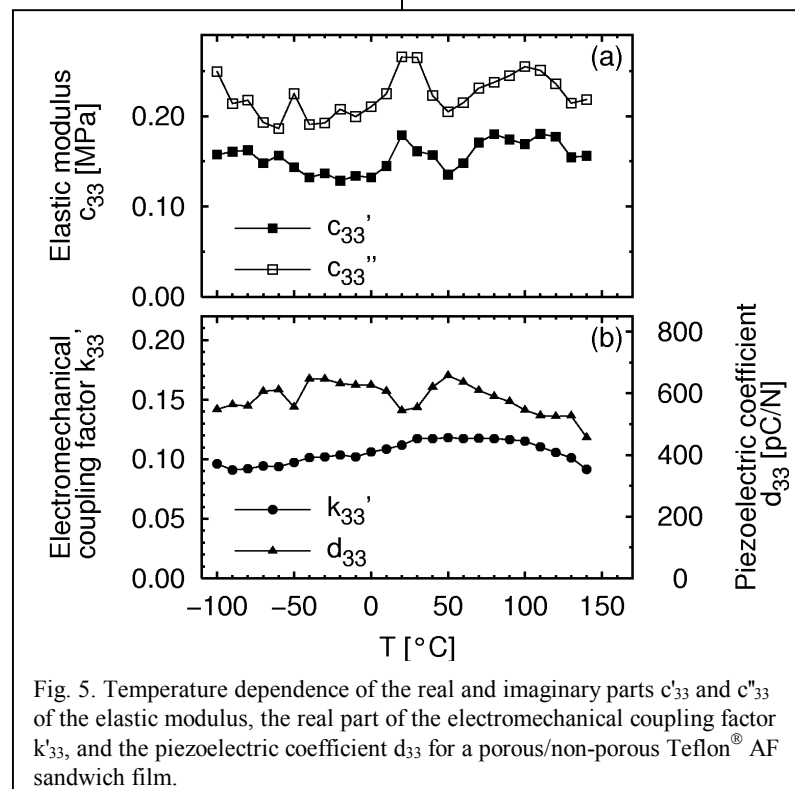Mail: axm@rz.uni-potsdam.de

Fig. 5. Temperature dependence of the real and imaginary parts c'_{33} and c''_{33} of the elastic modulus, the real part of the electromechanical coupling factor k'_{33}, and the piezoelectric coefficient d_{33} for a porous/non-porous Teflon® AF sandwich film.

Friedrich Kremer

How to Analyse the Conductivity Contribution in Dielectric Spectra?

The conductivity contribution in dielectric spectra is often an unwelcome artefact caused by charged impurities in a sample. Usually, it has in the imaginary part ε'' of the complex dielectric function a frequency dependence which can be described by the formal ansatz

$$\varepsilon''(\omega) = \frac{\sigma_0}{\omega^s \varepsilon_0} \cdot a \quad (1)$$

In this notation ε_0 is the vacuum permittivity, ω the angular frequency. For pure electronic conductors $s = 1$ and σ_0 describes the direct current (DC) conductivity with $a = 1$. In this case no contribution to ε' is observed. For hopping conduction [1] in disordered systems $s < 1$ and the conductivity contribution becomes complex (the constant a has then the dimension $[a] = (Hz)^{1-s}$). What is the molecular origin for this response and how should it be analysed?

