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Relaxation function for the non-Debye relaxation spectra description

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ABSTRACT

This study presents the new relaxation function describing the non-Debye relaxation phenomena. The relaxation function is based on a new theoretical model of the relaxation polarization. The non-Debye relaxation is explained with the model of nonlinear damped oscillator. It is shown that the relaxation function describes the relaxation spectra of the Davidson-Cole and Havriliak–Negami types as well as spectra with the left-skewed loss peak.

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1. Introduction

It is well known that broadband dielectric spectroscopy is a powerful tool for investigating a variety of dielectric processes both for electrical and non-electrical application. It provides the unique information pertaining to the structure, chemical composition and molecular processes in matter. In recent years, numerous experimental and theoretical studies have focused on understanding of the non-exponential dynamics in more detail.

At present a number of empirical formulas are used for the description of relaxation dielectric spectra. One of as of the best known is the Debye equation:

$$\varepsilon(\omega)=\varepsilon_s+\frac{\varepsilon_s-\varepsilon_\infty}{1+i\tau\omega} \tag{1}$$

where $\varepsilon(\omega)$ is the complex permittivity, τ is the time constant or the relaxation time, ε_∞ and ε_s are respectively the high and low frequency permittivity limits, ω is the cyclic frequency of an external electric field change, i is the complex unit [1–4]. Despite the extremely wide application of Eq. (1) in various branches of science and engineering, it does not explain the nature of relaxation polarization.

The inverse Fourier transform of the Debye formula gives the time-dependent exponential relaxation function:

$$P(t)=P_0e^{-\frac{t}{\tau}}, \tag{2}$$

here $P(t)$ is the polarization, P_0 is the polarization value at the moment $t = 0$.

Wide-ranging experimental information leads to the conclusion that pure Debye behavior is hardly ever found in nature. Eq. (1) describes the behavior of an assembly of non-interacting ideal dipoles that have the same time constant. In practice dispersion occurs over a wider frequency range. The Debye relaxation is generally limited to water in liquid state and weak solutions of polar liquids in non-polar solvents [1–3].

Cole and Cole (CC) suggested the following empirical equation

$$\varepsilon(\omega)=\varepsilon_s+\frac{\varepsilon_s-\varepsilon_\infty}{1+(i\tau\omega)^{1-\alpha}} \tag{3}$$

where α is the constant ($1 \geqslant \alpha > 0$) depending on a certain type of material, temperature and pressure [5]. Eq. (3) describes the dielectric spectra of many liquids and some polymers exhibiting symmetrical loss peak and wider dispersion area in comparison with the Debye formula [6].

In work [7] Davidson and Cole (DC) suggested the following formula for types of glass and glass-like substances having the asymmetric loss peak.

$$\varepsilon(\omega)=\varepsilon_s+\frac{\varepsilon_s-\varepsilon_\infty}{(1+i\tau\omega)^{1-\beta}} \tag{4}$$

here β is the constant ($1 > \beta \geqslant 0$) depending on material properties, temperature and pressure. The real and imaginary components of functions (1), (3), and (4) are plotted in Fig. 1.

Some polymers have CC-type spectra at low frequencies and DC-type spectra at high frequencies. In work [8] Havriliak and Negami (HN) proposed the following function:

$$\varepsilon(\omega)=\varepsilon_s+\frac{\varepsilon_s-\varepsilon_\infty}{\left(1+(i\tau\omega)^{1-\alpha}\right)^{1-\beta}}. \tag{5}$$

when $\alpha = \beta = 0$ the Debye function is obtained. Eqs. (4) and (5) describe the spectra exhibiting the right skewed loss peak (Fig. 1).

