

Relaxation function for the non-Debye relaxation spectra description



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ARTICLE INFO

Article history:

Received 28 June 2013

In final form 31 October 2013

Available online 9 November 2013

Keywords:

Dielectric relaxation

Non-Debye spectra

Relaxation function

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:

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

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:

$$P(t) = P_0 e^{-t/\tau}, \quad (2)$$

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

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

where α is the constant ($1 \geq \alpha > 0$) 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.

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

here β is the constant ($1 > \beta \geq 0$) 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:

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

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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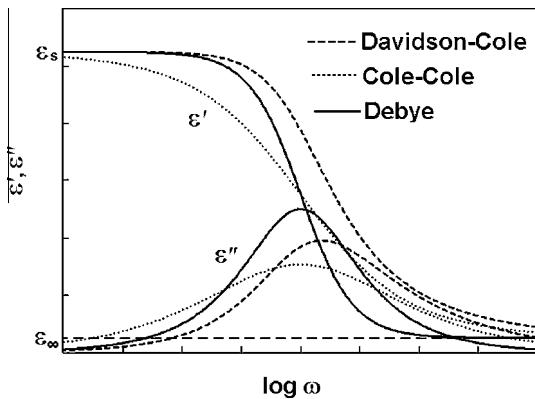


Fig. 1. The real and imaginary parts of dielectric constant vs. logarithmic frequency for Eqs. (1), (3), and (4).

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

$$P(t) = P_0 e^{-(t/\tau)^\gamma} \quad (6)$$

where γ is the constant ($1 \geq \gamma > 0$) [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]

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

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]:

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

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

$$x(t) = x_0 e^{-t/\tau} \quad (9)$$

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

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

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

$$f(x) = k \cdot x + k_1 \cdot x^n \quad (11)$$

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

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