Interpretation of non-ideal dielectric plots

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A semi-circular complex plane plot of permittivity corresponds to an ideal Debye dielectric, while that of impedance represents a parallel combination of a conductance and an ideal capacitor. Deviations from such semi-circular plots are normally observed in both situations and there is a tendency to interpret them in terms of distributions of relaxation times (DRT). As an interpretation of the permittivity response this may or may not be physically justified in any particular case, but there is no fundamental objection to its use for homogeneous media, since it implies the coexistence in the medium of *parallel* processes. On the other hand, the use of this approach in the interpretation of non-ideal complex impedance plots is inherently wrong in application to homogeneous media.

1. Introduction

The dielectric properties of most materials deviate more or less significantly from the classically expected simple behaviour which, according to the context, is associated with the ideal Debye response or the parallel combination of a loss-free capacitor with a conductor. Both these give simple semi-circular plots in the complex plane or permittivity and of impedance, respectively, the former being favoured by the "insulating" or dielectric school concerned primarily with low-loss materials, the latter by electrochemists interested in the response of relatively conducting liquid or solid electrolytes. In both situations, which correspond to physically very different systems, there is a tendency to "interpret", or more correctly explain away the deviations from the ideal behaviour in terms of "distributions of parameters" which may be characterized by suitable distribution functions and these are said to give a "measure" of the deviations from ideality.

Leaving aside for the present the question of the physical justification for the adoption of the "distributionist" approach, some objections to which having been discussed in reference [1], we propose in this communication to draw attention to certain more general limitations to the validity of this reasoning in the case of impedance plots.

The dielectric properties are commonly expressed as complex plane plots of permittivity, $\tilde{\varepsilon}(\omega) = \varepsilon(\omega) - i\varepsilon''(\omega)$ or of the equivalent complex capacitance which is given by

$$\tilde{C}(\omega) = C'(\omega) - iC''(\omega) = m\tilde{\varepsilon}(\omega) \qquad (1)$$

where m is a suitable geometrical factor. Alternatively, we may define the admittance $\tilde{Y}(\omega) = i\omega\tilde{C}(\omega)$ or impedance $Z(\omega) = \tilde{Y}^{-1}$, depending partly on the accepted "ethos" in the branch of science concerned.

The frequency dependence of the "ideal", i.e. Debye type is given by the expression for the dielectric susceptibility

$$\tilde{\chi}(\omega) = \chi'(\omega) - i\chi''(\omega) = \tilde{\varepsilon}(\omega) - \varepsilon_\infty = \Delta\varepsilon(1 + i\omega\tau)^{-1} \qquad (2)$$

where ε_∞ denotes the "high-frequency" limit of the permittivity, $\Delta\varepsilon = \varepsilon(0) - \varepsilon_\infty$ is known as the dielectric increment, $\varepsilon(0)$ is the low-frequency limit of ε and τ is the relaxation time. The imaginary part of the susceptibility $\chi''(\omega)$ reaches its peak at the loss peak frequency $\omega_p = 1/\tau$. The complex permittivity plot of a Debye system represents a semicircle, as shown in Fig. 1 and the corresponding impedance plot may be rather complicated, depending on the ratio $k = \Delta\varepsilon/\varepsilon_\infty = \varepsilon(0)/\varepsilon_\infty - 1$. If $k \gg 1$ the system behaves as a simple series R–C circuit, i.e. it gives a vertical line in the $\tilde{Z}$ plane, while in the more general case we may write

$$\tilde{Z}(x) = (\tau/\varepsilon_\infty)[ix + k(1 + 1/ix)^{-1}]^{-1} \qquad (3)$$

with $x = \omega\tau$ being a dimensionless frequency variable.

The most elementary complex impedance plot corresponds to a parallel combination of an ideal capacitor and a conductor and it represents a semicircle in the $\tilde{Z}$ plane which is completely analogous to the Debye permittivity circle shown in Fig. 1. Physically this might represent a system consisting of a loss-free "lattice" in which were embedded ideally conducting, i.e. infinitely rapidly responding charge carriers, such as ions or electrons. However, most real electrochemical systems show a completely different behaviour which will be discussed below.