The inverse Fourier transform of Eqs. (3)–(5) into the time domain are not analytic functions. For the polarization time

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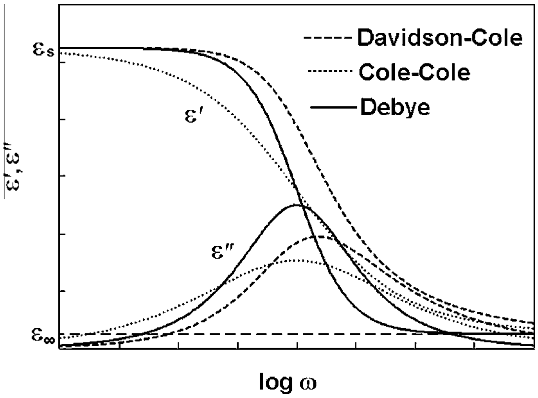

Fig. 1. The real and imaginary parts of dielectric constant vs. logarithmic frequency for Eqs. (1), (3), and (4).

dependence description the Kohlrausch–Williams–Watts (KWW) empirical relaxation function is used.

$$P(t) = P_0 e^{-\left(\frac{t}{\tau}\right)^{\chi}} \tag{6}$$

where γ is the constant ($1 \geqslant \gamma > 0$) [9]. The KWW is usually called the stretched exponential. It is easy to see that function (6) is a modified version of relaxation function (2). The digital Fourier transformation of function (6) into the frequency domain allows to describe the spectra of DC and HN type.

Obviously, functions (3)–(5) are the modified Debye equation. An experiment demonstrates that very few materials completely agree with Eqs. (3)–(5). In fact, slight (or not so slight) deviations from distributions (3)–(5) have been commonly observed for the majority of materials. Moreover, there are quite a few materials exhibiting the left-skewed loss peak; none of a known formulas, including (1)–(6), describes the spectra of such type.

None of the above mentioned functions explain the nature of non-Debye relaxation. There are a number of models explaining the non-Debye relaxation processes, the hopping model, the distribution of relaxation times, etc. [1–3], but none of them give an analytical relaxation function. The coupling model, suggested by Ngai et al. work [10] and citations, treated the non-Debye process as the non-linear vibrations of arrays of phase-coupled oscillators. The model is in good agreement with experimental data, a close fit for the calculated relaxation function to the KWW function. This one, however, does not give a relaxation function in analytical form.

2. Physical model of the relaxation polarization

2.1. Debye relaxation

It should be noted that in accordance with the Debye theory a water molecule rotates freely in the viscous continuous medium [4]. The microscopic mechanism of interaction between the given molecule and neighboring molecules was not considered. The average viscosity factor was used to describe the interaction. Hence we can conclude that the Debye relaxation model is macroscopic, since it considers an average molecule rotating in a viscous continuous medium with an average linear friction.

To find a simple relaxation function, we have to take into account the fact that a complicated microscopic model usually either gives a complicated solution or does not give an analytical solution at all.

In accordance with the definition, the dielectric polarization is relative displacement the charged particles or the orientation of dipoles towards the direction of external electric field [1–3]. In the alternating field the particle changes the move direction towards the direction of external field, i.e. the particle vibrates. It is also true for the relaxation polarization. Hence, the linear oscillator model [11] may be applied for the relaxation polarization description.

Thus, following the aforementioned arguments, consider an average molecule in a viscous medium. Obviously, the interaction between that molecule and its neighbors is due to Coulombic interaction, i.e. the molecule is located in the Coulombic potential well. Hence, the rotating molecule not only loses energy due to friction but it is also affected by the Coulombic restoring force. Therefore, consider an average vibrating particle in the potential well. Following Debye, introduce the average friction coefficient to take into account the energy loss. For the dipole orientation description the angle variable is used, for the particle movement the linear coordinate x is used. In both cases the linear oscillator equation has the same form. Below the coordinate x will be used.

Consider the linear oscillator equation [11]

$$\frac{d^2x}{dt^2} + 2\delta\frac{dx}{dt} + \omega_0^2 x = \frac{F(t)}{m}. \tag{7}$$

here x is the oscillator coordinate, m is the oscillator mass, ω_0 is the own frequency, δ is the damping coefficient, $F(t) = q\cdot E(t)$ is the external driving force, q is the elementary particle charge, and $E(t)$ is the external field strength. The own frequency is related to the spring constant k according to $\omega_0^2 = k/m$. The first term in Eq. (7) is responsible for the inertia force, the second for the damping force, and the third for the elastic restoring force.

