INTERCONNECTION BETWEEN
THE EMPIRICAL HAVRILIAK - NEGAMI
AND THE THEORETICAL "FIRST
PASSAGE" RELAXATION FUNCTION

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ABSTRACT

This paper provides the frequency domain analysis of the probabilistic representation of dielectric relaxation in dipolar systems. The present considerations complete the time domain results obtained earlier. Here it is found theoretically that the restriction (0,1) for both the power-law coefficients \( n \) and \( m \), describing the empirical behaviour of the complex dielectric susceptibility \( \chi(\omega) = \chi'(\omega) - i\chi''(\omega) \), is the necessary condition for the existence of the frequency-independent rules \( \chi''(\omega)/\chi'(\omega) = \cot(n\pi/2) \) for \( \omega > \omega_p \) and \( \chi''(\omega)/\chi'(\omega) = \cot(n\pi) \) for \( \omega < \omega_p \).

This paper provides also a graphical illustration of possible dielectric responses resulting from the probabilistic discussion. The interconnection between the empirical Havriliak-Negami and the theoretical "first passage" relaxation function is demonstrated.

KEY WORDS

Relaxing dipolar system, frequency domain analysis, probabilistic discussion.

INTRODUCTION

The dielectric response of dipolar solids has been long recognized [1] to deviate more or less strongly from the classical Debye spectrum given by the frequency dependence of the complex susceptibility:

\[
\chi_D(\omega) = \chi'_D(\omega) - i\chi''_D(\omega) = \frac{1}{1 + i\omega\tau_D}
\]

or the corresponding time dependence of the depolarisation current:

\[
i_D(t) = \alpha \exp\left(-\frac{t}{\tau_D}\right)
\]
where $\tau_D$ is the Debye relaxation time. It has been observed that the
dielectric response of most dielectrics is given by the following
universal responses in the frequency domain, at high frequencies
above any loss peak frequency $\omega_p$
\[ \chi'(\omega) \alpha \chi''(\omega) \alpha \omega^{-n} \text{ for } \omega >> \omega_p \]  
(1)
while below $\omega_p$ the corresponding relation may be written in the form
involving the polarisation decrement $\Delta \chi'(\omega) = \chi'(0) - \chi'(\omega)$
\[ \Delta \chi'(\omega) \alpha \chi''(\omega) \alpha \omega^{-m} \text{ for } \omega << \omega_p \]  
(2)
where both the power-low coefficients $n$ and $m$ fall in the range (0,1).
The corresponding time domain response in the respective ranges is
given by the following relations
\[ i(t) \alpha t^{-n} \text{ for } t << 1 / \omega_p \]  
(3)
and
\[ i(t) \alpha t^{-m-1} \text{ for } t >> 1 / \omega_p \]  
(4)
It has been pointed out [1, 2] that the experimental results (1) and
(2) imply the following frequency-independent rules
\[ \frac{\chi''(\omega)}{\chi'(\omega)} = \cot \left( \frac{n \pi}{2} \right) \text{ for } \omega >> \omega_p \]  
(5)
and
\[ \frac{\chi''(\omega)}{\Delta \chi'(\omega)} = \tan \left( \frac{m \pi}{2} \right) \text{ for } \omega << \omega_p \]  
(6)
which underline the differences in the nature of the high- and low-
frequency polarisation processes. Equ. (5) shows that when a system is
driven by an AC field the energy recoverable per cycle remains a con-
stant fraction of the work done by the field independent of frequency
in the frequency range $\omega >> \omega_p$. When a system is driven by an AC
field in the frequency range $\omega << \omega_p$, then it follows from equ.(6) that
the energy lost per cycle has a constant relationship to the extra en-
ergy that can be stored by a static field. The reason for the finite value
of the polarisation decrement $\Delta \chi'(\omega)$ lies in the inability of polarisation
to follow the magnitude of the field due to the inherent delays in
the process (3).

The fascinating and challenging property of the dielectric response
law is its applicability very largely regardless of the detailed physical
and chemical nature of the materials in which it is observed. The in-
terpretation of the physical basis of this universality has occupied
many workers [1-14]. Historically the earliest attempts to reconcile
the observed non-exponential relaxation with the classical Debye
process was the assumption of the Distribution of Relaxation Times
(DRT) [12] leading to a summation of the contributions of individual entities. The relaxation function of a system was expressed as a weighted average of exponential relaxation function. There is no mathematical objection to use of this formalism introduced 80 years ago but the most serious objection lies in the observed universality of the dielectric response, since this requires a proof why the same form of distribution of relaxation times should apply in all the different systems.

