Numerical simulation method for identification of experimental results according to frequency dispersion of dielectric permittivity by Havriliak-Negami

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Abstract. One of the problems physics of dielectrics which has not yet been completely solved is the determination of the form of the frequency dispersion of the dielectric constant. For relaxation mechanisms of polarization of dielectrics, there are many mathematical models. In practice, when analyzing experimental results, parameters are selected that correlate the results obtained with the proposed models. The goal of this paper is to search for basic equations to create a rapid method for identifying experimental results with the Havriliak-Negami model. The paper analyzes the influence of the parameters α and β in the dispersion model of Havriliak-Negami for relaxation dielectric permittivity by the method of numerical simulation. The tangents of the slope angle \( \lg \varepsilon'_{\text{rel}} \) are analyzed as functions of \( \log \omega \) at \( \omega < 1/\tau \) and \( \omega > 1/\tau \), and resolving formulas for α and β are obtained on the basis of these relationships. The relaxation time is found from the condition of independence from α and β on the basis of the analysis of the function \( \varepsilon'_{\text{rel}}/(\varepsilon' - \varepsilon_{\infty}) \). The values of \( \varepsilon_S \) and \( \varepsilon_{\infty} \) are found on the basis of the polynomial representation of the Argand (Cole-Cole) diagrams.

1. Introduction

One of the generalized models of the frequency dispersion of the dielectric constant is the Havriliak-Negami model [1]. According to this model

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

Depending on the parameters α and β, equation (1) goes:
- for α = 0 and β = 1 - Debye model;
- for \( 0 < \alpha < 1 \) and \( \beta = 1 \) - Cole-Cole model;
- for α = 0 and \( 0 < \beta < 1 \) - Davidson-Cole model.

Finding the fit of experimental results with the Havriliak-Negami model implies the determination of the following parameters of this model:
- high-frequency \( \varepsilon_{\infty} \) and low-frequency \( \varepsilon_S \) dielectric constant;
- relaxation time \( \tau \);
- dispersion parameters of the distribution of relaxation time α and β.

Different researchers approached the problem of identifying frequency dispersions in different ways. For example, Lukichev A.A. [2] modified the mathematical form of the Gavrilyaka-Negami...
frequency dispersion, but in the analysis applied the not quite correct ratio $\omega(\varepsilon''_{\text{max}})\tau=1$. In addition, it seems illogical to introduce the parameter $C=\log(\tau)/\log(\tau)$, where $\log(\tau)$ is selected based on the initial temperature of the experiment.

Bogatin A.S. [3] proposed an extrapolation method for determining the type of distribution of relaxers in dielectrics. However, the authors cite expressions for $\varepsilon'$ and $\varepsilon''$ as $\omega \to \infty$ are not entirely consistent with the expressions for the Havriliak-Negami model.

2. Getting the basic equations using the method of numerical simulation.

The expressions for the real and imaginary parts of the complex dielectric constant of the Havriliak-Negami model have the form [4]:

$$
\varepsilon' = \varepsilon_\infty + (\varepsilon_S - \varepsilon_\infty) \left(1 - \frac{1}{2}\right) \cos \beta \theta
$$

$$
\varepsilon'' = (\varepsilon_S - \varepsilon_\infty) \left(1 - \frac{1}{2}\right) \sin \beta \theta
$$

where

$$
r = \left[1 + \left(\frac{\omega \tau}{1 - \alpha}\right)^{1 - \alpha} \sin \left(\frac{\alpha \pi}{2}\right)\right]^2 + \left[\left(\frac{\omega \tau}{1 - \alpha}\right)^{1 - \alpha} \cos \left(\frac{\alpha \pi}{2}\right)\right]^2
$$

$$
\theta = \arctg\left[\frac{\left(\frac{\omega \tau}{1 - \alpha}\right)^{1 - \alpha} \cos \left(\frac{\alpha \pi}{2}\right)}{1 + \left(\frac{\omega \tau}{1 - \alpha}\right)^{1 - \alpha} \sin \left(\frac{\alpha \pi}{2}\right)}\right]
$$

Let us pay attention to the independence of the high-frequency $\varepsilon_\infty$ and static $\varepsilon_S$ dielectric constant on the parameters $\alpha$, $\beta$ and $\tau$. To determine $\varepsilon_\infty$ and $\varepsilon_S$, it is advisable to use the Argand (Cole-Cole) diagram technique. By constructing the dependence $\varepsilon''_{\text{rel}}=f(\varepsilon')$ and applying a polynomial representation of the function $\varepsilon''_{\text{rel}}=f(\varepsilon')$ in the limit as $\varepsilon''_{\text{rel}}\to0$, we obtain the values of $\varepsilon_\infty$ and $\varepsilon_S$.