For relaxation processes the inertia force is of little importance due to high friction. If the damping force is greater than the inertia force, then the first term in Eq. (7) may be neglected. In this case Eq. (7) becomes degenerated [11]:

$$\frac{dx}{dt} + \frac{1}{\tau}x = \frac{F(t)}{m\omega_0^2} \tag{8}$$

where $\tau = 2\delta/\omega_0^2$ is the time constant. The degeneracy condition is $\delta \geqslant 3\omega_0^2$ [12]. The general solution of Eq. (7) is:

$$x(t) = x_0 e^{-\frac{t}{\tau}}. \tag{9}$$

Further, it is easy to obtain the spectral function for the damped linear oscillator using the Fourier transform:

$$S(\omega) = \frac{x_0 \cdot \tau}{1 + i \cdot \omega \cdot \tau}. \tag{10}$$

Thus, taking into account the relationship $p = q \cdot x$ between polarization p and the charged particle displacement x, we can conclude that the spectral Debye function and relaxation function (2) are the consequences of damped linear oscillator Eq. (8). In other words, the Debye type polarization of a dielectric is damped linear vibrations of charged particles.

2.2. Non-Debye relaxation

Since very few materials completely agree with the Debye equation, it was supposed in work [13] that non-Debye relaxation may be described as the damped nonlinear vibrations of an average charged particle in a viscous medium.

Let us consider the special case of the damped oscillator with nonlinear spring force

$$f(x) = k \cdot x + k_1 \cdot x^n. \tag{11}$$

Here $k \cdot x$ is the linear spring force, $k_1 \cdot x^n$ is the nonlinear term, k, and k_1 are the spring constants, and n is the numerical parameter

($n > 1$). Following the above scheme, we introduce the own frequencies $\omega_0{}^2 = k/m$, $\omega_{01}{}^2 = k_1/m$ and the time constants $\tau = 2\delta/\omega_0{}^2$, $\tau_1 = 2\delta/\omega_{01}{}^2$.

Consider a simple physical model to show the validity of relation (11). Let the loosely bounded charge $+q$ is localized in the potential well created by the two strongly bounded charges $+Q_1$, and $+Q_2$ (Fig. 2(a)). Under action of the external field E the particle $+q$ is displaced from the point $x = 0$ to $x = \Delta x$. Two equal and opposite forces f_1 and f_2 act upon the charge $+q$ (Fig. 2(a)). The restoring force f_1 is caused by Coulombic interaction and the force $f_2 = q \cdot E$ is caused by the external electrical field. It is easy to find the restoring force using the Coulomb's law.

$$f_1 = Qq\left(\frac{4\Delta x}{\left(L^2 - (\Delta x)^2\right)^2}\right), \tag{12}$$

here $Q = Q_1 = Q_2$. Fig. 2(b) shows that the restoring force is approximately linear in the range $\Delta x \leqslant 0.1$ ($L/2$); under the condition $x > 0.1$ ($L/2$) it is significantly nonlinear. The graph of function (12) closely fit to (11) at $n = 3.8$. Here and below for function coincidence test the digital minimization procedure is used.

Further, using Eqs. (8) and (11) we get the degenerated equation for a damped nonlinear oscillator.

$$\frac{dx}{dt} + \frac{1}{\tau}x + \frac{1}{\tau_1}x^n = \frac{F(t)}{m\omega_0^2}. \tag{13}$$

This is the Bernoulli's equation [15], the solution of that is

$$x(t) = \left(C \cdot e^{(n-1)\frac{t}{\tau}} - \frac{\tau}{\tau_1}\right)^{-\frac{1}{n-1}} = C^{-\frac{1}{(n-1)}}\left(e^{(n-1)\frac{t}{\tau}} - a\right)^{-\frac{1}{n-1}} \tag{14}$$

here C is the constant determined by the initial condition, $a = \frac{\tau}{C \cdot \tau_1}$. For the rationality of function (14) it is necessary $a < 1$. Obviously, at $a = 0$ Eq. (14) transforms into the exponential relaxation function (9).

