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Phenomenological model of nonlinear dielectric losses related to the intrinsic conductivity of dielectrics

J.A. Małecki[a]

Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17, 60-179PL Poznań, Poland

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Abstract. A phenomenological approach was applied to the dynamics of the intrinsic electric conductivity of dielectrics in an electric field in order to analyze its contribution to dielectric losses. The proposed differential equation contains only two parameters – the effective time τ_F of conductivity decay in an electric field, and τ_R, the time describing the recovery rate of the conductivity after switching off the field. The proposed approach predicts a *linear dependence* of specific conductivity of dielectrics *on the sample thickness*, as experimentally confirmed by Du Pont [1] for Teflon FEP. The field and time (or frequency) dependences of intrinsic conductivity and related dependences of dielectric losses were calculated, analyzed and illustrated with the published experimental data. The results show that the discussed contribution in dielectric losses is characterized by two hyperbolas (instead of one) while the distance between the branches depends on the intensity of applied electric field.

PACS. 72.20.Ht High-field and nonlinear effects – 72.80.Sk Insulators – 77.22.Gm Dielectric loss and relaxation

1 Introduction

Developing a theoretical description of the intrinsic electric conductivity in dielectrics is a difficult and arduous task. An exact description of the mechanisms of electric conductivity in dielectrics leads to a set of partial differential equations, which are unsolvable analytically. Experimental study of intrinsic conductivity is also a complex task, since the application of the electric field usually involves some additional processes that disturb the time dependence of conductivity. For this reason, a large number of research papers and monographs devoted to the electrical conductivity of dielectrics focus on specific problems such as generation and annihilation of charge carriers and transport mechanisms.

Early studies of the nonlinear dielectric effect (NDE) of low conductance polar liquids [1–5], where *Joule heat* obscures the measurements, motivated studies of the electrical conductivity of dielectrics. Initial experiments [6] and theoretical work [7] began in the sixties. Silver applied of the gas conductivity model to the solid phase [8], and implementation of the dimensionless form of Thomson's equations has led to a description of the selected stationary and non-stationary states [9,10].

A well known phenomenon, which accompanies the application of an electric field to low conductivity media, is a decrease of the electric conductivity G and its recovery after switching off the field. Schematically this is shown in Figure 1, where we use the relative conductivity $g(t) \equiv G(t)/G_0$ rather than G, where G_0 denotes the equilibrium value for $E = 0$. This is usually a very complex process involving several contributions of different origin e.g. the generation and annihilation of natural charge carriers in the dielectric, creation of non-compensated spatial charge areas and, in a fluid state, the motion of charged macroscopic particles.

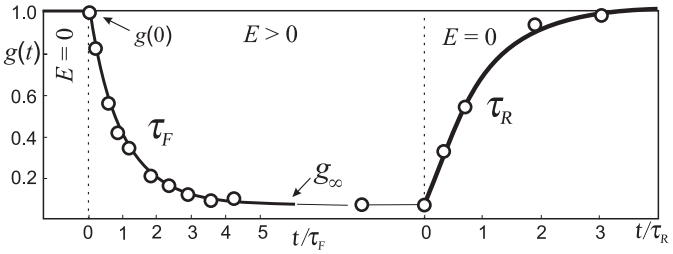

Fig. 1. Decay and recovery of relative, intrinsic conductivity of dielectrics (schematically, see text). Experimental points (circles) obtained for nitrobenzene illustrate the typical behavior.

No matter what kind of processes are responsible for the dynamics of the intrinsic, specific conductivity in an electric field, it should lead to a nonlinear dependence of dielectric losses (ε'') on the field strength. *The aim of this work is to find an approximate picture of this effect.* To achieve this goal we have to formulate the above defined

[a] e-mail: malecki@rose.man.poznan.pl

function $g(E,t)$ in such a way that it accounts for the experimental points (circles) shown in Figure 1.

