INFINITELY DIVISIBLE WAITING-TIME DISTRIBUTIONS UNDERLYING THE EMPIRICAL RELAXATION RESPONSES*

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The frequency-domain Havriliak–Negami and the time-domain Kohlrausch–Williams–Watts relaxation functions have found widespread acceptance in representing the relaxation data of dielectric systems. Since both functions yield an accurate description of real data in corresponding domains, a relationship between them is often suggested. In this paper we show that although a suitable choice of the parameters can lead in some ranges to a very small deviation between the plots of the functions, the empirical responses follow from clearly different mathematical reasons. We find a common probabilistic origin of both empirical relaxation functions. We obtain that the corresponding waiting-time distributions are infinitely divisible what may provide a clue to explain the universality observed in relaxation phenomena.

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1. Introduction

The "anomalous" nonexponential relaxation responses of various complex systems have attracted much attention of scientists for several decades. The natural description of such systems, introducing the notion of distribution

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functions of different physical quantities (random bonds, fields, relaxation times *etc.*, see *e.g.* [1–11]), clearly implies the use of probability theory technique.

The present paper is an attempt to shed some light on the probabilistic background of the empirical functions used to fit the dielectric relaxation data [1–4]. The frequency dielectric spectra are interpreted mainly by means of the Havriliak–Negami (HN) function defined as:

$$\frac{\chi(\omega) - \chi_\infty}{\chi_0 - \chi_\infty} = \phi^*_{\mathrm{HN}}(\omega) = \frac{1}{\left(1 + (i\tau_{\mathrm{HN}}\omega)^a\right)^b} \ , \tag{1}$$

where $0 < a, ab \leq 1$, the constant χ_∞ represents the asymptotical value of the dielectric susceptibility $\chi(\omega)$ at high frequencies and χ_0 is the value of the opposite limit. For $a = 1$ and $b < 1$ formula (1) takes the form known as the empirical Cole–Davidson (CD) function, for $b = 1$ and $a < 1$ it takes the form of the Cole–Cole (CC) function, while for $a = 1$ and $b = 1$ one obtains the classical Debye (D) formula.

On the other hand, the time-dependent response of dielectric systems to a steady electric field is usually described by the Kohlrausch–Williams–Watts (KWW) function

$$\phi_{\mathrm{KWW}}(t) = \exp\left(-\left(\frac{t}{\tau_{\mathrm{KWW}}}\right)^c\right) \ , \tag{2}$$

where $0 < c < 1$. For both functions the parameter τ with a respective index has the meaning of a time constant characteristic to the material.

The HN and KWW functions have both found a widespread acceptance in representing the relaxation data in the corresponding domains and therefore the interconnection between them has been the subject of several attempts to relaxation phenomena. Despite the dissimilarity of functional forms of the considered functions it has been claimed on the basis of numerical investigations [3, 12–14] that within experimental error the KWW function is a specific case of the HN function. One should notice, however, that the numerical similarity of the functions can be stated in some ranges only, see *e.g.* figure 1. The relation between the KWW and HN functions is hence worth being clarified by means of rigorous mathematical analysis concerning the underlying stochastic nature of both functions. Moreover, some mathematical rigour in physical considerations is surely needed to trace the origin of the existing distribution functions of random quantities and to indicate the universality of the observed relaxation responses.

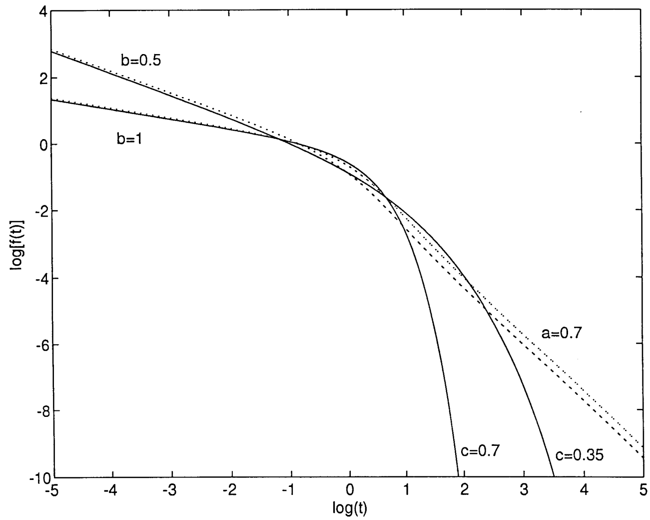

Fig. 1. The time-domain numerical comparison of the HN and KWW responses in the log–log scale. The dotted lines correspond to the Mittag–Leffler densities underlying the HN function, the solid lines — to the Weibull densities underlying the KWW function.