It is easy to see that Eq. (13) at $n = 1$ describes the damped linear oscillator with the time constant.

$$\tau^* = \frac{\tau \cdot \tau_1}{\tau + \tau_1} \tag{15}$$

Since the charged particle displacement is small ($x << 1$) at large n ($n > 10$) the third term in left part of Eq. (13) becomes negligible, i.e. at $n > 10$ Eq. (13) describes the linear oscillator with the time constant τ. Moreover, under condition $\tau_1 >> \tau$ the third term also becomes negligible. Hence, function (14) transforms into simple exponential form (2) if at least one of the following conditions hold: (i) $n \approx 1$; (ii) $n > 10$; (iii) $a \approx 0$. Also, function (14) does not depend on a and n if the listed conditions hold.

Thus, using the simple physical model we have obtained the new relaxation function. Below relaxation function (9) will be mentioned as linear, functions (6) and (14) as nonlinear. Here the term nonlinear means the nonlinearity of original Eq. (13).

The aim of the paper is to present the new relaxation function. The detailed analysis of the theoretical model will be the object of another article.

3. Nonlinear relaxation function properties

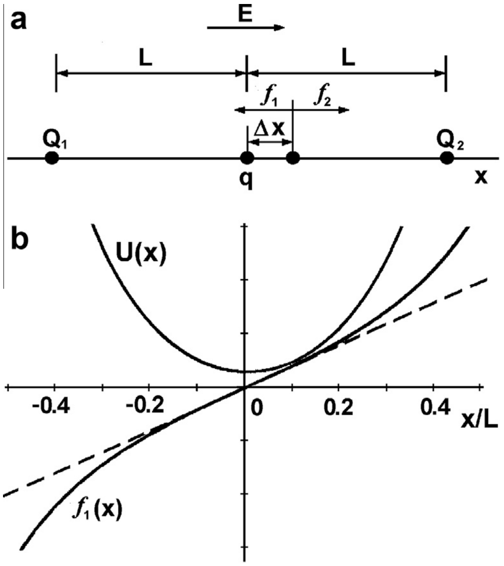

Fig. 2. (a) The particle $+q$ in the potential well. (b) $f_1(x)$ is the restoring force, the dashed line is the tangent to $f_1(x)$ at $x = 0$, $U(x)$ is the potential.

Find the frequency spectra of permittivity corresponding to relaxation function (14) using the Fourier transformation. Since the Fourier transform of Eq. (14) is not an analytic function, the digital procedure will be used below. Relaxation function (14) depends on the parameters n and a, therefore consider the influence of these parameters on the spectra shape separately. The real $\varepsilon'(\omega)$ and imaginary $\varepsilon''(\omega)$ parts of permittivity, both normalized by $\varepsilon'(0)$, for various values of n at $a = 0.99$ are shown in Fig. 3. Since the parameter a is limited ($a < 1$), the graphs are plotted for $a = 0.99$ to show the highest possible curves distortion caused by the nonlinearity.

As follows from the above the spectral functions shown in Fig. 3(a) at $n = 1$ and at $n > 10$ correspond to the spectral function of linear oscillator (the Debye shape). At $n = 1$ the loss peak maximum is located in the point $\omega_{m2} = 1/\tau$, and at $n > 10$ in the point $\omega_{m1} = 1/\tau^*$. In the range of $n = 1$ to 10 the spectra shape depends on n. The raising of n ($n > 1$) causes a significant widening of the loss peak. In the range $1 < n < 1.84$ the loss peak is skewed to left (negative asymmetry); at $n > 1.84$ it is skewed to right; at $n = 1.84$ the peak is symmetric. At $n \approx 2$ the peak exhibits a near HN shape. At $n \approx 2.5$ the real and imaginary parts are described by the HN distribution with sufficient accuracy. In the case of $n = 3$ Eq. (13) describes the Duffing oscillator [11]. As shown in work [14], the Duffing oscillator spectral function coincides with the DC distribution to within ≈5%. At higher values of n ($n > 3$) the spectra completely coincides with the DC function and tends

