Relaxation and Resonance Absorption in Dielectrics

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An alternative approach to the dielectric relaxation and resonance absorption is proposed. Two assumptions were taken into consideration. One, that there exists a dielectric in which particular molecules have different freedom of motion. The other, that the value of the motion damping coefficient can be described by the distribution function. The obtained formula for the description of the experimental data of dielectric relaxation and resonance absorption measurements is presented.

Key words: Dielectrics; Debye Relaxation; Poley Absorption.

Introduction

The behaviour of dielectrics in an electromagnetic field is of great interest to many researchers. A lot of papers have been and are still being published on this subject [1, 2].

In the historical Debye model the molecules have a limited freedom of motion, so only the relaxation with one relaxation time \( \tau \) is possible [3]. Expanding this model gave a relatively good agreement with the experimental data by using the semi-experimental Cole-Cole [4] and Cole-Davidson [5] relations. For dielectrics which cannot be described by the Debye model (one relaxation time), several relaxation times or even their distribution are postulated [6]. Different functions were suggested for describing the distribution of the relaxation times [6, 7]. In the Cole-Davidson formula, either the existence of several relaxation times or a non-symmetrical distribution function of the relaxation times is assumed. The most general and perhaps best suggestion describing the dielectric behaviour in the electrical field is the one proposed by Dissado and Hill [8].

The above mentioned works concern absorption connected with relaxation, i.e. dipole reaction to the external electrical field of frequencies up to microwave ones. This absorption gives a curve which is never narrower than relation (3). Apart from this absorption, which is relatively well described in literature, there exists another one at higher frequencies.

Distortions in the range of high frequencies have been observed in alcohols [9] and also in benzene derivatives [10]. It was also found that they have a resonance character [11]. Models explaining this phenomenon have been described [12 - 15].

In [2] a good description of the behaviour of \( \text{CH}_3\text{Cl} \) (at 193 K) in an alternating “enlarged” electrical field is given. This dielectric spectrum has two maxima, one in the microwave region \( (\omega_{\text{max}} = 2.5 \cdot 10^{10} \text{ Hz}) \) and the other one in the infrared range \( (\omega_0 = 2.5 \cdot 10^{12} \text{ Hz}) \).

The described method of treating molecules in a dielectric is different from any approaches existing so far. Two assumptions were taken into consideration. One, that there exist dielectrics in which particular molecules have a different freedom of motion. The other one, that the motion damping coefficient can be described by the distribution function. Different functions defined as distribution functions of the damping coefficient are discussed here.

It seems that the proposed explanation of the behaviour of molecules in a dielectric is quite reasonable. Thus it is worth looking at the results obtained with these assumptions.

Theory

According to Debye’s theory [3] the polarisation of a dielectric resulting from permanent dipole moments of molecules decays exponentially. This can be expressed by the relaxation equation

\[
\frac{dP}{dt} + \frac{1}{\tau}P = 0,
\]

\[
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\]
If an alternating electric field

\[ E = E_0 \exp(i \omega t) \]

is applied to a dielectric, the polarisation equation takes the form

\[ \frac{dP}{dt} + \frac{1}{\tau} P = aE \]

and the polarisation is obtained in the form

\[ P = P_0 \exp \left( i(\omega t + \varphi) \right) = \frac{a\tau}{1 + \omega^2 \tau^2} E. \]  \hspace{1cm} (1)

The experiment provides the dielectric susceptibility [16, 17, 19]

\[ \chi(\omega) = \frac{dP}{dE}. \]  \hspace{1cm} (2)

In our case

\[ \chi_D(\omega) = \frac{\chi_0 \tau}{1 + i\omega\tau}, \]

or

\[ \chi_D''(\omega) = \frac{\chi_0 \omega^2 \tau}{1 + i\omega\tau}, \chi_D'(\omega) = \frac{\chi_0 \omega \tau}{1 + i\omega\tau}, \]  \hspace{1cm} (3)

where \( a = \chi_0 \) in relation (1), since for \( \omega = 0 \), \( \chi_D'(0) = \chi_0 \), \( \chi_D''(0) = 0 \), and for \( \omega \to \infty \chi_D'(\infty) = 0 \) and \( \chi_D''(\infty) = 0 \). (The dielectric permittivity \( \varepsilon(\omega) \) is often introduced: \( \varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \), \( \chi(\omega) = \varepsilon'(\omega) - 1 \), \( \chi''(\omega) = \varepsilon''(\omega) - 1 \).

These are Debye’s relations that describe well the behaviour of dispersion and of absorption caused by permanent dipole moments of many dielectrics.