Recently there has been introduced a probabilistic representation [15-17] of the cluster model [4] for dipolar dielectric relaxation which extends the plausible on physical grounds DRT concept in such a way that it can yield the fractional power-law response (3) and (4). The rigorous mathematical approach to the dielectric relaxation is based on a revised definition of relaxation function [15] which expresses the probability that the whole system has not changed its initial state, imposed by an external field, up to time $t$. This attempt not only explains why the fractional power-law (or its special case: the Williams-Watts response) should be so universally applicable but also supplies the necessary and sufficient conditions for it.

The frequency domain analysis presented here completes the time domain results [17] and shows how the rules (5) and (6) follow from the new probabilistic representation of relaxing dipolar systems. Moreover, it yields the theoretical restriction $(0,1)$ for the power-law coefficients $n$ and $m$, while the time domain analysis has led only to the following results: $0 < n < 1$ and $m > 0$. The extension of Havriliak-Negami function is introduced. It is compared with the theoretical results by means of numerical methods.

**FREQUENCY DOMAIN ANALYSIS OF „FIRST PASSAGE” RELAXATION FUNCTION**

The time domain analysis of the probabilistic representation of relaxing dipolar systems, presented in [17], has led to the general relaxation equation

$$\frac{d\phi}{dt}(t) = -\alpha A(At)^{\alpha-1}\left(1 - \exp\left(-\frac{(At)^{-\gamma}}{k}\right)\right)\phi_t$$

(7)

which is fulfilled by the relaxation function

$$\phi(t) = \lim_{N \to \infty} P(r(N, \min(\theta_{1N}, \ldots, \theta_{NN}) \geq t))$$

(8)

where $\theta_{iN}$ represents the random switching time of the $i$-th ipole in a system of $N$ initially aligned dipoles. The relaxation function (8) stands for the survival probability of a dipolar system and is called „first passage” relaxation function [18].
The parameters $0 < \alpha < 1$, $\gamma > 0$, $A > 0$ and $k > 0$ are defined by the Lévy-stable [19] and max-stable [20] laws. If the parameter $k$ tends to 0, equ. (7) takes on the well-known form [2, 6, 9, 11]

$$\frac{d\phi(t)}{dt} = -\alpha A(At)^{\alpha-1}\phi(t)$$

with the solution

$$\phi(t) = \exp\left(-\left(At\right)^{\alpha}\right)$$

which is just the Williams-Watts relaxation function.

The time dependence of the depolarisation current is determined by the response function $f(t)$ given as the negative time derivative of the relaxation function $\phi(t)$. It has been shown [17] that the response function $f(t)$, obtained from the solution of equ.(7), has the fractional power-law coefficients $n$ and $m$ equal

$$n = 1 - \alpha,$$

$$m = \begin{cases} \frac{\alpha}{k} & \text{if } \gamma = \alpha, \\ \gamma - \alpha & \text{if } \gamma > \alpha. \end{cases}$$

At this point we have to note that the two cases $\gamma = \alpha$ and $\gamma > \alpha$ impose a difference in long-time behaviour of the relaxation function (8), [17]: Namely, for $t \rightarrow \infty$

$$\phi(t) \rightarrow \begin{cases} 0 & \text{for } \gamma = \alpha \\ \text{const} > 0 & \text{for } \gamma > \alpha \end{cases}$$

Moreover, although the restriction $(0,1)$ is imposed by empirical data for both the power-law coefficients $n$ and $m$, the time domain analysis has led only to the results $0 < n < 1$ and $m > 0$ [17].

The mathematical basis for the treatment of the frequency domain response rests on the Fourier transformation of the response function $f(t)$, which defines the complex frequency-dependent susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$.

Hence, in terms of the result (7), the dielectric susceptibility $\chi(\omega)$ has the form:

$$\chi(\omega) = \int_0^\infty \alpha A(At)^{\alpha-1}\left(1 - \exp\left(-\frac{(At)^{\gamma}}{k}\right)\right)\phi(t)e^{-i\omega t} dt$$

Consequently, in the high-frequency region we have

$$\omega^\alpha \chi(\omega) = \int_0^\infty \alpha A(At)^{\alpha-1}e^{-i(1 - \exp\left(-\frac{(At)^{\gamma}}{k}\right)\phi\left(\frac{t}{\omega}\right)} dt$$

$$\xrightarrow{\omega \rightarrow \infty} \text{const} \int_0^\infty t^{\alpha-1}e^{-i t} dt$$
Therefore we get
\[
\frac{\chi(\omega)}{\omega^{n-1}} \xrightarrow{\omega \to \infty} \text{const} \int_0^\infty t^{-n} e^{-it} dt
\]
where \( n \) is the high-frequency power-law coefficient, see equ.(9). From the time domain analysis [17] we have \( 0 < n < 1 \) and so there exists integral
\[
\int_0^\infty t^{-n} e^{-it} dt
\]
Hence the dielectric susceptibility \( \chi(\omega) \), given by equ.(10), fulfills the high-frequency relation (1). Moreover, it follows from the theory of complex functions (see [21]) that
\[
\lim_{\omega \to \infty} \frac{\chi''(\omega)}{\chi'(\omega)} = \cot \frac{n \pi}{2}.
\]
The above result, which holds also for the Williams-Watts relaxation function [22], is in agreement with the experimental rule (5).