Difficulties in obtaining a rigorous theoretical description of electrical conductance of dielectrics lead us to abandon the idea of modeling the mechanisms responsible for the observed processes. Instead, we choose a phenomenological approach. We seek therefore an analytical solution $g(E,t)$ describing the conductivity decay in the static electric field E, and its recovery after switching off the field. Finally we need a function $\varepsilon''(E,\omega)$ to simulate the intrinsic conductivity background that obscures the dielectric spectra at low frequencies. A similar approach reported earlier [11,12] has lead to the explanation of the unusual stability of the electret charge as well as to an understanding of the effect of improved stability of the electrets decreasing thickness.

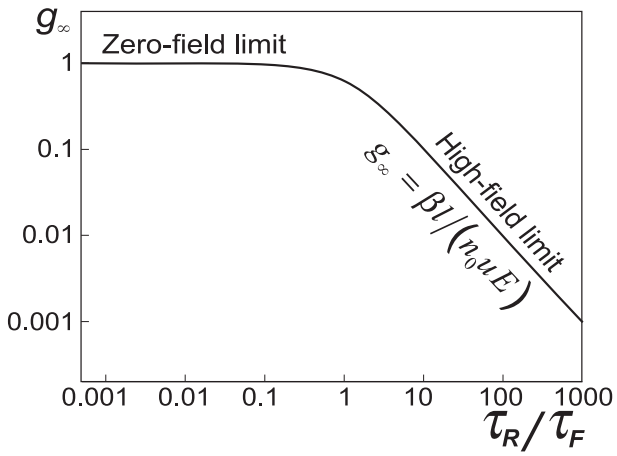

Fig. 2. The dependence of final relative conductivity g_∞ on the ratio τ_R/τ_F.

2 Phenomenological approach

Considering the mathematical complication we will not attempt a description of the mechanisms responsible for the conductivity evolution in an electric field. Instead, we will confine our attempt to a phenomenological approximation of the time dependences of current and conductivity. Therefore, we propose the following semi-empirical differential equation describing the conductivity decay and its recovery:

$$\frac{dg\,(t)}{dt} = \frac{1-[g\,(t)]^2}{\tau_R} - \frac{g\,(t)}{\tau_F}. \tag{1}$$

The equation contains only two parameters: times τ_F and τ_R – the effective time of conductivity decay in an electric field, and the time of the recovery of conductivity after switching off the field, respectively (see Fig. 1).

Equation (1), resembling Thomson's model, suggests the approximate intuitive physical meaning of the parameters. Namely, τ_F, in a crude approximation, expresses the mean time of flight $\tau_F \cong l/(E\sqrt{u^+u^-})$, whereas the approximate relation $\tau_R \cong 1/\sqrt{\alpha\,\beta}$ describes the rate of conductivity recovery. In the above relations l denotes the distance between electrodes and u – the carrier mobilities, α – recombination coefficient and β – the rate of carrier-pair creation. With

$$\Delta \equiv \tau_R^2 + 4\,\tau_F^2 \text{ and } B = \frac{\sqrt{\Delta}+\tau_R+2g\,(0)\;\tau_F}{\sqrt{\Delta}-\tau_R-2g\,(0)\,\tau_F}$$

the solution of equation (1) becomes:

$$g\,(t) = \frac{\sqrt{\Delta}}{2\tau_F}\,\frac{\sinh\left[\dfrac{\sqrt{\Delta}}{\tau_F\tau_R}\,t+\ln|B|\right]}{\cosh\left[\dfrac{\sqrt{\Delta}}{\tau_F\tau_R}\,t+\ln|B|\right]+\mathrm{sgn}\,(B)} - \frac{\tau_R}{2\tau_F}. \tag{2}$$

If the electric field is on, the parameter B is negative, and the function $g\,(t)$ is described by a hyperbolical cotangent. After switching the field off, $B>0$ and the function $g\,(t)$ now adopts the form of a hyperbolical tangent. Since it is analytical, the equation (2) can be used to compare with the experimental data.

In Figure 1 only one example – the decay and recovery of conductivity observed in nitrobenzene is shown, but a similar fit was made for a number of organic compounds including nitro and cyano derivates and higher alcohols, and their solutions in nonpolar and polar solvent. The results show that to a reasonable degree of approximation, the proposed phenomenological approach reproduces the dynamics of the intrinsic conductivity of dielectrics.