The motion of a hopping charge is accompanied by an electrical relaxation: An ionic or electronic (in case of a polaron) charge is surrounded by negative or positive counter charges. A hop of a charge carrier to a new site can lead to a successful charge transport only if the polarisation cloud follows. Otherwise the charge carriers will jump back with a high probability. This mutual movement of the charge carrier and the surrounding polarisation cloud requires an electrical relaxation time τ_σ. If the frequency of the outer electrical field is higher than $1/\tau_\sigma$ its effect on the charge transport averages out. For lower frequencies than $1/\tau_\sigma$ the relaxation of the polarisation cloud is in phase with the outer electrical field. For that case the field supports the propagation of the charges. Hence this electrical relaxation gives rise to a contribution in the complex dielectric function which increases with decreasing frequency. This is the essence of the Debye / Hückel / Falkenhagen theory [2-4]. It explains the experimental
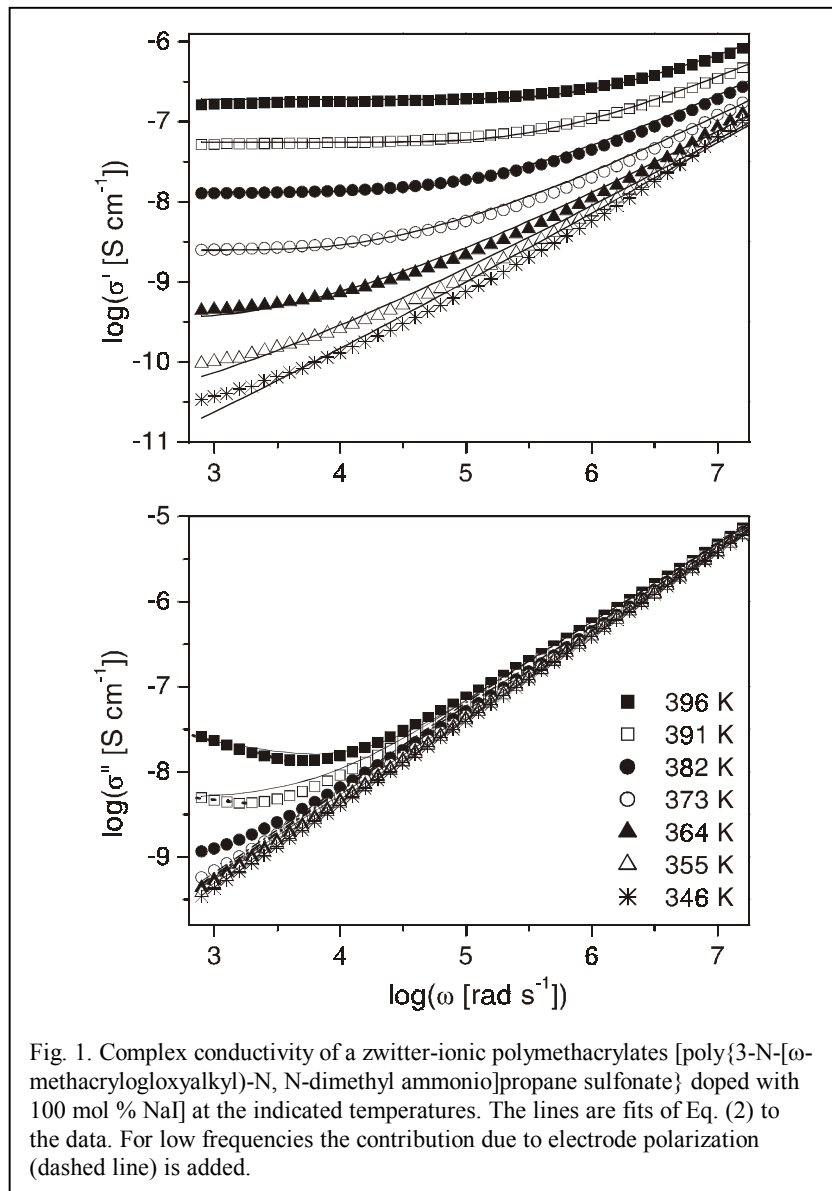

Fig. 1. Complex conductivity of a zwitter-ionic polymethacrylates [poly{3-N-[ω-methacrylogloxyalkyl)-N, N-dimethyl ammonio]propane sulfonate} doped with 100 mol % NaI] at the indicated temperatures. The lines are fits of Eq. (2) to the data. For low frequencies the contribution due to electrode polarization (dashed line) is added.

observation that for electrolytes the real part ε' increases with decreasing frequency. (Additionally one has to expect electrode polarisation effects in ionic conductors.)

The random free energy barrier model as developed by Dyre [5] assumes that conduction takes place by hopping of charge carriers in a randomly varying energy landscape. It provides a basis to analyse the charge transport in disordered systems. Within the Continuous–Time-Random Walk (CTRW) approximation [6] the following expression for the complex conductivity $\sigma^*(\omega)$ is obtained

$$\sigma^*(\omega) = \sigma_0 \left[\frac{i\omega\tau_e}{\ln(1 + i\omega\tau_e)} \right] \quad (2)$$

where τ_e is the attempt frequency to overcome the largest barrier determining the DC-conductivity. Splitting into real and imaginary parts delivers:

$$\sigma'(\omega) = \frac{\sigma_0 \omega\tau_e \arctan(\omega\tau_e)}{\frac{1}{4}\ln^2(1 + \omega^2\tau_e^2) + (\arctan\omega\tau_e)^2}$$

$$\sigma''(\omega) = \frac{\sigma_0 \omega\tau_e \ln(1 + \omega^2\tau_e^2)}{\frac{1}{2}\ln^2(1 + \omega^2\tau_e^2) + 2(\arctan\omega\tau_e)^2}$$