In the low-frequency region we have to investigate two distinct cases: \( \gamma > \alpha \) and \( \gamma = \alpha \). When \( \gamma > \alpha \)
\[
\frac{\chi(0) - \chi(\omega)}{\omega^{\gamma-\alpha}} =
\]
\[
= \int_0^\infty \alpha A / k (At)^{\alpha/\gamma - 1} (1 - e^{-it}) \frac{1 - \exp(-\omega^\gamma (At)^{-\gamma} / k)}{\omega^\gamma (At)^{-\gamma} / k} \phi \left( \frac{t}{\omega} \right) dt
\]
and
\[
\frac{\chi(0) - \chi(\omega)}{\omega^{\gamma-\alpha}} \xrightarrow{\omega \to 0} \text{const} \int_0^\infty t^{\alpha - \gamma - 1} (1 - e^{-it}) dt
\]
(11)

When \( \gamma = \alpha \)
\[
\frac{\chi(0) - \chi(\omega)}{\omega^{\alpha/k}} =
\]
\[
= \int_0^\infty \alpha A / k (At)^{-\alpha/k - 1} (1 - e^{-it}) \frac{1 - \exp(-\omega^\gamma (At)^{-\gamma} / k)}{\omega^\gamma (At)^{-\gamma} / k} \left( \frac{t}{\omega} \right)^{\alpha/k} \phi \left( \frac{t}{\omega} \right) dt
\]
and
\[
\frac{\chi(0) - \chi(\omega)}{\omega^{\alpha/k}} \xrightarrow{\omega \to 0} \text{const} \int_0^\infty t^{-\alpha/k - 1} (1 - e^{-it}) dt
\]
(12)

From the above results, eqs.(11) and (12), we get
\[
\frac{\chi(0) - \chi(\omega)}{\omega^m} \xrightarrow{\omega \to 0} \text{const} \int_0^\infty t^{-m-1} (1 - e^{-it}) dt
\]
(13)
where \( m \) is the low-frequency power-law coefficient, see equ(9). Hence the limit (13) depends on the value taken by the integral.
\[ \int_0^\infty t^{-m-1} (1-e^{-it}) dt \]

which exists if and only if \( 0 < m < 1 \). Consequently, when \( 0 < m < 1 \) the low-frequency relation (2) is fulfilled. Moreover, it follows from the theory of complex functions (see [21]) that

\[ \lim_{\omega \to 0} \frac{\chi''(\omega)}{\chi'(0) - \chi'(\omega)} = \tan\left( m \frac{\pi}{2} \right) \]

which is in agreement with the low-frequency empirical result (6).

**DISCUSSION OF EMPIRICAL AND THEORETICAL DIELECTRIC SUSCEPTIBILITY**

In this chapter we compare the most commonly used empirical function proposed by S. Havriliak and S. Negami [1, 12] and the theoretically derived dielectric susceptibility function \( \chi(\omega) \), equ.(10), for \( \gamma = \alpha \). Equ.(10) in its general form cannot be solved analytically, therefore we present the numerical results obtained by applying the Fast Fourier Transform procedure [23].

The Havriliak-Negami function is a combination of two empirical, Cole-Cole and Cole-Davidson functions and can be written in the form:

\[ \chi(\omega) = \chi_\infty + \frac{\chi(0) - \chi_\infty}{(1 + (i\omega \tau_p)^{\alpha})^{\beta}} \]  

(14)

where \( \chi(0) \) is a static dielectric susceptibility, \( \chi_\infty \) is the susceptibility at infinitely high frequencies, \( \tau_p = 1/\omega_p \) and \( 0 < \alpha, \beta < 1 \). It should be stressed that the empirical parameters \( \alpha \) and \( \beta \) have no physical sense. Expression (14) has the respective limiting behaviours (1) and (2) with \( n - 1 = -\alpha, \beta \) and \( m = \alpha \):

\[ \chi'(\omega) \propto \chi''(\omega) \propto \omega^{-\alpha\beta} \quad \text{for} \quad \omega >> \omega_p \]

\[ \Delta \chi'(\omega) \propto \chi''(\omega) \propto \omega^{\bar{\alpha}} \quad \text{for} \quad \omega << \omega_p \]