Very important and interesting is the *boundary case* – the dynamic equilibrium in the electric field is achieved for $t\to\infty$ with the respective minimum value of the conductivity g_∞ (see Fig. 2). Evaluating the approximate formula

$$\tau_R/\tau_F \cong n_0 uE/(\beta l) \tag{3}$$

g_∞ can be expressed as

$$\lim_{t\to\infty} g\,(t) \equiv g_\infty = \frac{1}{2}\left(\sqrt{\left(\frac{\tau_R}{\tau_F}\right)^2+4}-\frac{\tau_R}{\tau_F}\right) = \frac{2\beta l}{\sqrt{n_0^2u^2E^2+4\beta^2l^2}+n_0uE}. \tag{4}$$

Figure 2 shows a plot of equation (4). Two limiting values can be distinguished:

(a) For small values of the fraction τ_R/τ_F, i.e. in *weak–field limit* $E \ll \beta\,l/n_0u$, one obtains $g_\infty = 2\beta\,l/(2\beta\,l+n_0u\,E)\approx 1$. Such a situation is often observed in high conductivity materials, where the carrier creation rate β reaches relatively large values.

(b) On the other hand, in the strong field limits, i.e. when $E \gg \beta\,l/n_0u$, we get

$$g_\infty = \beta\,l/(n_0\,u\,E) \tag{5}$$

and the *current density does not depend* on the electric field strength (Eq. (6)).

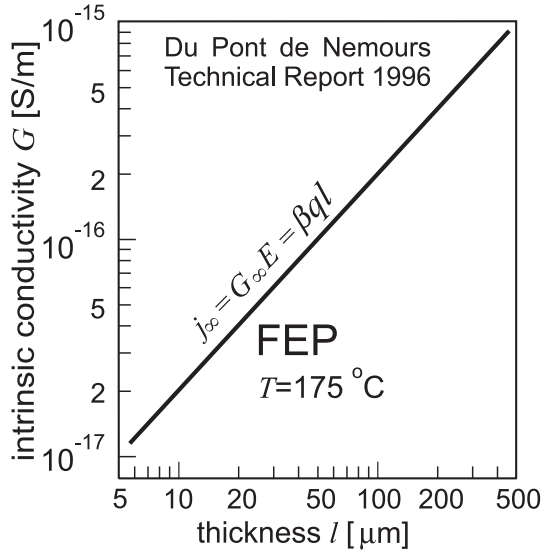

Fig. 3. Dependence of the intrinsic conductivity G of Teflon ® FEP on sample thickness [13].

Effectively, under the strong field condition, almost all the generated current carriers reach the electrodes. This means that the current density j_∞ is determined by the rate of carrier generation β and, as follows from equation (5), linearly depends on sample thickness (l):

$$j_\infty = G_\infty E = \beta q l \tag{6}$$

where q denotes the carrier charge. Somewhat unexpectedly, such behavior of the specific conductivity has been confirmed by Du Pont laboratories [13] for Teflon ® FEP (Fig. 3). This particular form of the conductivity dependence $G_\infty(l)$ reflects the volume character of the carrier generation process. Under equilibrium conditions, on the other hand, their annihilation in the electric field occurs within the two dimensional space of the electrode surface.

One should still bear in mind the strong limitations of this proposed method resulting from its phenomenological character. Above all, the physical interpretation of parameters τ_F and τ_R as related to physical quantities (such as carrier mobility and rate of creation and recombination coefficient) is a very crude approximation. In particular, as a result of the formation of space charge, both the electric field distribution and the proposed approximate physical meaning of the parameters τ_F and τ_R can be strongly disturbed. For the same reason, the equation (4) describing the conductivity g_∞ for dynamic equilibrium has also only an approximate meaning. Less significant is the field effect on mobilities u^+ and u^-, since it is observed for very strong fields, normally not applied in dielectric relaxation studies as discussed below.

3 Conductivity in alternating electric field

Numerous studies of dielectrics are carried out in alternating electric fields with a wide range of frequencies ω.