The first stage of the implementation of numerical simulation involves the clarification of the nature of the parameters $\alpha$ and $\beta$.

On Figure 1 shows the Argand diagrams and the dependences $\log\varepsilon''_{\text{rel}}=f(\log\omega)$ at $\tau=10^{-3}$, $\varepsilon_\infty=3$, and $\Delta\varepsilon=5$.

![Figure 1](image.png)

**Figure 1.** Dependences $\log\varepsilon''_{\text{rel}}=f(\log\omega)$ for different values of the parameters $\alpha$ and $\beta$.

Note the observed features. Parameter $\alpha$ at increase:

- reduces the maximum value $\varepsilon''=f(\varepsilon')$;
- symmetrically broadens the frequency dispersion $\varepsilon''$ and lowers the maximum value of $\varepsilon''$;
- actively reduces $\tan\gamma_1$ and $\tan\gamma_2$. 


Parameter $\beta$ when decreasing:
- reduces the maximum $\varepsilon''=f(\varepsilon')$ and moves its position on the $\varepsilon'$ scale to the side of large values;
- shifts the maximum $\varepsilon''=f(\omega)$ towards high frequencies;
- actively reduces $\tan\gamma_2$ at $\omega>1/\tau$.

The essence of numerical simulation is that the selected parameter, for example $\tan\gamma$, is found as a function of $\beta$:

$$\tan\gamma_1 = a_0(\alpha) + a_1(\alpha)\beta + a_2(\alpha)\beta^2.$$  

A separate study are dependencies $a_0=f_0(\alpha)$, $a_1=f_1(\alpha)$, $a_2=f_2(\alpha)$.

The results of studies on the effect of the parameter $\alpha$ for different values of $\beta$ and, respectively, $\beta$ for different $\alpha$ on $\tan\gamma_1$ and $\tan\gamma_2$ are presented on Figure 2

![Figure 2](image)

**Figure 2.** The dependences of $\tan\gamma_1$ and $\tan\gamma_2$ for different values of $\alpha$ and $\beta$.

The result presented on figure 2 allows for the experimental values of $\tan\gamma_1$ to determine the value of $\alpha$:

$$\alpha = \frac{1 - \tan\gamma_1}{1.048} \approx 1 - \tan\gamma_1$$  

(6)

From figure 2a, it can be seen that the dependence $\tan\gamma_1=f(\beta)$ is insignificant. Using the results of figure 2b:

$$\beta = \frac{\tan\gamma_2 + 0.0358\alpha - 0.0004}{1.0020 - 1.00732\alpha} \approx \frac{\tan\gamma_2 + 0.036\alpha}{1 - \alpha}$$  

(7)

where $(1-\alpha)\beta = \tan\gamma_2$.

The time of relaxation $\tau$ can be determined in two ways. The first way involves the calculation for different frequencies of expressions

$$B = \frac{1}{(1-\alpha)} \left[ \frac{A}{\log(\omega)} \right]^{\alpha \pi} - \log(\omega)$$  

(8)

$$A = \arctg \left( \frac{\varepsilon''}{\varepsilon' - \varepsilon_n} \right) = f(\omega \tau)$$  

(9)

The last relations are performed under the condition of independence from the corresponding values of $\alpha$ and $\beta$.

Then $B=f(\log(\omega))$ will give the averaged values of the time of relaxation $\tau = 10^0$.  

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The second way is based on the fact that the displacement of a point with the maximum value of $\varepsilon''_{\text{rel}}$ on the scale $\omega$ is determined by

$$\log(\omega_{\text{max}}\tau) = (0.355-0.25\alpha)+(0.17+0.24\alpha)(1-\beta)$$  \hspace{1cm} (10)$$

and this ratio can be used to determine the relaxation time $\tau$.