2. Empirical approximations

It is a well-established fact that the behaviour of solid materials deviates more or less strongly from the ideal Debye response [1], and may be described by the empirical "universal" form which is given at high frequencies by

$$\tilde{\chi}(\omega) = B(\omega/\omega_p)^{n-1} \quad \text{for } \omega/\omega_p \gg 1, \quad \text{with } 0 < n < 1 \qquad (4)$$

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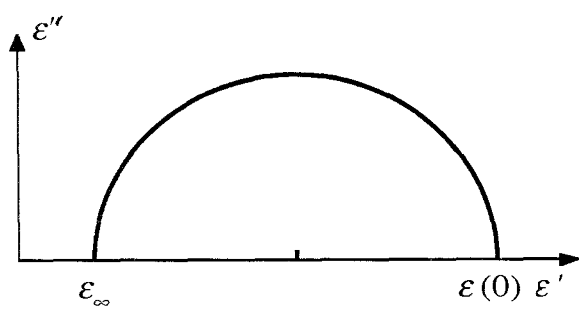

Figure 1 The complex permittivity plot corresponding to the ideal Debye response, showing the characteristic values of the real part at zero and infinitely high frequencies.

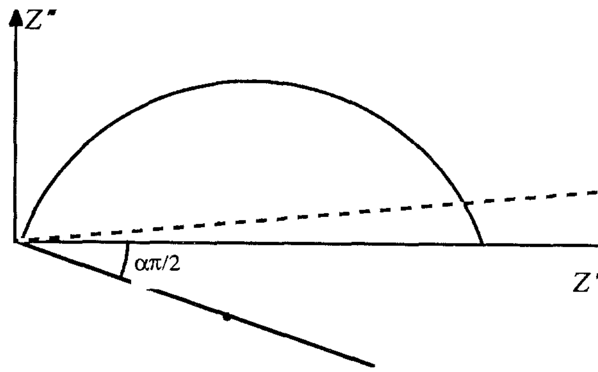

Figure 2 The inclined circular arc representing a non-ideal impedance following the Cole–Cole formula of Equation 7. An exactly similar form of plot would be applicable to the permittivity of certain non-Debye systems. The dotted line corresponds to LFD response as explained in the text.

which implies that

$$\chi''(\omega) = \cot(n\pi/2)\chi'(\omega) \propto \omega^{n-1} \quad (5)$$

and at low frequencies by the expressions [2]

$$\chi''(\omega) \propto \chi(0) - \chi(\omega) \propto \omega^{m} \quad \text{for } \omega/\omega_p \ll 1, \quad (6)$$
$$\text{with } 0 < m < 1$$

The resulting $\tilde{C}(\omega)$ plots are correspondingly distorted from the simple semi-circular shape of the ideal Debye system and they may be approximated by one of the empirical forms [3], namely the Cole–Cole relation

$$C(\omega) \propto [1 + (i\omega\tau)^{1-\alpha}]^{-1} \quad (7)$$

which introduces an empirical factor α causing a tilting of the circular arc by an angle $\alpha\pi/2$, or the Cole–Davidson relation

$$\tilde{C}(\omega) \propto (1 + i\omega\tau)^{\beta-1} \quad (8)$$

which results in a pear-shaped $\tilde{C}(\omega)$ arc, or finally the Havriliak–Negami function which combines the other two

$$\tilde{C}(\omega) \propto [1 + (i\omega\tau)^{1-\alpha}]^{\beta-1} \quad (9)$$

Similar relations may be applied to non-ideal impedance plots, an example of which is shown in Fig. 2.

We note that the Cole–Cole and Cole–Davidson expressions are one-parameter functions, while the Havriliak–Negami function uses two parameters and is therefore more realistic in representing the behaviour of real materials. A more complete discussion of these functions and of their relation to Expressions 4–6 is given in [1] and [2]. We stress again the fact that these empirical expressions have nothing to do with any particular physical model – they represent mathematical devices for modelling the shapes of the observed complex $\tilde{C}(\omega)$ or $\tilde{Z}(\omega)$ arcs.

It is equally established that similar deviations apply to the complex impedance plots $\tilde{Z}(\omega)$, especially in materials in which mobile ions contribute significantly to the dielectric response, such as fast ionic conductors [4]. Analogous empirical expressions to those given by Equations 7–9 have been used in that context as well, again purely as mathematical devices for modelling the observed behaviour.