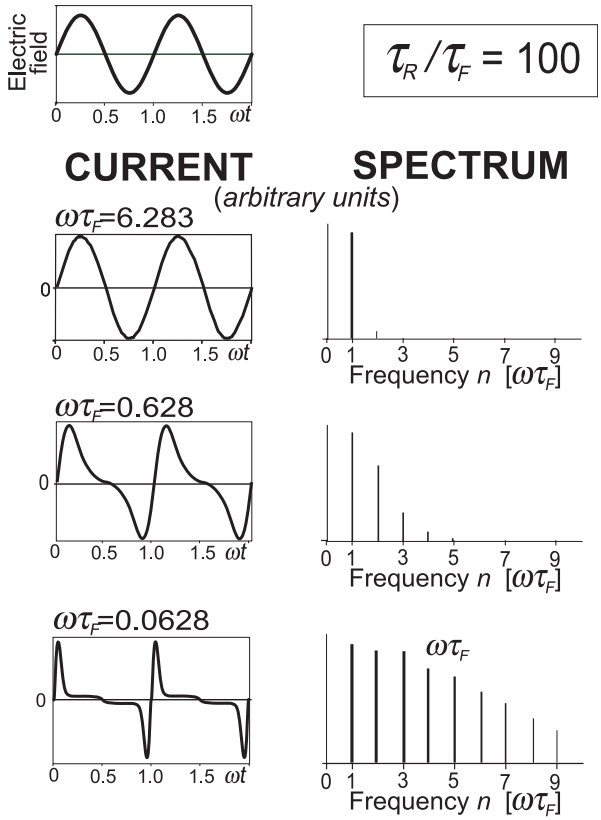

Fig. 4. Current densities versus time and respective spectra (both in arbitrary units) for three selected values of the frequency $\omega\,\tau_F$.

The dielectric relaxation studies in low frequency range are difficult to accomplish owing to a troublesome background effect related to the DC conductivity. The phenomenological approach proposed here provides a means to evaluate and to account for the relative contribution of this conductivity. Adopting a sine-wave electric field of the form $E = E_0 \sin(\omega t)$ we may, just as before (Eq. (1)), write the rate equation of relative electrical conductivity as

$$\frac{d\,g(t)}{d\,t} = \frac{1 - g^2(t)}{\tau_R} - \frac{\sin(\omega t)\,g(t)}{\tau_F}, \tag{7}$$

where $\tau_F \cong l/(E_S\,u)$ is now related to the effective field strength value E_S. Unfortunately, this equation cannot be solved analytically and numerical methods have to be used.

Dependence of the conductivity on time and the electric field strength leads to a nonlinear relationship between the current densities and these parameters. Current versus time, and respective spectra expressed in arbitrary units for $\tau_R/\tau_F = 100$ are illustrated in Figure 4 for three selected values of frequency. Similar graph are obtained for constant frequency versus the ratio τ_R/τ_F (or electric field strength). The outcome of the calculation is that, irrespective of the field strength, the ratio τ_R/τ_F is one of the decisive factors, rather than the magnitude E_S itself. In practice, we apply a field that can be considered as

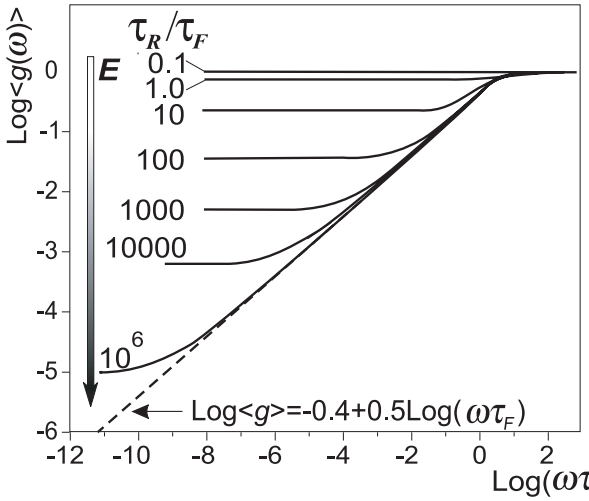

Fig. 5. Logarithm of the average conductivity $\mathrm{Log}\langle g(\omega)\rangle$ versus Log ω. The ratio τ_R/τ_F, which can be taken as a measure of the electric field strength, is the varied parameter.

