Nonlinear Model of non-Debye Relaxation

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Abstract

We present a simple nonlinear relaxation equation which contains the Debye equation as a particular case. The suggested relaxation equation results in power-law decay of fluctuations. This equation contains a parameter defining the frequency dependence of the dielectric permittivity similarly to the well-known one-parameter phenomenological equations of Cole-Cole, Davidson-Cole and Kohlrausch-Williams-Watts. Unlike these models, the obtained dielectric permittivity (i) obeys to the Kramers-Kronig relation; (ii) has proper behaviour at large frequency; (iii) its imaginary part, conductivity, shows a power-law frequency dependence \( \sigma \sim \omega^n \) where \( n < 1 \) corresponds to empirical Jonscher’s universal relaxation law while \( n > 1 \) is also observed in several experiments. The nonlinear equation proposed may be useful in various fields of relaxation theory.

The frequency dependence of the dielectric permittivity \( \varepsilon(\omega) \) plays a crucial role in numerous aspects of condensed matter science. Among the great number of publications, we can mention the textbooks [1, 2] and review articles [3, 4]. Classical theory of polar dielectric relaxation, which is connected with the \( \varepsilon(\omega) \), is based on the linear Debye equation

\[
\frac{dW}{dt} = -\frac{1}{\tau}(W - W_0). \tag{1}
\]

Here \( W \) is the angular distribution of dipoles, \( W_0 \) is its equilibrium value and \( \tau \) is a relaxation time. The solution of the Eq. (1) describes an exponential relaxation, which results in the Debye dielectric permittivity

\[
\varepsilon(\omega) = \varepsilon_{\infty} + \varepsilon_D(\omega), \quad \varepsilon_D(\omega) = \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + i\omega\tau}. \tag{2}
\]
where $\varepsilon_\infty$ is the dielectric permittivity at $\omega \gg 1/\tau$ and $\varepsilon_s \equiv \varepsilon(0)$. However, the dependence (2) occurs quite seldom in experiments [1, 2, 3, 4]. Explanation of a non-Debye dispersion $\varepsilon(\omega)$ is carried out in frames of the models which can be tentatively divided into three directions. (i) Models which assume the relaxation time $\tau$ to be a stochastic variable. Taking different distributions for $\tau$ one can obtain from the equation (2) different $\varepsilon(\omega)$ dependencies, including those matching the experimentally observed curves (see, for instance, Refs. [5, 6]). Apparently this theoretical approach to explain the experimental data is not faultless. (ii) Electrical network model used for the microstructural media [7]. (iii) Models which consider influence of manybody effects on the relaxation [1, 4, 8, 9]. The model suggested here is close to the latter type.

The kinetic equation for spatial distribution of dipoles includes a collision integral which model is right hand side of Eq. (1) (see, for instance, Ref. [10]). In general kinetic theory this integral is a nonlinear functional of the distribution. It is therefore natural to take the right hand side of the relaxation equation as a nonlinear function. The simplest nonlinear generalization of the Debye equation (1) is the following relaxation equation:

$$\frac{dW}{dt} = -\frac{(W - W_0)^{q+1}}{\tau}. \quad (3)$$

The parameter $q$ in the equation (3) defines the relaxation law, shape of absorption line and dispersion dependence for the real part of $\varepsilon$. In this regard the parameter $q$ is analogous to the parameters of Cole-Cole, Davidson-Cole, Kohlrausch-Williams-Watts phenomenological curves [6]. In the present case the fitting parameter is introduced at an earlier stage, i.e., into a differential relaxation equation. This leads to a number of principal differences comparing to the aforementioned phenomenological curves.

A nonlinear relaxation equation

$$\frac{dW}{dt} = -\frac{W^{q+1} - W_0^{q+1}}{\tau},$$

which is similar to the Eq. (3), also includes the only shape parameter $q$, though it leads to more sophisticated mathematical formulae.