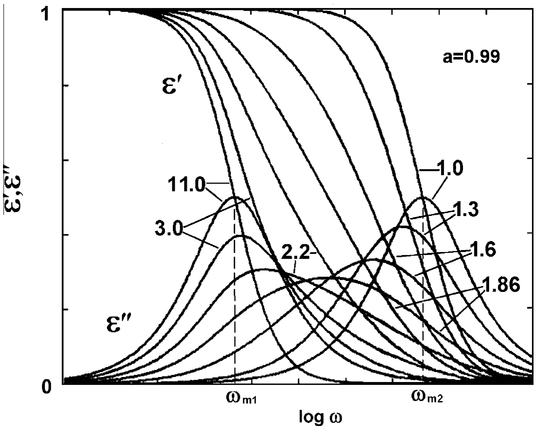

Fig. 3. The real and imaginary parts of normalized spectral function of the nonlinear oscillator for various values of n at $a = 0.99$.

towards Debye shape with further increase in n. At $n > 10$ the spectra with high accuracy (<1%) coincides with the Debye function.

The dependence of nonlinear spectra shape on a at $n = 1.5$ is shown in Fig. 4. At $a \approx 1$ the loss peak is skewed to left and shifted to the high frequency region; the ratio $\varepsilon''(\omega_m)/\varepsilon'(0)$ is less than that for the Debye distribution. At $a \approx 0.9$ the peak is symmetrical. At $a < 0.9$ the spectra obeys the DC law, and tends to the Debye shape with further decrease in a. At $a \leqslant 0.2$ the spectra completely coincides with the Debye graph; the loss peak maximum shifts to the point ω_{m1}.

So we can conclude that the spectra have the negative asymmetry if the following conditions hold: $a > 0.9$, $n < 1.8$. The n rising leads to the following transformation of the spectra shape: the Debye shape – the left asymmetry – symmetrical – the right asymmetry – the Debye shape; correspondingly the loss peak width rises at $n < 1.85$ and decreases at $n > 1.85$. The spectra transformations caused by the a decreasing are: the left asymmetry – symmetrical – the right asymmetry – the Debye shape; the loss peak width decreases in the mentioned range.

4. Discussion

Let us compare the spectral functions of KWW and function (14) obtained by Fourier transform. In Fig. 5 the graphs for the various values of KWW parameter γ are plotted. One can see that the spectra of KWW and the new relaxation function are sufficiently fitted with each other. Hence all kinds of curves described by KWW are described by function (14). Since the new relaxation function describes the spectra with positive and negative symmetry, the function (14) area of use is wider than that of KWW.

To show the applicability of function (14) for the relaxation spectra description the digital modeling of a number of experimental relaxation spectra were performed. The experimental spectra taken in [16–18] obey the HN law and taken in [19] does not obey the one. The digital modeling gives the good agreement of calculated curves with the experiment with accuracy to within 3–5%.

Fig. 3 shows that function (14) describes the relaxation spectra with the negative asymmetry. In practice, it is not unusual to find a material exhibiting the relaxation spectra with the left-skewed loss peak. Let us consider the spectra of nematic liquid crystal at various bias voltages obtained by Ösder et al. in work [20] (Fig. 6). One can say, that the spectra should be described by the distribution of relaxation times model. But the application of the model leads to the question: Why does the bias rising cause the transformation of multi-τ spectra into the single-τ. From the point of view of above suggested model the nematic crystal exhibits single-τ spectra and the bias rising causes linearization of molecules vibration.