As example [7] spectra of the zwitter-ionic polymer [poly{3-N-[ω-methacrylogloxyalkyl)-N, N-dimethyl ammonio]propane sulfonate} doped with 100 mol % NaI] are analysed. It shows that the above formulae describe well the measured complex conductivity (Fig. 1). For the real part $\sigma'(\omega)$ on the low frequency side a plateau value is obtained which can be extrapolated to the DC-conductivity
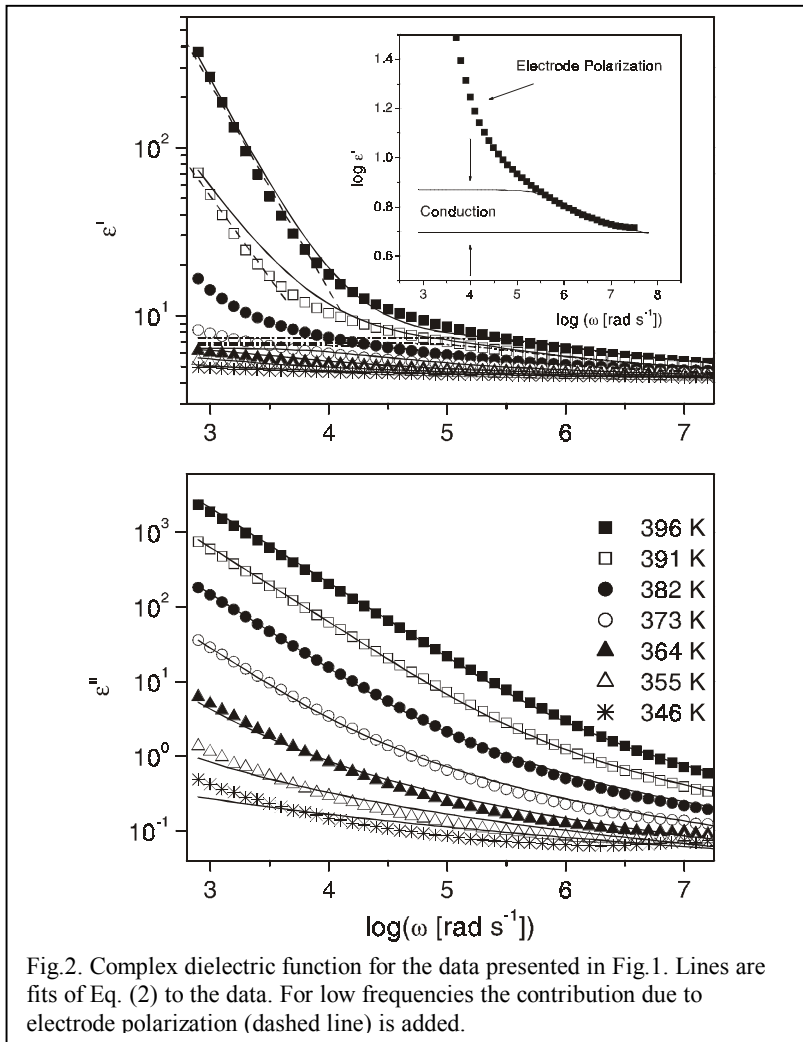
Fig.2. Complex dielectric function for the data presented in Fig.1. Lines are fits of Eq. (2) to the data. For low frequencies the contribution due to electrode polarization (dashed line) is added.

σ_0 for $\omega \rightarrow 0$ (see Fig1). At a critical frequency $\omega_c = 2\pi\nu_c$ the dispersion of σ' sets in. The later can be determined by smoothing the data and calculating numerically the maximum in $\partial^2\sigma'/\partial\omega^2$. The imaginary part of the complex conductivity decreases with decreasing frequency. The increase at low frequencies indicates electrode polarisation. Of course it does not make a difference if the data are displayed in another representation, e. g. in

$$\varepsilon^* = \frac{\sigma^*}{j\omega\varepsilon_0} + 1 \text{ or in the electrical}$$

modulus $M^* = \dfrac{1}{\varepsilon^*}$ (Fig. 2 resp.