The results of numerical modeling of dependences on the parameters $\alpha$ and $\beta$ allow us to determine the order of possible processing of experimental results: determining $\varepsilon_\infty$ and $\varepsilon_S$ based on Argand diagrams, then determining $\alpha$ based on equation (6), then finding $\beta$ using (7), based on (8), (9) or (10) is determined by $\tau$.

The above analysis is based on the analysis of the frequency dispersion of the imaginary part of the complex dielectric constant $\varepsilon''$. The time of relaxation obtained with this approach corresponds, according to the relation $\varepsilon''=\sigma/(\varepsilon_0\omega)$, to the relaxation time of the specific electrical conductivity $\tau_\sigma$. In 1964, Jacquard [5] theoretically proved that the dielectric constant relaxation time is $\tau_\varepsilon$ against $\tau_\sigma$ ($\tau_\varepsilon>\tau_\sigma$).

As a result of a search for a processing technique based only on the frequency dependence of the real part of $\varepsilon'$, the following procedure was proposed, involving the use of numerical simulation. For the model calculation of $\varepsilon'$, the following parameters were used: $\tau_0 = 10^{-3}$ s, $\varepsilon_\infty = 3$, $\varepsilon_S = 13$. According to equations (2) - (5), in the Havriliak-Negami model, tables of values were compiled for $\beta=1$ and $\alpha=0$; 0.1; 0.2; 0.4; 0.6 and at $\alpha=0$ and values $\beta=1; 0.8; 0.6; 0.4$. In the Debye frequency dispersion, the time of relaxation is $\tau_0$, as in the Havriliak-Negami model. At frequency $\omega$, relaxers with a time of relaxation $\tau$ resonate so that $\omega\tau=1$. The distribution of relaxers in frequency is determined by the parameters $\alpha$ and $\beta$ [6]. Debye's frequency dispersion formula is converted to:

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + \omega^2\tau_0^2} = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + \left(\frac{\tau_0}{\tau}\right)^2}\hspace{1cm} (11)$$

From (11) we obtain

$$\frac{\tau_0}{\tau} = \sqrt{\frac{\varepsilon_S - \varepsilon_\infty}{\varepsilon' - \varepsilon_\infty} - 1}$$ \hspace{1cm} (12)$$

Let us find out the dependence of $\tau_0/\tau$ on $\omega$. According to the model of Havriliak-Negami:

$$\frac{\tau_0}{\tau} = \sqrt{\frac{r^2}{\cos\beta\theta} - 1}$$ \hspace{1cm} (13)$$

where the parameters $r$ and $\theta$ are determined by equations (4) and (5), respectively.

The result of the model calculation is shown in Figure 3.
From figure 3 it follows that $\tau/\tau_0$ has a value close to 1 at $\omega=1/\tau_0$. In the frequency range $\omega < 1/\tau_0$, $\frac{d\lg\left(\frac{\tau}{\tau_0}\right)}{d\lg\omega} \approx 1 - \alpha$ and in the frequency range $\omega > 1/\tau_0$, $\frac{d\lg\left(\frac{\tau}{\tau_0}\right)}{d\lg\omega} \approx (1 - \alpha)\frac{\beta}{2}$. When processing the experimental results, based on (12), a graph is plotted $\lg\left(\frac{\tau}{\tau_0}\right) = f(\omega)$. Then the kink gives the frequency $\omega=1/\tau_0$, and further $\tan\alpha = \left(\frac{d\lg\left(\frac{\tau}{\tau_0}\right)}{d\lg\omega}\right)_{\omega=1/\tau_0} = 1 - \alpha$ and $\tan\beta = \left(\frac{d\lg\left(\frac{\tau}{\tau_0}\right)}{d\lg\omega}\right)_{\omega=1/\tau_0} = (1 - \alpha)\frac{\beta}{2}$.

The technique of numerical simulation allowed us to find empirical relationships that allow us to speed up the processing of experimental results to find the parameters of the frequency dispersion of the dielectric constant using the Havriliak-Negami model.

Note that the described methods become uninformative when the frequency $\omega=1/\tau_0$ falls on the edge of the frequency interval used in the experiment. Artificial expansion of the number of experimental points can be achieved using the polynomial representation $\varepsilon'' = f(\varepsilon')$ and establishing a connection between $\varepsilon'$ and $\omega$ near $\varepsilon_S$ or $\varepsilon_\infty$.

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