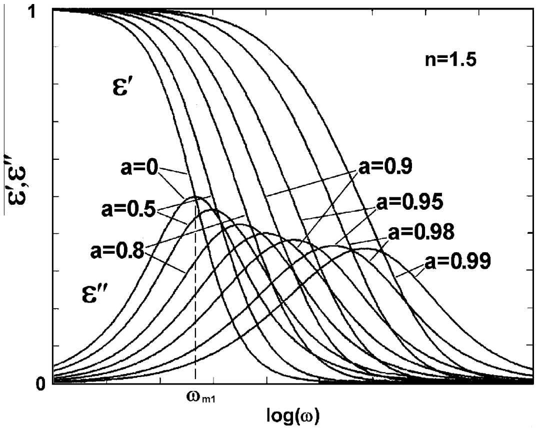

Fig. 4. The real and imaginary parts of normalized spectral function of the nonlinear oscillator for various values of a at $n = 1.5$.

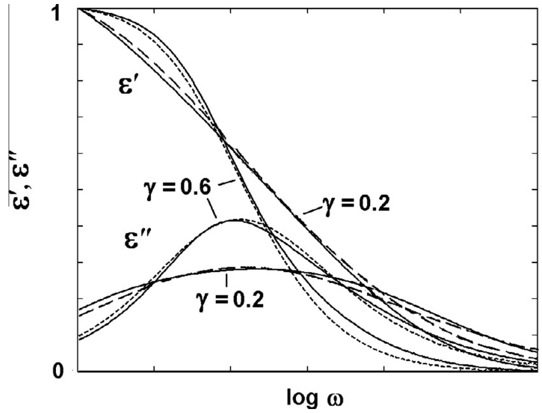

Fig. 5. The real and imaginary parts of permittivity obtained by the Fourier transform of the KWW (dashed) and function (14) (solid). The KWW parameter γ values are shown in the graphs.

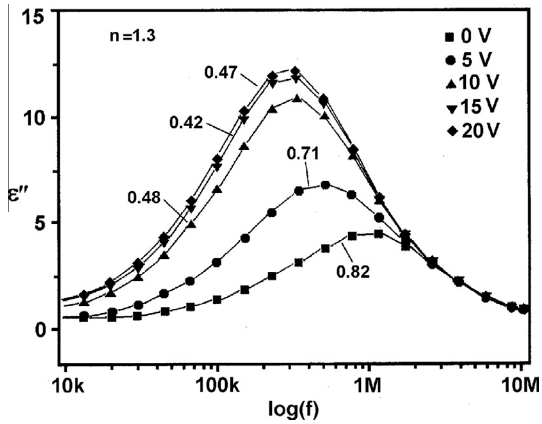

Fig. 6. The imaginary part of nematic liquid crystal permittivity at various constant bias voltages obtained in work [20] (with permission of Elsevier). The a and n values giving the close fit to the experimental curves are shown in the graphs.

One can see that at low bias (0 V, 5 V) the loss peaks have the left asymmetry. The shape of peaks 10 V, 15 V, and 20 V are estimated by the graphical method [21]. The peaks 10 V and 15 V have the slight negative asymmetry, the peak 20 V has the near CC shape, i.e. with the bias increase the left-skewed peak tends to the CC shape. As follows from Fig. 3, the parameter n rising ($n < 1.85$) leads to the significant loss peak widening, at the same time the a decreasing ($a > 0.9$) leads to the insignificant narrowing of the one. The simple measurement by a ruler of the loss peak half-height width in Fig. 6 shows the insignificant rising of the one with the bias rising. Hence the bias rising causes the parameter a decreasing. The digital Fourier transform of function (14) shows close fit of calculated functions to the curves shown in Fig 6. The n and a parameter values giving close fit of calculated functions to the experimental curves are shown in the figure.

5. Conclusions

In the present work the novel theoretically validated relaxation function is obtained. It has some advantageous in comparison with the KWW function. The presented theoretical model gives a key to understanding the nature of relaxation phenomena. Moreover, the new approach to the relaxation polarization problem solving is shown.

The private case of oscillator with nonlinear spring force (11) is considered above. The restoring force function may be more complicated; moreover the friction force may be nonlinear too, i.e. a set of relaxation functions may be unlimited.

The subject of relaxation covers all types of stress relief in solids – dielectric, mechanical, chemical and so on. Therefore, the all of the above conclusions in the stated model may be used in various branches of science and engineering.

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