An approach to the dielectric relaxation spectrum as a continuous distribution of Debye processes

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Abstract

Assuming that the system can be described by Debye’s model at each frequency, a method is proposed for the direct estimation at each frequency of the relaxation time \( \tau_D(\omega) \), static permittivity \( \varepsilon_\infty(\omega) \), infinite-frequency permittivity \( \varepsilon_{\infty,D}(\omega) \) and dielectric strength \( \Delta\varepsilon_0(\omega) = \varepsilon_{\infty,D}(\omega) - \varepsilon_{\infty}(\omega) \), proper of these relaxation processes, as function of angular frequency, \( \omega \). \( \Delta\varepsilon_0(\omega) \) values are a clue to the presence and magnitude of effective electric dipoles in the sample responding to the applied field at different frequency domains. Estimating the relaxation time \( \tau_D(\omega) \) at each frequency allows to contrast these values with the electric field oscillation period and i\( \omega \tau \) as basic principle that the polarization decays exponentially, the complex permittivity is given by Debye’s function, follows the branch of a rectangular hyperbola for the CC function or behaves as a Boltzmann-type sigmoid in the case of CD function. Present method is exemplified with literature data.

1. Introduction

Relaxation processes in alternating fields of angular frequency \( \omega \) are suitably represented by the relative complex permittivity \( \varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \), which is an inherent property of matter. The real part \( \varepsilon'(\omega) \) is the permittivity and the imaginary part \( \varepsilon''(\omega) \) is the loss factor, both parts being accessible to the experiment, and i\( \omega \tau \) as basic principle that the polarization decays exponentially, the complex permittivity is given by Debye’s function

\[
\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega \tau_D}
\]

(1)

Here \( \varepsilon_\infty \) is the infinite-frequency permittivity, \( \varepsilon_0 \) is the static permittivity and \( \tau_D \) is the relaxation time, which is the characteristic time constant for the relaxation process.

In eqn (1), \( \varepsilon_0 - \varepsilon_\infty = \Delta\varepsilon \) is the dielectric strength which is related to the molecular dipole moment, \( \mu \), by [1]

\[
\Delta\varepsilon = \frac{1}{3\varepsilon_0} \frac{\mu^2}{k_B T} n_v
\]

(2)

where \( n_v \) is the volume density of dipoles, \( \varepsilon_0 \) is the permittivity of vacuum, \( k_B \) is the Boltzmann constant and \( T \) is the temperature. In this expression, \( F = 1 \) in dilute solutions where local field effects can be disregarded, \( F = (\varepsilon_0 + 2\varepsilon_\infty)(\varepsilon_\infty + 2)/9 \) in case Lorentz model for polar molecules is employed, \( F = \varepsilon_0(\varepsilon_\infty + 2)^2/[3(2\varepsilon_\infty + \varepsilon_\infty)] \) in terms of Onsager theory of the reaction field and \( F = g\varepsilon_0(\varepsilon_\infty + 2)^2/[3(2\varepsilon_\infty + \varepsilon_\infty)] \), where \( g \) is the Kirkwood correlation factor, within Kirkwood model for associating condensed phases.

Analysis of complex permittivities is conveniently done by plotting \( \varepsilon^*(\omega) \) against \( \varepsilon'(\omega) \), a representation known as Argand diagram or Cole–Cole plot, in which the Debye equation describes a semi-circle linking \( \varepsilon_\infty \) to \( \varepsilon_0 \). However, since most systems do not follow eqn (1), their description is made empirically: either as a superposition of Debye functions with different relaxation times by introducing the concept of relaxation time distribution or distribution function, [2,3] \( f(\tau) \),

\[
\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \left(\varepsilon_0 - \varepsilon_\infty\right) \int_0^\infty \frac{f(\tau)\,d\tau}{1 + i\omega \tau}
\]