Obviously, for noninteger $q$ the right hand side of the Eq. (3) displays nonanalytic (in the sense of Cauchy–Reimann conditions) behaviour which cannot follow from kinetic theory. For small deviations from the equilibrium, $U = W - W_0$,

$$U = W - W_0, \quad (4)$$

the right hand side of the relaxation equation should have Debye form (1). However, this is a rather difficult question whether $U$ can be considered as
Figure 1: Hypothetical view of the collision integral \( I(U) = U + U^2 \) (solid curve) and approximation of it in the Debye linear model \( I(U) \simeq U \) (dashed curve) and in the proposed nonlinear model \( I(U) \simeq 2U^{1.5} \) (points). Multiplier 2 in the latter equation defines the difference between the relaxation times in the linear and nonlinear models.

small enough. We assume that the \( U \) values relevant to the experiment are not small so that the relaxation equation can be approximated by the simple formula (3) (see Fig. 1).

From the Eq. (3) one easily obtains the relaxation function

\[
U(t) = (qt/\tau + C)^{-1/q},
\]

where \( q \) is positive number to satisfy the condition \( W \to W_0 \) at \( t \to \infty \). The constant \( C = U_0^{-q} \) ensures the initial condition \( U(0) = U_0 \). Then

\[
U(t) = U_0(1 + qtU_0^q/\tau)^{-1/q}.
\]

Function (6) coincides with the Debye relaxation function \( U(t) = U_0 \exp(-t/\tau) \) for \( q \to + 0 \).

The general relation between the electric field \( E(t) \) and the electric displacement field \( D(t) \) will be used. The principle of causality gives for the isotropic media [11]

\[
D(t) = \varepsilon_\infty E(t) + \int_{-\infty}^{t} \kappa(t - \theta) E(\theta) d\theta,
\]
where $\kappa$ may differ from the relaxation function $U(t)$ only by a constant positive multiplier \[12\]

$$\kappa(t) = A(1 + t/\tau^*)^{-1/q}, \quad (8)$$

and an effective relaxation time

$$\tau^* = \frac{\tau}{qU_0^q} \quad (9)$$

is introduced.

Multiplier $A$ can be calculated for $q < 1$ from the equation (7) with the dc field $E$. Taking into account the equation $D = \varepsilon_s E$ for this case,

$$A = 1 - \frac{q}{q\tau^*} (\varepsilon_s - \varepsilon_\infty), \quad q < 1. \quad (10)$$

For $q > 1$ the field $E$ cannot be assumed as a dc since integral in the equation (7) diverges. Multiplier $A$ cannot be calculated in this case. This problem is discussed below.

To determine an ac permittivity $\varepsilon(\omega)$ let us consider a periodic field $E(t) = E_0 e^{-i\omega t}$ in the Eq. (7). Then

$$\varepsilon(\omega) = \varepsilon_\infty + \varepsilon(\omega), \quad (11)$$

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 = A \int_0^\infty (1 + t/\tau^*)^{-1/q} e^{i\omega t} dt$$

$$= \frac{iA}{\omega} (-i\omega\tau^*)^{1/q} e^{-i\omega\tau^*} \Gamma (1 - 1/q, -i\omega\tau^*),$$

where $\Gamma(\cdot, \cdot)$ is an incomplete $\Gamma$-function \[13\]. In a more common form one can write $\varepsilon(\omega)$ as

$$\varepsilon = \varepsilon_1 - i\varepsilon_2 = -\frac{iA}{\omega} (i\omega\tau^*)^{1/q} e^{i\omega\tau^*} \Gamma (1 - 1/q, i\omega\tau^*). \quad (12)$$

It is easy to see the dependence $\varepsilon$ on $\omega$ is determined by effective relaxation time $\tau^*$. The actual relaxation time, $\tau$, which enters the Eqs. (5), (10), can be measured by the methods of time domain spectroscopy \[14, 15\]. Since $\varepsilon(\omega)$ is Fourier-Laplace transform of a smooth function it obeys to the Kramers-Kronig relation \[12\]. Function $\varepsilon(\omega)$ has an integrable singularity at $\omega = 0$ when $q > 1$ and this singularity is an inaccuracy of the model. In fact, it is well known that behaviour of a function in frequency domain near $\omega = 0$ is determined by the function in time domain at $t \to \infty$. However, for very
large $t$ the function $W$ is close to the function $W_0$ and equation (3) becomes incorrect. So the equation (12) cannot be used with $q > 1$ in the narrow frequency region near $\omega = 0$.