2. Probabilistic representation of empirical responses

Relaxing physical system can be considered as a system undergoing an irreversible transition from initial state A, imposed at time $t = 0$, to state B that differs from A in some physical parameter. The transition $A \to B$, defined as the change of this particular parameter (although changes in all other parameters may also have an influence on the process), takes place at a random instant of time θ that value is equal to the system's waiting time for the transition. The conditional probability $p(t, dt)$ that the system will undergo the transition during the time interval $(t, t + dt)$ provided that the transition did not occure before time t can be expressed by means of the random variable θ:

$$p(t, dt) = \Pr(t \leq \theta \leq t + dt \,|\, \theta \geq t)\,. \tag{3}$$

As $dt \to 0$, probability (3) can be rewritten in a form more useful for further considerations, namely,

$$p(t, dt) = -d \ln \Pr(\theta \geq t)\,,$$

where $\Pr(\theta \geq t)$ is the system's survival probability in the initial state by a time interval not less than t, *i.e.* the probability that the transition of the system from its initial state did not happen prior to the time instant t (for details, see [15]).

The survival probability $\Pr(\theta \geq t)$ determines relaxation response in both, time and frequency domains. The time-domain relaxation function $\phi(t)$ equals [5, 6, 15]:

$$\phi(t) = \Pr(\theta \geq t) = 1 - F_\theta(t)\,, \tag{4}$$

where $F_\theta(t)$ denotes the waiting-time distribution for the system to change its initial state. The frequency–domain response $\phi^*(\omega)$ is related to the function $\phi(t)$ by the one-sided Fourier transform:

$$\phi^*(\omega) = \int_0^\infty \mathrm{e}^{-i\omega t}\left(-\frac{d\phi(t)}{dt}\right) dt\,,$$

that, using the notion of the random waiting time θ introduced above, can be rewritten as

$$\phi^*(\omega) = \left\langle \mathrm{e}^{-i\omega\theta}\right\rangle = \int_0^\infty \mathrm{e}^{-i\omega t} f(t)\, dt\,. \tag{5}$$

The waiting-time probability density function $f(t) = \frac{dF_\theta(t)}{dt}$ in (5) is equal to $-\frac{d\phi(t)}{dt}$ and can be recognized as the response function. The representation of the time- and frequency-domain relaxation functions by means of the random variable θ, Eqs. (4) and (5), permits us to indicate the common probabilistic scheme underlying the appearance of the empirically established relaxation functions.

For the KWW function (2) it is easy to recognize that the waiting time θ in (4) has the Weibull distribution, defined by its density function [16, 17]

$$w_c(t) = \frac{c}{A}\left(\frac{t}{A}\right)^{c-1} \exp\left(-\left(\frac{t}{A}\right)^c\right), \quad t > 0,$$

with the shape parameter equal to c and the scale parameter $A = \tau_{\mathrm{KWW}}$.

In order to study properties of the distribution of the waiting time θ that corresponds to the HN function (1) let us take into account the following formula

$$\theta = A\, S_a\, (\Gamma_b)^{1/a}, \quad 0 < a \leq 1,\ b > 0\,, \tag{6}$$

for the random variable θ. Here S_a is such a random variable that its Laplace transform is the stretched exponential function

$$\langle \mathrm{e}^{-sS_a}\rangle = \int_0^\infty \mathrm{e}^{-st}\, h_a(t)\, dt = \mathrm{e}^{-s^a}, \quad 0 < a \leq 1\,, \tag{7}$$

and it is a well-known fact that when $a < 1$ the random variable S_a has to be distributed according to one-sided Lévy-stable law with the probability density function $h_a(t)$ (given by the series representation, for details see [18, 19]). In case $a = 1$ we have $S_1 = 1$ with probability 1 so that $h_1(t) = \delta_0(t-1)$ is the Dirac delta function. Moreover, the distribution of S_a tends to the degenerate distribution of S_1 as $a \to 1$.