Let us consider a dielectric in which the molecules are freer than in the dielectric analysed by Debye. This dielectric, as the previous one, is placed in a harmonic electric field. Now the polarisation will be described by [18, 19]

\[ \frac{d^2P}{dE^2} + 2a\frac{dP}{dt} + \omega_1^2 P = aE. \]

A solution of the form

\[ P = P_0 \exp \left( i(\omega t + \varphi) \right) = \frac{aE}{\omega_1^2 + \omega^2 + 2i\omega_1 \omega} \]

\[ \chi(\omega) = \frac{\chi_0 \omega_1^2}{\omega_1^2 + \omega^2 + 2i\omega_1 \omega}, \]

and the real and imaginary parts of the dielectric susceptibility can be written as

\[ \chi'(\omega) = \frac{\chi_0 \omega_1^2 (\omega_1^2 - \omega^2)}{(\omega_1^2 - \omega^2)^2 + 4\alpha^2 \omega_1^2 \omega^2}, \]

\[ \chi''(\omega) = \frac{2\chi_0 \omega_1^2 \omega^2}{(\omega_1^2 - \omega^2)^2 + 4\alpha^2 \omega_1^2 \omega^2}, \]  \hspace{1cm} (4)

where \( \alpha \) is a coefficient responsible for the damping of the motion of the molecules. Now \( \alpha = \chi_1 \omega_1^2 \), since for \( \omega = 0 \), \( \chi''(0) = \chi_0 \), \( \chi'(0) = 0 \), and for \( \omega \to \infty \), \( \chi'(\infty) \) and \( \chi''(\infty) = 0 \).
The function $\chi''(\omega)$ (4) has a maximum for
\[
\omega_{\text{max}} = \frac{\omega_0^2 - 2\alpha^2 + 2\sqrt{\alpha^4 - \alpha^2 \omega_0^2}}{3}.
\] (5)

Figure 1 shows changes of the functions $\chi''(\omega)$ and $\chi''(\omega)$ versus $\alpha$. For $\alpha \geq 10$ ($\omega_0 = 1$) the diagrams of $\chi''(\omega)$ and $\chi''(\omega)$ differ and can be very big, while $\chi''(\omega)$ and $\chi''(\omega)$ do not differ (visually) from the diagrams of the Debye's relations (3) ($\chi''(\omega)$, $\chi''(\omega)$).

The relations (4) are a description of the molecular motion when all the molecules are equally damped. Let us assume that we deal with a medium in which the damping of the motion is different for each molecule. The freedom of motion depends on the distribution of the damping coefficient of the molecules at a given moment, and first of all on the closest neighbours of a particular molecule. Thus, at a given moment $\alpha$ takes different values for each molecule. For further consideration, the distribution of the damping coefficient must be determined.

**Distribution of the Damping Coefficient**

In order to obtain the absorption maximum that is observed in dielectrics, the distribution function of the damping coefficient must be a "bell" function and, since it also has to describe the dielectric behaviour shown by the Cole-Cole relation [4], it must be symmetrical. Let $f(\alpha)$ fulfill our requirements and have the maximum at $\alpha = \alpha_0$. Thus the dielectric susceptibility can be written as

\[
\chi''(\omega) = \sum_i \frac{b_i \chi_0 \omega_0^2}{(\omega_0^2 - \omega^2)^2 + 4\alpha_i^2 \omega^2},
\]

\[
\chi'(\omega) = \sum_i \frac{b_i \chi_0 \omega_0^2}{(\omega_0^2 - \omega^2)^2 + 4\alpha_i^2 \omega^2},
\]

where $b_i$ is the normalised value of our distribution function $f(\alpha)$ for $\alpha_i$.

We know that for $\alpha < 10$ (Fig. 1) the maximum values of $\chi''(\omega)$ (4) differ and can be very big, while for $\alpha > 10$ all the $\chi''(\omega)$ components reach the maximum value of 0.5 ($\chi_0 = 1$, $\omega_0 = 1$).

Thus, one should expect that two maxima will occur for $\chi''(\omega)$ (6), one derived from the small values of $\alpha < 10$, situated close to $\omega_0$, and the other one for $\alpha > 10$. This maximum will occur at $\omega_{\text{max}}$ (5) when $\alpha = \alpha_0$. This is the value at which the distribution function $f(\alpha)$ has the maximum, hence $\chi''(\omega)$ will also take the highest value.