(3)

or by using empirical functions that have been proposed to describe non semi-circular Argand diagrams, [1,3]. Most of them are generalizations of Debye equation, as the Cole–Cole [4], Cole–Davidson [5], and Havriliak–Negami [6] functions, which lead to a single characteristic relaxation time. Another empirical approach consists in superposing two or more of the aforementioned functions and therefore to assume the occurrence of two or more relaxation times. As remarked by Böttcher and Bordewijk, [3] the relaxation time distributions experimentally determined are often ambiguous because different types of relaxation behaviour may be consistent with the dielectric data. Furthermore, in some cases the distribution function may not have a direct physical meaning. This notwithstanding, it is conventional to report and collect parameter values for the different functions or their superposition, even though many researchers prefer to draw conclusions directly from
dispersion diagrams of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$, [1], because those parameters lack physical meaning.

The theoretical advances in recent decades have been mainly directed to improve the mathematical methods for establishing distribution functions [7], or the fitting of dielectric functions [8], and the experimental techniques for dielectric characterization have also greatly improved. However, models for interpreting experimental data have not progressed much and continue to lack a sound physical basis, although recently Lukichev [9] developed an interesting damped oscillator model with non-linear spring force which appears to be able to describe both non-Debye and Debye-like relaxation spectra.

We have devised an alternative method for the analysis of dielectric dispersion data which discards empirical equations. Our method focus on the direct estimation of the underlying physical real processes leading to novel views on the interpretation of dielectric relaxation spectra.

We exemplify this method with a system that was obtained from literature.

2. The theoretical method

For systems described by the Debye equation (eqn (1)), the real and imaginary parts of the complex permittivity are given by [1]:

$$
\varepsilon'(\omega) = \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + \omega^2 \tau_D^2} \quad (4)
$$

$$
\varepsilon''(\omega) = \frac{\Delta \varepsilon}{1 + \omega^2 \tau_D^2} \omega \tau_D \quad (5)
$$

To express the derivative $d\varepsilon''(\omega)/d\varepsilon'(\omega)$ in an Argand diagram we begin by differentiating eqn (4) and (5):

$$
\frac{d\varepsilon'(\omega)}{d\omega} = -\frac{2\Delta \varepsilon \tau_D^2 \omega}{\left(1 + \omega^2 \tau_D^2\right)^2} \quad (6)
$$

$$
\frac{d\varepsilon''(\omega)}{d\omega} = \frac{\Delta \varepsilon \tau_D (1 - \omega^2 \tau_D^2)}{\left(1 + \omega^2 \tau_D^2\right)^2} \quad (7)
$$

Hence

$$
\frac{d\varepsilon''(\omega)}{d\varepsilon'(\omega)} = \frac{d\varepsilon''(\omega)/d\omega}{d\varepsilon'(\omega)/d\omega} = -\frac{1 - \omega^2 \tau_D^2}{2\omega \tau_D} \quad (8)
$$

Therefore $\tau_D$ can be obtained from the derivative $d\varepsilon''(\omega)/d\varepsilon'(\omega)$ as the solution of the quadratic eqn (8).

Next we consider the Argand diagram for a general sample having the shape depicted in Fig. 1.

At frequency $\omega_i$ the derivative $d\varepsilon''(\omega)/d\varepsilon'(\omega)$ is given by the slope of a straight line tangent to the experimental curve at that frequency. We consider the approach that this straight line is also the tangent to a semi-circle containing the data point ($\varepsilon'_i = \varepsilon'(\omega = \omega_i)$; $\varepsilon''_i = \varepsilon''(\omega = \omega_i)$) (see Fig. 1) which can be described by the Debye-like parameters $\varepsilon_{\infty,i}$, $\varepsilon_\infty$ and $n_{\infty,i}$. Since $\varepsilon'_i$ and $\varepsilon''_i$ are experimentally accessible, and the derivative $(d\varepsilon''(\omega)/d\varepsilon'(\omega))_{\infty} = \omega_i$ can be calculated by using analytical or numerical methods, we would have the means to evaluate the Debye-like relaxation time $n_{\infty,i}$ at each experimental frequency.