Fig. 3). From the fits the DC-conductivity σ_0 and the electrical relaxation time τ_e is obtained. As shown in Fig. 4 the Barton/Nakajima/Namikawa

(BNN) [8a-c] relationship $\dfrac{1}{\tau_e} \sim \sigma_0$

is well fulfilled. This proves that DC- and AC- conduction are based on the same mechanism of charge transport.

It is remarkable that the complex conductivity σ^* is similar in its frequency- and temperature- (including also charge carrier
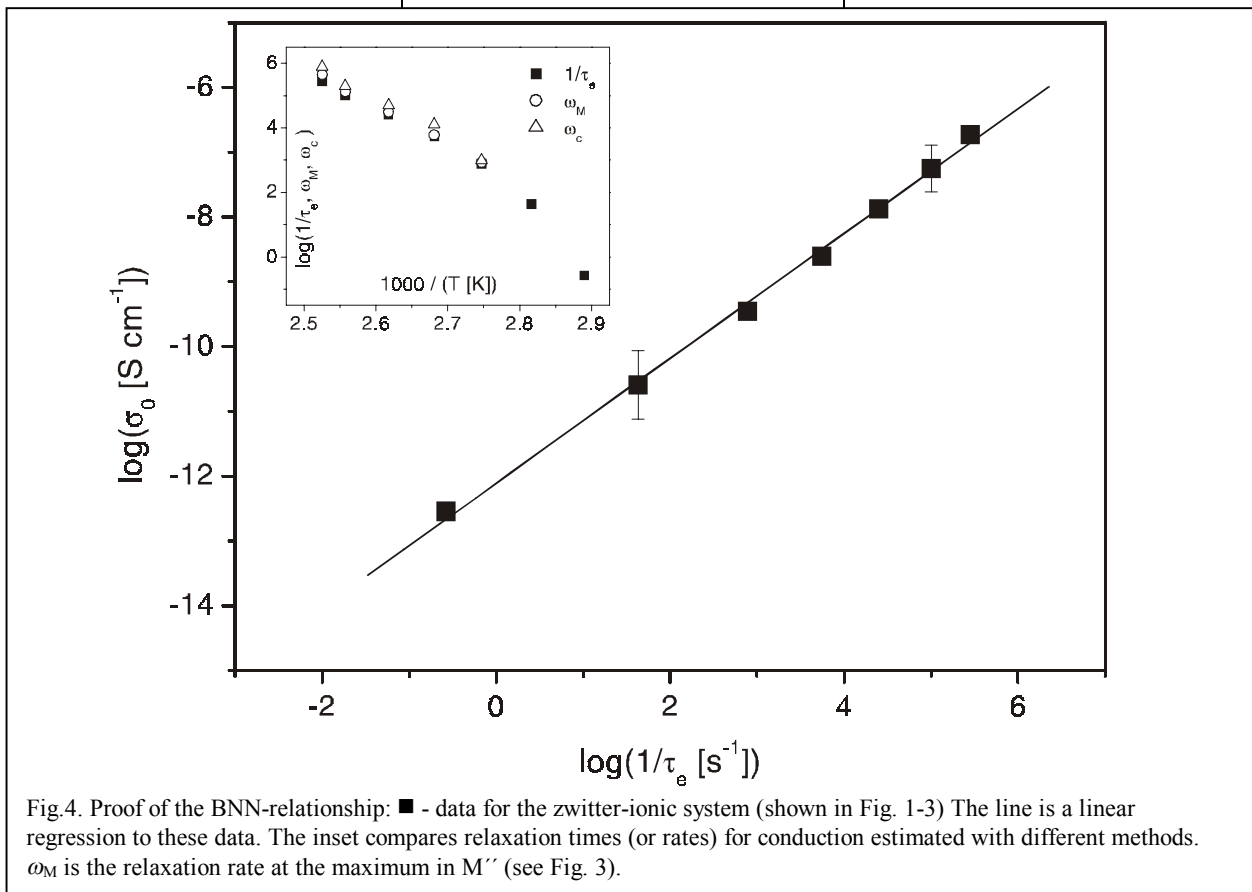