Imaginary part of the permittivity, $\varepsilon_2$, is connected with the conductivity of a matter, $\sigma$, by the well-known equation

$$\sigma(\omega) = \frac{\omega}{4\pi} \varepsilon_2(\omega)$$

(13)

and $\sigma(\omega)$ has no singularity at $\omega = 0$ for any $q$. Its behaviour at small $\omega$ is the following

$$\sigma(\omega) \simeq \begin{cases} \frac{A}{4\pi(\omega^\tau)^2} \cos(\pi/2q) (\omega\tau^*)^{1/q}, & q > 1/2 \\ \frac{A}{2\pi(1-2q)} \omega < 1/2 \end{cases}$$

(14)

It is interesting to note that the dependence $\sigma \sim \omega^2$, which follows from the Eq. (14) for $q < 1/2$, coincides with its dependence in Debye theory when $q = 0$. The dependence $\sigma \sim \omega^n$ with $n < 1$ has been observed in many experiments (Jonscher’s universal relaxation law [2, 3, 16, 17]). Such a dependence follows from the equation (14) for $q > 1$. Dependence $\sigma \sim \omega^n$ with $n > 1$ which follows from the equation (14) for $1/2 < q < 1$ has been also observed in some types of materials, e. g., in glassy 0.3(xLi$_2$O.(1-x)LiO)0.7B$_2$O$_3$ [18], in mixed compounds of (NH$_4$)$_3$H(SO$_4$)$_1.42$(SeO$_4$)$_{0.58}$ [19] and K$_3$H(SeO$_4$)$_2$ single crystals [20]. Sometimes at very low frequencies, $\omega < \omega_0$, in both ($n < 1$ and $n > 1$) cases the frequency dependence of conductivity is weak, plateau-like. It does not contradict the proposed model since in the low-frequency region the conductivity may be connected with other processes, magnitude of which becomes equal to (14) when $\omega \simeq \omega_0$ [21].

For $\omega \to \infty$

$$\varepsilon_1 \simeq \frac{A}{\omega^2\tau^*}, \quad \varepsilon_2 \simeq \frac{A}{\omega},$$

(15)

that coincides with the asymptotic behavior of $\varepsilon_D$ [2]. We remind that the dependence $\varepsilon_1 \sim \omega^{-2}$ is a general feature of a dielectric permittivity at large frequencies [11]. Nevertheless, for many materials the decrease of $\varepsilon_1$ with the increasing frequency is slower than $\omega^{-2}$. It may be connected with the influence of faster relaxation processes which induce extra high-frequency maxima on the dielectric losses curve.

Clearly, the suggested model requires a detailed experimental verification. Here we demonstrate that it may be adjusted with the well-known empirical dependencies, e. g., with the Cole-Cole equation

$$\varepsilon_{CC} = \frac{\Delta \varepsilon}{1 + (i\omega\tau_{CC})^\alpha}, \quad \Delta \varepsilon \equiv \varepsilon_s - \varepsilon_\infty.$$
Figure 2: Imaginary part of the dielectric permittivity, $\varepsilon_2$, calculated according to the equation (12) (solid curve) and to the Cole-Cole equation (16) (dashed curve). All parameters are given in the text.

Figure 2 shows the frequency dependence of $\varepsilon_2$ for $\alpha = 1/2$. The parameters of nonlinear relaxation are chosen as $q = 0.732$ and $\tau^* = 4.66 \tau_{CC}$. Such a large difference of $\tau^*$ and $\tau_{CC}$ implies a shift of dielectric losses curve maximum to the low-frequency region.

In conclusion, the nonlinear relaxation equation is proposed. The equation leads to a power decay of the fluctuations. Frequency dependencies of the dielectric permittivity and dielectric losses are in agreement with the well-known empirical dependencies. Derived relaxation equation may be useful to describe different relaxation processes. If a relaxation of the dimensional values is under consideration, $U$ in (4) should be equal to $W/W_0 - 1$.

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