However, following this procedure the curvature of Argand diagrams is rather large and measurements in the frequency domain would need to be at very small intervals for a proper evaluation of that derivative. Fortunately, Cole [10], proposed two additional procedures for the analysis of dielectric data, namely plotting $\varepsilon'(\omega)$ against $\varepsilon''(\omega)/\omega$ or against $\omega \varepsilon''(\omega)$ which lead to the following linear relationships in the case of simple Debye dispersions:

$$
\frac{\varepsilon'(\omega)}{\omega} = \varepsilon_{\infty} + \frac{\varepsilon'_i}{n_i} \quad (9)
$$

$$
\varepsilon'(\omega) = \varepsilon_{\infty} - \tau_D \frac{\varepsilon''(\omega)}{\omega} \quad (10)
$$

By combining these equations we obtain the following one:

$$
\frac{\varepsilon''(\omega)}{\omega} = \Delta \varepsilon n_D - \tau_D \frac{\omega \varepsilon''(\omega)}{n_i} \quad (11)
$$

Hence for Debye dispersions the plot of $\varepsilon''(\omega)/\omega$ against $\omega \varepsilon''(\omega)$ is a straight line with slope $-\tau_D^2$ and intercept $\Delta \varepsilon n_D$. Consequently, this slope is the same at all frequencies and $\tau_D$ is given by

$$
\tau_D = \left[ \frac{d\left(\frac{\varepsilon''(\omega)}{\omega}\right)}{d\left(\omega \varepsilon''(\omega)\right)} \right]^{1/2} \quad (12)
$$
Now, for a sample not exhibiting Debye behaviour, the representations in terms of eqn (9)–(11) do not come into view as straight lines.

This notwithstanding, if we accept that at each frequency \( \omega = \omega_0 \) the sample verifies a Debye equation (eqn (1)) then we would find a relaxation time \( \tau_{D,i} \) at frequency \( \omega_0 \) given by

\[
\tau_{D,i} = \left[ \frac{\partial \varepsilon''(\omega)}{\partial \omega} \right]^{-1/2}_{\omega = \omega_0} \quad \text{or} \quad \tau_{D,i} = \left[ \frac{\partial \varepsilon''(\omega)}{\partial \omega} \right]^{-1/2}_{\omega = \omega_0}
\]

(13)

In case no analytic expression is employed, eqn (13) can be implemented numerically using the approximation \( d\omega \approx \Delta\omega \) which leads to

\[
\tau_{D,i} = \left[ \frac{\varepsilon''(\omega + \Delta\omega)}{\omega + \Delta\omega} - \frac{\varepsilon''(\omega)}{\omega} \right]^{-1/2}_{\omega = \omega_0 + \Delta\omega/2}
\]

(14)

Once \( \tau_{D,i} \) values have been estimated, eqn (9) yields \( \varepsilon_{\infty,i} \),

\[
\varepsilon_{\infty,i} = \frac{\varepsilon'(\omega = \omega_0)}{\tau_{D,i}} - \frac{\varepsilon''(\omega = \omega_0)}{\tau_{D,i}}
\]

(15)

and eqn (10) gives \( \varepsilon_{\infty,i} \) as

\[
\varepsilon_{\infty,i} = \varepsilon'(\omega = \omega_0) + \varepsilon''(\omega = \omega_0)
\]

(16)

Finally, from eqn (15) and (16) or directly from eqn (11) we obtain \( \Delta\varepsilon_i \) as

\[
\Delta\varepsilon_i = \varepsilon_{\infty,i} - \varepsilon_{\infty,i} = \tau_{D,i} \varepsilon''(\omega = \omega_0) + \frac{1}{\tau_{D,i}} \varepsilon''(\omega = \omega_0)
\]

(17)

The running of the quantities \( \Delta\varepsilon_i, \varepsilon_{\infty,i} \) and \( \varepsilon_{\infty,i} \) while varying the experimental angular frequency allows interpreting any relaxation spectrum as the result of consecutive Debye-like dispersion processes.