The random variable Γ_b in (6) is independent of S_a and distributed according to the gamma law [16] defined by the probability density function

$$g_b(t) = \frac{1}{\Gamma(b)} t^{b-1} \mathrm{e}^{-t}, \quad t > 0\,,$$

with $\Gamma(\cdot)$ being the special gamma function [16]. It is worth noting that the Laplace transform of Γ_b takes the form

$$\left\langle \mathrm{e}^{-s\Gamma_b} \right\rangle = \int_0^\infty \mathrm{e}^{-st}\, g_b(t)\, dt = \frac{1}{(1+s)^b}\,. \tag{8}$$

Finally, the positive constant A is a scale parameter.

For θ given by (6) one obtains from the time-frequency relation (5) and properties (7), (8) that

$$\begin{aligned} \phi^*(\omega) &= \left\langle \mathrm{e}^{-i\omega A\, S_a\, (\Gamma_b)^{1/a}} \right\rangle = \int_0^\infty \left(\int_0^\infty \mathrm{e}^{-i\omega A s t^{1/a}}\, h_a(s)\, ds \right) g_b(t)\, dt \\ &= \int_0^\infty \mathrm{e}^{-(i\omega A t^{1/a})^a}\, g_b(t)\, dt = \int_0^\infty \mathrm{e}^{-(i\omega A)^a t} g_b(t)\, dt = \frac{1}{(1+(iA\omega)^a)^b}\,. \end{aligned}$$

Therefore the waiting time θ of the form (6) with $0 < ab \leq 1$ and $A = \tau_{\mathrm{HN}}$ represents the HN function (2) and, moreover, in the time domain we have

$$\phi_{\mathrm{HN}}(t) = \int_0^\infty \left\{ 1 - G_b\left(\left(\frac{t}{\tau_{\mathrm{HN}} s} \right)^a \right) \right\} h_a(s)\, ds\,, \tag{9}$$

where $G_b(x) = \int_0^x g_b(t)\, dt$.

On the other hand, the distribution of the random variable θ given by (6) is known as the generalized Mittag–Leffler distribution [20] and hence the time-domain relaxation function related to the HN function has the following series representation

$$\phi_{\mathrm{HN}}(t) = 1 - \sum_{k=0}^\infty \frac{(-1)^k\, \Gamma(b+k)}{\Gamma(b)\, k!\, \Gamma(1+a(b+k))} \left(\frac{t}{\tau_{\mathrm{HN}}} \right)^{a(b+k)}\,. \tag{10}$$

The corresponding response function

$$f_{\rm HN}(t) = \sum_{k=0}^{\infty} \frac{(-1)^k\,\Gamma(b+k)}{\Gamma(b)\,k!\,\Gamma(a(b+k))}\,\frac{1}{\tau_{\rm HN}}\left(\frac{t}{\tau_{\rm HN}}\right)^{a(b+k)-1} \tag{11}$$

can be recognized as the Riesz function. It should be mentioned that already two decades ago it has been suggested [21] that the Riesz function (11) may represent any arbitrary arrangement of Debye decays in the time domain.

Formula (6) and hence the time-domain relaxation function (9) take on simpler forms in case of the CD, CC and D responses. For the CD function ($a = 1$, $0 < b < 1$) one gets the gamma waiting-time distribution and

$$\phi_{\rm CD}(t) = 1 - G_b\,\frac{t}{\tau_{\rm CD}}\,.$$

The respective response function equals $f_{\rm CD}(t) = g_b(t/\tau_{\rm CD})/\tau_{\rm CD}$. Similarily, in case of the D function ($a = b = 1$) the corresponding waiting time is distributed according to the exponential law and

$$\phi_{\rm D}(t) = 1 - {\rm e}^{-t/\tau_{\rm D}}, \quad t > 0\,.$$

For the CC response $b = 1$ so that the gamma part of formula (6) becomes an exponentially distributed random variable and the waiting time θ has the Mittag–Leffler distribution [20]. The series representation (10) is simplified to

$$\phi_{\rm CC}(t) = 1 - \sum_{k=0}^{\infty} \frac{(-1)^k}{\Gamma(1+a(1+k))}\left(\frac{t}{\tau_{\rm CC}}\right)^{a(1+k)}.$$