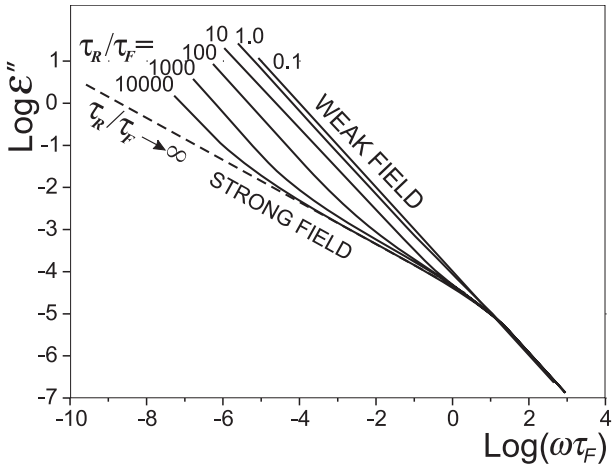

Fig. 6. Logarithm of the dielectric losses versus Log $(\omega\tau_F)$. The equilibrium conductivity was taken to be $G_0 = 10^{-13}$ S/m.

"strong" when the following condition of the E_S/l ratio is fulfilled:

$$\frac{\tau_R}{\tau_F} \cong \frac{G_0}{\beta q}\frac{E_S}{l} > 1. \tag{8}$$

In the "strong" field, in this meaning, the sine–like function of the current density appears distorted. For this reason, in the case of the AC electric field, we have to define an *average* electric conductivity

$$\langle G(\omega)\rangle \equiv \frac{\int_0^{T/2} G(\omega,t)\,E(\omega,t)\;dt}{\int_0^{T/2} E(\omega,t)\;dt}. \tag{9}$$

Results of the numerical calculations performed in a wide range of frequencies and τ_R/τ_F ratios (or electric field – see Eq. (3)) are shown in Figure 5. These show that in alternating field the unique parameter τ_R/τ_F is significant, in contrast to the steady field case where the two separate times describing the time evolution of conductivity are involved (see Eq. (2)). This property was tested empirically by calculations performed in the range of 10 orders of magnitude for τ_F and 15 orders of magnitude for the ratio τ_R/τ_F.

The ratio τ_R/τ_F directly relates to the rate of carrier generation β (Eq. (3)). It can be determined by measuring $g_\infty \equiv G_\infty/G_0$ in a steady electric field because, according to equation (4),

$$\frac{\tau_R}{\tau_F} = \frac{1-g_\infty^2}{g_\infty}. \tag{10}$$

Two measurements must be made to achieve this goal: (i) with the careful choice of time $t > \tau_F$ one obtains G_∞, (ii) during $t \ll \tau_F$ one measures G_0 in a pulse mode. Sometimes it is more convenient to apply the above unambiguous relation between $\langle g(\omega)\rangle$ and τ_R/τ_F, outlined with the results in Figure 5. Hence, resorting to only two measurements of the conductivity – in low frequency range (G_∞), and at high frequencies (G_0) – one can experimentally determine the effective value of τ_R/τ_F ratio. It should be noted however, that in the case of AC field E means the effective electric field strength.

4 Component of dielectric losses related to the intrinsic conductivity

We will now use the well-known relationship between specific electrical conductivity and dielectric losses:

$$\varepsilon''(\omega) = G/\varepsilon_0\omega. \tag{11}$$

When the conductance G does not depend on external parameters, as commonly assumed, one obtains the well-known, hyperbolical relation between dielectric losses and frequency. However in our case, when conductance depends on time and the intensity of electric field, the dependence becomes more complex.

Results of our calculations are shown in Figure 6. As an example, we have assumed the initial, equilibrium conductivity $G_0 = 10^{-13}$ S/m – a sample of relatively low conductivity. The results show, as one might expect, that for *weak* electric field (comp. Eq. (8))

$$E_S < \frac{\beta g l}{G_0}\frac{\tau_F}{\tau_R}$$

the hyperbolical dependence of dielectric losses is predicted. One obtains such dependence also at *high* frequencies $(\omega\tau_F > 10)$. However, for stronger fields and lower frequencies the model predicts a clear-cut deviation from hyperbolical dependence.