Let us observe that for Havriliak-Negami response the parameters \( n \) and \( m \) are formally related in the following way:

\[ m = \frac{1-n}{\bar{\beta}}, \quad \text{where} \quad 0 < \bar{\beta} < 1 \]  

(15)

The "ad hoc" assumptions \( 0 < \bar{\alpha} < 1 \) and \( 0 < \bar{\beta} < 1 \) imply then:

\[ 0 < 1-n < m \quad \text{and} \quad 0 < m < 1 \]

or equivalently
\[ 0 < n < 1 \text{ and } 1 - n < m < 1. \]

Therefore for the Havriliak-Negami function there is formally obtainable the typical range of dielectric response [24] \( 0 < n < 1, 1 - n < m < 1 \), while the less typical range \( 0 < n < 1, 0 < m < 1 - n \) is unavailable since this would require \( 0 < \bar{\alpha} < 1 / \bar{\beta}, \bar{\beta} > 1 \).

On the other hand, from the theoretical considerations [17] we get in the case \( \gamma = \alpha \) the relation

\[
m = \frac{1 - n}{k}, \quad \text{where } 0 < n < 1, \ k > 1 - n \tag{16}
\]

which covers the typical as well as the less typical ranges of dielectric response.

As one can see from the above discussion, the parameters \( \alpha \) and \( \beta \) of the Havriliak-Negami function do not cover the full range \( 0 < n, m > 1 \). To obtain an extension to the full range we propose a revised form of this function

\[
\chi(\omega) = \chi_\infty + \frac{\chi(0) - \chi_\infty}{1 + (i\omega \tau_p)^{\alpha/k}} \tag{17}
\]

where \( \alpha, \ k \) are the parameters of the theoretical function (10), \( 0 < \alpha < 1 \) and \( k \geq \alpha \). The case \( k > 1 \) stands for the less typical responses which cannot be described by the original Havriliak-Negami function (14).

Below, on Fig.1 and Fig.2, we present the numerically obtained solutions of equ.(10) plotted with the revised Havriliak-Negami function. The abbreviations denote:

- \( \text{D} \) - Debye response,
- \( \text{C-C} \) - Cole-Cole response,
- \( \text{C-D} \) - Cole-Davidson response,
- \( \text{H-N} \) - extended Havriliak-Negami response.

The theoretical function (10) has the same power-law properties as the empirical Havriliak-Negami function; however, these are not exactly the same functions. To stress the difference for the theoretical function we put the above abbreviations in quotation marks, e.g., "C-C" denotes the Cole-Cole-like theoretical response. Note that the Debye-like response "D" can be recognized as a broadened Debye response BD [1].
Fig. 1. Numerical comparison of Havriliak-Negami function and the theoretical susceptibility. Solid line denotes the empirical response, dashed line - the theoretical response. a) C-D and "C-D" response: $\alpha=0.3$ and $k=0.3$; b) H-N and "H-N" response: $\alpha=0.3$ and $k=0.5$; c) C-C and "C-C" response: $\alpha=0.3$ and $k=1.0$; d) H-N and "H-N" response: $\alpha=0.3$ and $k=1.2$.

Fig. 2. Numerical comparison of Havriliak-Negami function and the theoretical susceptibility. Solid line denotes the empirical response, dashed line - the theoretical response. a) C-D and "C-D" response: $\alpha=0.8$ and $k=0.8$; b) H-N and "H-N" response: $\alpha=0.8$ and $k=1.2$; c) D and "D = BD" response; d) H-N and "H-N" response: $\alpha=0.83$ and $k=1.2$. 
CONCLUSIONS

In this paper we have presented the frequency domain analysis of the probabilistic representation of a relaxing dipolar system proposed in [15-18]. We have obtained theoretically not only the experimentally observed high-frequency result (5) (as was found in the case of the Williams-Watts response, see [22]) but also the low-frequency rule (6). Moreover, the power-law coefficient $m$ has been shown to fall in the range $(0,1)$ (as is imposed by empirical data) which completes the time doznin considerations presented in [17].

We have also proposed a, revised form of the original Havriliak-Negami function in order to cover by this function the full range of the dielectric responses. Then we have compared numerically the extended Havriliak-Negami function with the dielectric susceptibility (10) obtained theoretically. The results can be summarized in diagrams, Fig. 3 and 4. Note that the abbreviations KWZ and FL in Fig. 4 denote the Kohlrausch-Williams-Watts and the flat response respectively, not described by the extended Havriliak-Negami function.

![Fig. 3. Graphical representation of empirical dielectric response.](image1)

![Fig. 4. Graphical representation of theoretical dielectric response.](image2)

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