It was pointed out [1, 5, 6] that the most commonly observed tilted circular arc $\tilde{Z}(\omega)$ represented by and expression analogous to the Cole–Cole relation (Equation 7) corresponds directly to dielectric permittivity obeying the high-frequency "universal" relationship (Equation 4).

A special limit of the "universal" relation (Equation 4) is found in all cases in which some slowly mobile electronic or ionic charge carriers dominate the polarisation at low frequencies, when the familiar dipolar loss peak is replaced by a second power law of the type (Equation 4) but with a much lower value of the exponent $n_2 \ll 1$. This type of response is referred to as low-frequency dispersion (LFD) [1, 7–9] and becomes dominant in virtually all dielectric materials at elevated temperatures when the ionic mobilities become sufficiently high. LFD is especially clearly visible in fast ionic conductors [5, 6] and is also the dominant form of behaviour in surface conduction on, for example, humid insulators [10].

The manifestation of LFD in the impedance plots is a straight line inclined at a very low angle to the horizontal, as shown by the dotted line in Fig. 2, and this tends to enhance the "flatness' of the impedance plot. There are many examples of this type of behaviour and they tend to cause a good deal of confusion in the interpretation of dielectric data by the conventional approaches, while being easily accommodated in the framework of the "universal" theory.

3. Conventional interpretation

It has become customary to interpret any deviations from the straight semi-circular arc plots in the complex plane of *either* capacitance *or* impedance in terms of the concept of *distribution of relaxation times* (DRT) [3, 11]. Oddly enough, the argument runs along similar lines equally for the capacitance and impedance plots, despite the fact these represent very different physical conditions and it is not possible to obtain an inclined circular arc in the capacitance plane from one in the impedance plane. It is argued that no system can be completely uniform and many systems are manifestly strongly non-uniform, so that there are many different dipolar species which must have different activation energies and characteristic relaxation times. Because of this, it is argued, the ideal expression for capacitance or susceptibility (Equation 2) must be replaced by a summation over all the different relaxation times, which in the limit of a continuous distribution of these relaxation times becomes an integration:

$$\tilde{C} = \int_0^\infty \frac{g(\tau)}{1 + i\omega\tau} d\tau \qquad (10)$$

where $g(\tau)$ is a suitable distribution function of relaxation times. The mathematical sense of Equation 10 is that the empirically observed dielectric response is expressed as an integral transform in terms of ideal Debye functions – an operation which is probably justified in most cases of practical interest. The physical sense of this operation is the postulation of the existence in the given material of a wide range of *parallel* polarization processes coexisting in the same medium, a very acceptable proposition. This reasoning does not in any way answer the question as to the justification for the *particular form* of distribution function required to give the observed dielectric response – it merely states that the experimentally observed capacitance relation *is consistent with* a certain distribution of relaxation times.

What is important *physically* is that the DRT approach presupposes the existence in the dielectric medium in question of a continuous – or in certain circumstances discontinuous – distribution of *parallel* polarization processes. This does not present any serious conceptual difficulty, since a parallel arrangement is the natural outcome of the existence in the material of a range of different contributory processes.

The situation is very different in the case of the interpretation of impedance plots in terms of DRT. Here an integral expression of the type of Equation 10 would imply the presence in the system under consideration of a *series combination* of elements, in this instance of a continuously graded *stratification* of the medium. While it is possible in principle to envisage such a peculiar medium, it is evident that this consequence of the application of the DRT interpretation to non-semicircular impedance plots has escaped people who were proposing this approach. As far as we can see, in all such cases the materials in question were thought to be homogeneous.

It is evident, therefore, that while the DRT interpretation may possibly be valid in the case of non-ideal complex permittivity or capacitance plots, it cannot be applied to the case of *homogeneous* materials showing inclined circular arc or otherwise non-ideal impedance plots.

4. Conclusions

We have shown that, whatever the physical justification for the interpretation of non-ideal, i.e. non-Debye behaviour of dielectric permittivity in terms of distributions of relaxation times, there is no justification for applying the same approach to the case of non-ideal impedance plots for homogeneous materials.

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