Schematically the results for the frequency dependence of the intrinsic conductivity and dielectric losses are shown in Figure 7. The conductivity dependence $G(E,\omega)$ is characterized by two dynamical equilibrium states: starting

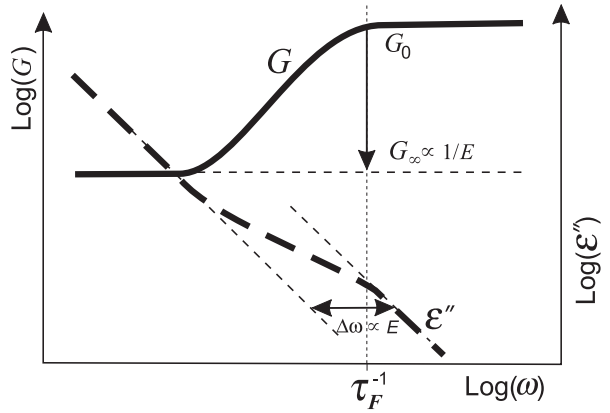

Fig. 7. Schematic representation of the frequency dependence of the intrinsic conductivity G and the related contribution of dielectric losses ε'' presented in double logarithmic scale.

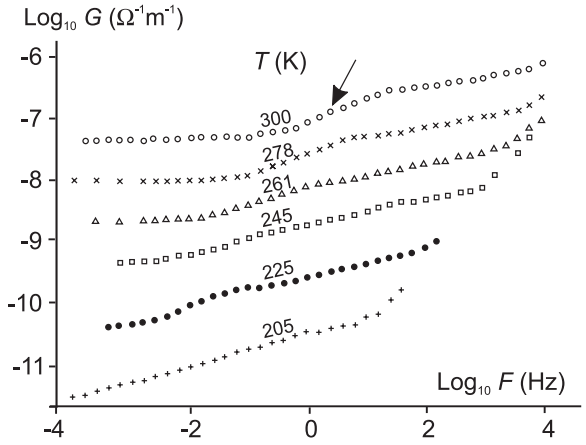

Fig. 8. The frequency dependence of the conductivity of chalcogenide glass for a range of temperatures [14]. A drop in conductivity is clearly seen.

from the value G_0 at frequency $\omega > \omega_F$ and reaching G_∞ at low frequency range for $\omega \ll \omega_F$, with an almost linear region in between. Using a double logarithmic scale, the two linear branches characterize the dielectric losses $\varepsilon''(E, \omega_E)$.

5 Comparison with experimental results

The characteristic decay time τ_F is, in crude approximation, equal to the mean time of flight $\tau_F \cong l/(E\,u)$ of the current carriers. In dielectric liquids the carrier's mobility is usually of the order of 10^{-6}–10^{-10} m^2 V^{-1} s^{-1}. With one volt applied to 1mm thick sample, the characteristic frequency is of the order of 10^{-1}–10^3 Hz. In solid state, the effective mobilities may attain values over a much broader range, consequently the discussed phenomena can be observed in a wider range of frequencies.

Adopting similar procedures one may evaluate the critical intensity E_c of electric field using equations (3) and (8) and assuming $\tau_R/\tau_F = 1$:

$$E_c = \frac{bql}{G_0} = \frac{j_\infty}{(dj_\infty/dE)_{E=0}}.$$

In practice, for weakly conducting sample E_c is of the order of 1 V or even less.

In the literature one finds the results of experimental study of intrinsic conductivity and dielectric losses in low frequencies, between 10^{-3}–10^3 Hz. In Figure 8 we give the results of conductivity measurements published by Jonscher and Frost [14] for chalcogenide glass over a low frequency range. The shape of the plots suggests that the mechanism we propose and discuss may be responsible for the observed drop in conductivity occurring between 0.1–10 Hz.