The frequency of the relaxation maximum $\omega_{\text{max}}$ depends on $\epsilon_0$ and $\omega_0$ and is always smaller than $\omega_0$. We relate $\omega_{\text{max}}$ to the frequency of the absorption maximum described by Debye, and the resonance maximum for frequency $\omega \approx \omega_0$ to the one described by Poley.
For simplicity it was assumed that all the molecules are represented by only one frequency $\omega_1$. For testing this it was assumed that $\omega_1 = 1$ and $\chi_0 = 1$ (Table 1, Table 2).

### Application

The Gauss function was used as the distribution function $f_0(\alpha)$ of the damping coefficient

$$f_0(\alpha) = A \exp \left\{ - (\alpha_1 - \alpha) c_0^2 \right\}.$$  \hspace{1cm} (7)

The parameters $c_0$, $\alpha_0$, $\alpha_1$, $\alpha$ (the smallest and the largest values of the damping coefficient) decide about the shape of $\chi'(\omega)$ and $\chi''(\omega)$ (6). The results obtained by using Debye’s (3), the Cole-Cole [4] and Dissado-Hill [8] relations as the “standard” together with the results obtained from the above discussed formulas are presented in Tables 1 and 2.

Table 1 shows that the higher $\alpha_0$ and $c_0$, the closer are the results to the values of $\chi'_0(\omega)$ and $\chi''_0(\omega)$ obtained with the Debye relation (3). However, one does not obtain full agreement of the results. With increase of frequency the way the values of $\chi'_0(\omega)$ and $\chi''(\omega)$ tend to zero is different. $\chi''(\omega)$ is always bigger than $\chi'(\omega)$. 

Table 2 presents results of the Cole-Cole and Dissado-Hill formulas and the ones discussed above. The calculations were carried out for $\eta = 0.6$ of the Dissado-Hill formula parameters. For these parameters $\chi''_{max} = 0.32550$. The parameters of the other formulas, i.e. Cole-Cole (h) and the tested ones were chosen in such a way that in all cases the same value of maximum was obtained as in the case of the Dissado-Hill relation. As can be seen, the results in all columns are different.

The Gauss function as a distribution function does not fulfil all the expectations. The resonance peak occurs for lowered Cole-Cole arcs ($\alpha_0 < 4$, $\chi''_{max} < 0.4$). However, for benzene derivatives it was experimentally found that there exists a relaxation which can be well described by the Debye’s formula [10] ($\chi'' = 0.5$) and a peak in the high frequency range.

Thus the question arises about the conditions the distribution function should fulfil additionally to the ones mentioned earlier. First of all it should more “gently” tend to zero than the Gauss function, so that the resonance peak would occur simultaneously with the relaxation described by Debye’s formula (3). The shape of the function is also important. It must retrace the lowered arcs at the curve of $\chi''(\omega)$ versus $\chi'(\omega)$ (Cole-Cole diagram). The function that is the sum of two Gauss functions was then tested as the distribution function of the damping coefficient:

$$f_1(\alpha_1) = A \left\{ \exp \left[ - (\alpha_1 - \alpha_0)^2 c_0^2 \right] + d \exp \left[ - (\alpha_1 - \alpha_0)^2 c_1^2 \right] \right\}.$$  \hspace{1cm} (8)

### Table 2

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<th>$\omega_1$</th>
<th>Cole-Cole</th>
<th>Dissado-Hill</th>
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Table 2. b) $\chi''(\omega)$ calculated from the Cole-Cole, Dissado-Hill and discussed formulae (6) for different distribution functions of the damping coefficient ($\chi''_{max} = 0.32550$).
Fig. 2. Acetone-cyclohexane. Circles: experimental points [20], solid line: formula (6) with function (9) ($\epsilon_0 = 20, \frac{\omega_1}{\omega_0} = 10, \frac{\omega_2}{\omega_0} = 0.25, \frac{l}{\omega_0} = 25.1, \frac{s}{\omega_0} = 0.008$).

Fig. 3. Acetone-decaline. Circles: experimental points [20], solid line: formula (6) with function (9) ($\epsilon_0 = 7, \frac{\omega_1}{\omega_0} = 9, \frac{\omega_2}{\omega_0} = 0.28, \frac{l}{\omega_0} = 16.0, \frac{s}{\omega_0} = 0.043$).

Fig. 4. Undecanone-6-cyclohexane. Circles: experimental points [20], solid line: formula (6) with function (9) ($\epsilon_0 = 10, \frac{\omega_1}{\omega_0} = 75, \frac{\omega_2}{\omega_0} = 0.35, \frac{l}{\omega_0} = 149.6, \frac{s}{\omega_0} = 0.022$).