Fig.4. Proof of the BNN-relationship: ■ - data for the zwitter-ionic system (shown in Fig. 1-3) The line is a linear regression to these data. The inset compares relaxation times (or rates) for conduction estimated with different methods. ω_M is the relaxation rate at the maximum in M'' (see Fig. 3).
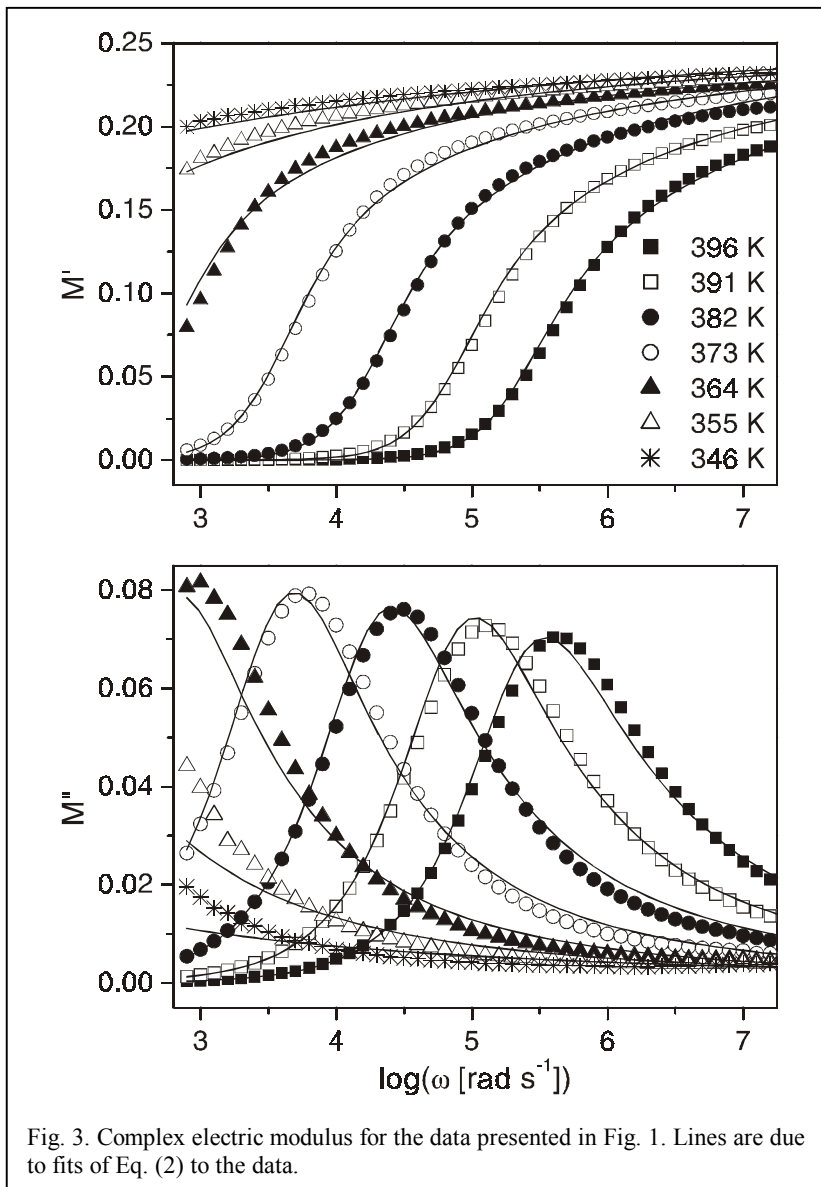
Fig. 3. Complex electric modulus for the data presented in Fig. 1. Lines are due to fits of Eq. (2) to the data.

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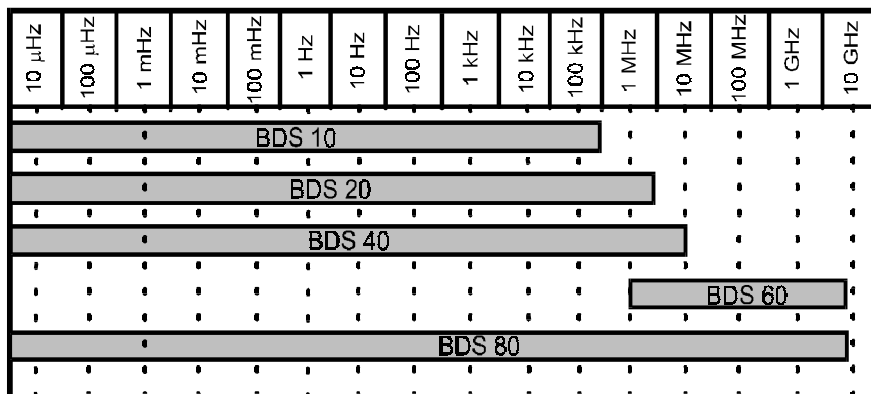04103 Leipzig, Germany
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