It is worth noting that all the waiting-time distributions underlying the considered empirical relaxation responses are infinitely divisible [22, 23]. In case of the HN function it follows directly from the form (1) of frequency-domain function $\phi^*(\omega)$, for the KWW function it is the consequence of infinite divisibility of the Weibull distribution with the shape parameter less than 1 [24].

In order to find a relation between the HN and KWW functions it should be taken into account that the random variable $\Gamma_1^{1/c}$ has the Weibull distribution with the shape parameter equal to c. Therefore the waiting times representing the functions can be considered as specific cases of a random variable of the form

$$\theta = A\;S_a\,(\Gamma_b)^{1/ac} \tag{12}$$

with $0 < a, c \leq 1$ and $b > 0$. One gets here the KWW function for $a = b = 1$, $0 < c < 1$ and $A = \tau_{\rm KWW}$, the HN function if $c = 1$, $0 < a, ab \leq 1$, for details see Table I.

TABLE I

Waiting-time distributions underlying the empirical relaxation responses

Empirical response	Waiting time $\theta = A\ S_a\ (\Gamma_b)^{1/ac}$	Waiting time distribution $F_\theta(t)$
HN	$c = 1,\ 0 < a, ab < 1$ $\theta = \tau_{\mathrm{HN}}\ S_a\ (\Gamma_b)^{1/a}$	Generalized Mittag–Leffler distribution with the scale constant $\tau_{\mathrm{HN}} > 0$ and the parameters $0 < a, ab < 1$
CC	$b = 1,\ c = 1,\ 0 < a < 1$ $\theta = \tau_{\mathrm{CC}}\ S_a\ (\Gamma_1)^{1/a}$	Mittag–Leffler distribution with the scale constant $\tau_{\mathrm{CC}} > 0$ and the parameter $0 < a < 1$
CD	$a = 1,\ c = 1,\ 0 < b < 1$ $\theta = \tau_{\mathrm{CD}}\ \Gamma_b$	Gamma distribution with the scale constant $\tau_{\mathrm{CD}} > 0$ and the parameter $0 < b < 1$
KWW	$a = 1,\ b = 1,\ 0 < c < 1$ $\theta = \tau_{\mathrm{KWW}}\ (\Gamma_1)^{1/c}$	Weibull distribution with the scale constant $\tau_{\mathrm{KWW}} > 0$ and the parameter $0 < c < 1$
D	$a = 1,\ b = 1,\ c = 1$ $\theta = \tau_{\mathrm{D}}\ \Gamma_1$	Exponential distribution with the scale constant $\tau_{\mathrm{D}} > 0$

3. Concluding remarks

The relationship between the frequency-domain HN and the time -domain KWW functions has been studied in terms of the probabilistic approach to relaxation. The common probabilistic origin of both relaxation functions given by the general formula (12) for the system's waiting time for the transition from the initial nonequilibrium state has been found. Although both functions follow from the same formula (12), they result from different mathematical constraints imposed on the parameters of the waiting-time distribution $F_\theta(t)$, see Table I. The ranges of the parameters determine the dissimilar functional forms of the empirical relaxation functions, as well as the different stochastic mechanisms [9, 15] underlying them, and it is hence clear that the KWW function cannot be considered as a specific case of the HN function. However, the "equivalence" of both functions, expected on the basis of experimental data and numerical studies [3, 12–14], can be reached by such a choice of scale constants and distribution parameters that the distinction between graphical representations of both functions in the range taken into account is very small [13, 14], see also figure 1.

It is still an open question what a stochastic relaxation mechanism, physically acceptable, can meet the condition (12) uniquely determining the common origins of the HN and KWW relaxation functions. The obtained property of the empirical types of dielectric responses, namely, the infinite divisibility of the corresponding waiting-time distributions, may provide a clue to better understanding of the origins of relaxation phenomena.

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