### 3. Application of the method

We applied the proposed method to the dielectric spectrum analysis of different samples which follow dielectric functions. Literature was largely random, apart from the availability of reproducing the experimental values of \( \varepsilon''(\omega) \). Here we present the results for dimethyl sulfoxide (DMSO).

Kaatz et al.[11] found that the DMSO relaxation spectrum can be described by the CD function:

\[
\varepsilon''(\omega) = \varepsilon'(\omega) - i\varepsilon_n(\omega) = \varepsilon_n + \frac{\varepsilon_{\infty} - \varepsilon_n}{(1+i\omega\tau_{CD})^\beta}
\]

(18)

where \( \beta \) is an empirical fitting parameter. The application of our procedure to DMSO is displayed in Fig. 2.

Fig. 2a reveals that \( \tau_{D,i} \) is constant up to \( \omega \approx 5 \times 10^{10} \) s\(^{-1}\), thus indicating a single relaxation time in this frequency range. This is in accordance with the well-known result [3] that the CD function at low frequencies approaches the Debye function with a relaxation time equal to \( \beta\tau_{CD} \). However, the value of \( \beta\tau_{CD} = 18.53 \) ps [11] whereas with the proposed method we have obtained \( \tau_0 \) (low frequency) = 20.03 ps. Hence the two different approximations do not yield the same value, although we have verified that both reproduce accurately \( \varepsilon''(\omega) \) values at low frequencies.

The logarithmic scale in Fig. 2b helps to compare the behaviour of \( \tau_{D,i} \) with that of the oscillation period of the electric field upon \( \omega \) increase. Fig. 2c indicates that, up to \( \omega \approx 10^{10} \) s\(^{-1}\), all polarization mechanisms contribute to a total permittivity of about \( \varepsilon_{\infty,i} \approx 46 \) which includes the amount of \( \varepsilon_{\infty,i} = 7.1 \) due to processes that are fast-responding to the applied field. \( \varepsilon_{\infty,i} \) decreases slightly for \( \omega > 10^{10} \) s\(^{-1}\) until reaching a constant value of 4 at high frequency. At \( \omega \approx 10^{10} \) s\(^{-1}\) a particular mechanism should take place to reinforce polarization with the effect of keeping \( \varepsilon_{\infty,i} \) constant and \( \varepsilon_{\infty,i} \) decreasing, so that \( \Delta\varepsilon_i \) attains a slightly maximum value. Fig. 2d discloses that \( \varepsilon_{\infty,i} \) and \( \varepsilon_{\infty,i} \) values became identical at frequencies above \( 20 \times 10^{12} \) s\(^{-1}\). This feature strongly suggests that, upon frequency increase, some mechanisms fail to respond to the field and hence only the electronic polarization is operating at high frequencies. Fig. 2d shows the profile of the frequency-dependent dielectric strength \( \Delta\varepsilon_i \). In view of eqn (2), this should be, broadly speaking, the behaviour of the effective mean molecular dipole moment \( \mu(\omega) \). Consequently \( \mu(\omega) \) would be constant at low frequencies, then would attain a maximum value, and would decrease upon further increase in frequency. In terms of Onsager’s model we estimated \( \omega_{\mu,max} \approx 0.2 \times 10^{12} \) s\(^{-1}\), a frequency at which \( \mu(\omega_{\mu,max}) \) = 13.5 ps. Note that \( \mu(\omega_{\mu,max}) < \tau_{CD} \).

Finally, the expression from Diaz-Calleja [12] for the CD function gives a relaxation time associated with the loss-peak maximum \( \tau_{\mu,max} = 19.05 \) ps. Our approach reproduces that value.

Analyzing other substances we have found that there is a useful link between the profile of \( \tau_0(\omega) \) plots and the models Debye, CC and CD. Thus, \( \tau_0(\omega) \) is a constant in samples complying with the Debye function, follows the branch of a rectangular hyperbola for the CC function or behaves as a Boltzmann-type sigmoid in the case of CD function (Fig. 2a). Therefore, the best empirical model to describe a given spectrum can be inferred from examining the shape of the experimental \( \tau_0(\omega) \) plots.
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5. References