Fig. 5. Fluoromethane. Circles: experimental points [21], solid line: formula (6) with function (9) ($\epsilon_0 = 20, \frac{\omega_1}{\omega_0} = 28.5, \frac{\omega_2}{\omega_0} = 0.12, \frac{l}{\omega_0} = 46.7, \frac{s}{\omega_0} = 0.002$).
It turns out that the contribution of the second component, \( A \cdot d \exp[-\alpha_t - \alpha_0] c_1^* \), is small (0.2 \( \div 4\% \)) and is almost constant in the range of summing \( \alpha_t \mid \alpha_t \mid \alpha_0 \). Hence a simpler form of the distribution function of the damping coefficient can be used, namely

\[
f_2(\alpha_t) = A \exp[-\alpha_t - \alpha_0] c_0^* + \epsilon, \tag{9}\]

where \( \epsilon \) is constant for a given dielectric.

Literature data for five dielectrics [2, 20, 21] were used for testing. All these dielectrics show two absorption maxima: the relaxation and the resonance one (Figs. 2 - 6). Using (6), a probable shape of \( \chi''(\omega) \) was reproduced by fitting the curve to the experimental data. Two functions were used as the distribution functions of the damping coefficient, that is \( f_1(\alpha_t) \) (8) and \( f_2(\alpha_t) \) (9). For all dielectrics the fittings of the two functions did not differ.

The fitting parameters are shown below the figures. Scales from the original works were used. It seems that the maxima assigned to the relaxations are well described by the curves. However, the fittings of the curves to the experimental points of the resonance maxima are a matter of concern. A tendency to shift from the experimental points can be observed in the high frequency range. However, the general fitting of the curves to the experimental data is good.

Discussion

The approach presented here seems to be quite natural and the results fit both to the experimental data and to the formulas used earlier. We sought for a formula describing both Debye’s and Poley’s absorptions.

As it was already said (Table 1), the formulas (6) with the distribution function of the damping coefficient (7) give results that agree well with the results of Debye’s relation (3). The functions \( f_1(\alpha_t) \) (8) and \( f_2(\alpha_t) \) (9) can also be used as the distribution function of the damping coefficient.

As can be seen from Table 2, Gauss’s function as a damping coefficient distribution function gives results that differ most from the results obtained with the Cole-Cole relation. The results obtained from the function \( f_2(\alpha_t) \) (9) seem to fit best to this relation.

The agreement with the Cole-Cole or Dissado-Hill relation will depend on the parameters of the second component of the function \( f_1(\alpha_t) \) (8) and \( f_2(\alpha_t) \) (9) (Table 2, last column).

The relation \( \chi''(\omega) \) (6) is also useful for the description of the experimental data concerning relaxation and resonance maxima (Figs. 2 - 6).

In order to describe the experimental data concerning relaxation, we need the parameter \( \epsilon_0 \) describing the width of the distribution function of the damping coefficient (equivalent of \( h \) in the Cole-Cole formula) and the parameter \( \epsilon_0 \). Thus, the relaxation time \( \tau \) is not needed for the dielectric description. We know, however, that the experimental relaxation time is determined from \( \omega_{\text{max}} \tau = 1 \). In our case, \( \omega_{\text{max}} \) is a function of \( \alpha_t \) and \( \omega_1 \) (5). It is easy to obtain for \( \omega_0 \geq 10 \) (the range of values \( \omega_0 \) corresponding to the dielectric relaxation, see Fig. 1), the simplified relation \( \omega_{\text{max}} \approx \frac{\omega_0}{2} \alpha_t \). Thus the damping coefficient \( \alpha_t \)
can be related to the relaxation time $\tau$ by $\alpha \approx \frac{1}{2} \tau \omega_0^2$. Hence, the coefficient $\alpha$ is linearly related to the relaxation time $\tau$. Therefore all known relations connected with the relaxation time will be true for the damping coefficient, among others the relation concerning the viscosity coefficient $\eta$ [22 - 24].

One can also interpret the damping coefficient with the use of Fröhlich’s model [6]. Namely, from Fröhlich’s interpretation of Eyring’s formula we obtain $\tau = \frac{\tau_0 e^{\Delta H/RT}}{1}$, where $\Delta H$ is the height of the potential barrier between the equilibrium positions of dipoles. And since there is a relation between $\alpha$ and $\tau$, one can say that the distribution function of the damping coefficient results from the distribution of the height of the potential barrier between the equilibrium positions of dipoles in a dielectric.

Concluding one can say:

The assumption that a dielectric is a set of molecules with different degrees of motion free-

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