In the next two figures (Figs. 9–10) we quote the original results of the frequency dependence of the dielectric losses in ionic conductor Hollandite [15] and $PbTiO_3$–PVDF composites [16], correspondingly. In both

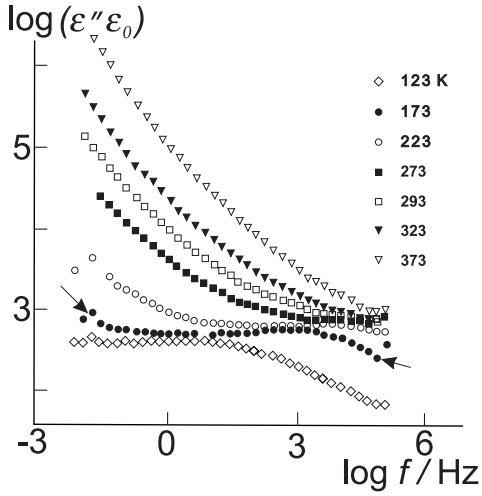

Fig. 9. The frequency dependence of the dielectric losses of the ionic conductor Hollandite $K_{1.8}Mg_{0.9}Ti_{7.1}O_{16}$ [15]. The arrows indicate the most characteristic dependence (comp. Fig. 8).

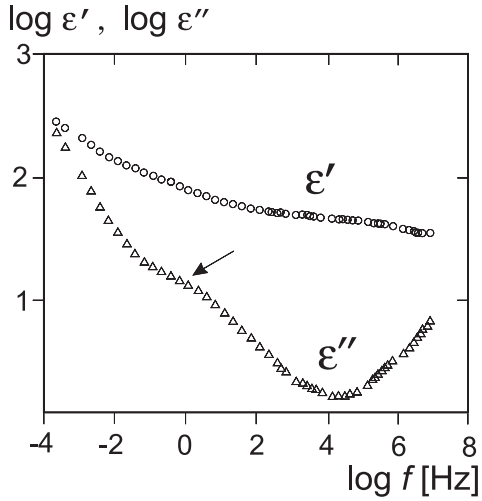

Fig. 10. The low frequency dielectric relaxation of $PbTiO_3$–PVDF composite [16]. The two linear branches can be distinguish in the frequency dependence of dielectric losses ε'' (comp. Fig. 8).

cases the characteristic two linear branches can be identified. In the literature, one can find many similar results, although the slopes of the linear branches are usually far from unity. Moreover, for an unambiguous interpretation of these data it would be required to examine the effect of magnitude of the electric field on the magnitude of the decrease in electrical conductivity, or on the magnitude of the frequency shift in the case of dielectric losses. Unfortunately, there are no such systematic studies available in the literature, which would provide the data for a sufficiently large range of electric field intensities.

6 Conclusions

A semi-empirical description of the dynamics of the intrinsic electrical conductivity of dielectrics using two parameters τ_F and τ_R is shown. These parameters have some *intuitive, approximate* physical meaning: τ_F denotes the effective, apparent time of conductivity decay, which may be associated with the time of flight $\tau_F \cong l/(E\sqrt{u^+u^-})$ of the current carriers in an electric field. τ_R denotes the apparent recovery time of conductivity after switching the field off, and can be approximated as one over the square root of the product of the recombination coefficient α and the carrier creation rate β, i.e. $\tau_R \cong 1/\sqrt{\alpha\,\beta}$.

The proposed approach predicts the *linear dependence of specific conductivity of low-conducting substances on the sample thickness*. The results previously reported by Du Pont [13] for Teflon FEP agree with the above predictions.

The phenomenological model was applied for calculations of the electric field and frequency dependence of the dielectric losses component $\varepsilon''(E,\omega)$ related to the dynamics of the intrinsic conductivity $G(E,t)$ of dielectrics.

Numerical methods were used for calculating $\varepsilon''(E,\omega)$. We find that the influence of field E becomes essential when its frequency $\omega < 1/\tau_F$ and $\tau_R/\tau_F \gg 1$, e.g. for "strong" electric field $E \gg \beta\, l/(n_0 u)$.

The conductivity dependence $G(E,\omega)$ is characterized by two dynamical equilibrium states: starting from the value G_0 at frequency $\omega > 1/\tau_F$, reaching G_∞ at low frequency range $\omega \ll 1/\tau_F$, with a nearly linear transition in between (Figs. 6, 7). The related dielectric losses $\varepsilon''(E,\omega)$ are characterized by two linear branches (Figs. 5, 7). Such behavior can be found in the published experimental data.

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