HAVRILIAK–NEGAMI RESPONSE IN THE FRAMEWORK OF THE CONTINUOUS-TIME RANDOM WALK*

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We show how to modify the random-walk scenario underlying the classical, exponential relaxation response in order to derive the empirical Havriliak–Negami function, commonly used to fit the dielectric permittivity of complex-material data. The turnover from the exponential Debye to the power-law Havriliak–Negami relaxation response is associated with a new type of a coupled memory continuous-time random walk (CTRW) driving a fractional dynamics.

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1. Introduction

Dielectric relaxation is commonly defined as an approach to equilibrium of a dipolar system driven out of equilibrium by a step or alternating external electric field. It is represented in terms of the temporal relaxation function $\phi(t)$ that has a meaning of the system's survival probability in an initially

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imposed state until time t and hence is associated with the random waiting time θ of the system for the transition from the initial state. Namely, we have $\phi(t) = \Pr(\theta \geq t) = 1 - F_\theta(t)$ where $F_\theta(t)$ denotes the probability distribution function of the random time θ.

Experimentally the systems are often probed in the frequency domain under an harmonic external driving force yielding the complex permittivity $\varepsilon^*(\omega)$ as a function of the driving frequency ω. By definition, $\varepsilon^*(\omega)$ is connected to the temporal relaxation function $\phi(t)$ through the Fourier transform

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \Phi^*(\omega) = -\int_0^\infty e^{-\mathrm{i}\omega t} d\phi(t)\,,$$

where ε_0 is the static permittivity, and ε_∞ is the infinite-frequency permittivity of the sample. Equivalently, $\Phi^*(\omega) = \int_0^\infty e^{-\mathrm{i}\omega t} dF_\theta(t) = \langle e^{-\mathrm{i}\omega\theta} \rangle$ where $\langle\cdot\rangle$ denotes the average value.

As it is already well known, [1–3], all dielectric data are characterized well enough by a few empirical functions. Among them, the most popular analytical expression applied to the complex permittivity is given by the Havriliak–Negami function

$$\Phi^*(\omega) = \frac{1}{(1 + (\mathrm{i}\omega/\omega_\mathrm{p})^\alpha)^\gamma}\,, \tag{1}$$

where $0 < \alpha, \gamma < 1$, and ω_p denotes the loss peak frequency defining the characteristic system's time scale $\tau_\mathrm{p} = 1/\omega_\mathrm{p}$. Substituting $\alpha = 1$ and $\gamma = 1$ in formula (1) one obtains the spectral representation of the Debye relaxation function

$$\phi(t) = \exp(-\omega_\mathrm{p} t) \tag{2}$$

related to the exponentially distributed system's waiting time θ. In general, the relaxation function $\phi(t)$ corresponding to the Havriliak–Negami function (1) can be given in the following series representation

$$\phi(t) = 1 - \sum_{k=0}^{\infty} \frac{(-1)^k\, \Gamma(\gamma + k)}{\Gamma(\gamma)\, k!\, \Gamma(1 + \alpha(\gamma + k))} \left(\omega_\mathrm{p} t\right)^{\alpha(\gamma + k)}\,, \tag{3}$$

which can be also expressed in terms of the H-function [4]

$$\phi(t) = 1 - \frac{1}{\Gamma(\gamma)} H^{11}_{12}\left([\omega_\mathrm{p} t]^\alpha \,\Big|^{(1,1)}_{(\gamma,1)(0,\alpha)} \right).$$

The relaxation function (3) is associated with a generalized Mittag–Leffler distribution $F_\theta(t) = 1 - \phi(t)$ of the system's waiting time θ [5–7]. To make this distribution more user-friendly let us discuss its structure by means of the random-variable notation. It has been shown [6] that in case of the Havriliak–Negami response (1) the random waiting time θ (having a generalized Mittag–Leffler distribution) can be expressed as a product of two independent random variables $\mathcal{G}_\gamma$ and $\mathcal{S}_\alpha$; namely,

$$\theta = \frac{1}{\omega_{\mathrm{p}}} \mathcal{G}_\gamma^{1/\alpha} \mathcal{S}_\alpha \,, \tag{4}$$

where $\mathcal{G}_\gamma$ is distributed according to the gamma distribution with scale parameter 1 and shape parameter γ (defined by the density function $g_\gamma(t) = \frac{1}{\Gamma(\gamma)} t^{\gamma-1} e^{-t}$ for $t > 0$, and 0 otherwise), and $\mathcal{S}_\alpha$ is the completely asymmetric Lévy-stable random variable such that $\langle e^{-\mathrm{k}\mathcal{S}_\alpha} \rangle = e^{-\mathrm{k}^\alpha}$. According to formula (4), a generalized Mittag–Leffler distribution can be represented by a mixture of a generalized gamma distribution corresponding to $\mathcal{G}_\gamma^{1/\alpha}$ and the Lévy-stable distribution of $\mathcal{S}_\alpha$. Let us note that when $\alpha = 1$ and $\gamma = 1$, formula (4) simplifies to $\theta = (1/\omega_{\mathrm{p}})\mathcal{G}_1$ what denotes the exponentially distributed waiting time θ of the Debye model.

The most natural theoretical attempt to model the nonexponential relaxation phenomena is based on the diffusion of defects in the system under considerations. Originally, this concept was introduced by Zener [8, 9] in order to explain the relaxation of the strain field in a linear solid. The model of Zener was adapted by Glarum [10] assuming that vacancies such as microscopic cavities or random orientations of crystallities diffuse within the system, and when they meet an initially prepared excited state (an imposed orientation of a dipole, stress, *etc.*), the latter is allowed to relax. This idea was generalized by Shlesinger [11] and Blumen *et al.* [12] who proposed the target model for processes of anomalous statistics. The technique used by them was based on the notion of a continuous-time random walk (CTRW) introduced by Montroll and Weiss [13] for description of many types of kinetic phenomena. Recently, a new approach to study the CTRW, applying the random-variable formalism, has been developed [14–18]. As we shall show below, this mathematical tool allows us to avoid the technical difficulties present in the classical approach to the CTRW [13, 19]; and, on the other hand, it gives a possibility of constructing new types of coupled memory CTRWs driving the fractional transport dynamics in complex systems.

In this paper we introduce a coupled memory CTRW which governs the Havriliak–Negami relaxation pattern. We show that the power-law exponents of the Havriliak–Negami function follow from scaling properties imposed on the jump and coupling parameters of the new type of the CTRW. We also show that this relationship helps us to find interpretation of the fractional operators in the corresponding fractional kinetic equation.

2. New type of a coupled CTRW with random-sum structure of time and space steps

Let us consider a random walk generated by a sequence $\{(R_i,T_i), i = 1,2,\ldots\}$ of jump parameters where R_i indicates both the length and the direction of the i-th jump while $T_i > 0$ is the residence time between the i-th jump and the next one. We assume that (R_1,T_1), $(R_2,T_2),\ldots$ are independent and identically distributed (i.i.d.) random vectors. The total distance $R(t)$ reached by the walker at time $t \geq 0$ defines a stochastic process called the CTRW. It is classified as decoupled if random variables T_i and R_i are independent; as coupled in case of dependent time and space steps. By definition, $R(t)$ has a form of the following random sum over the space steps R_i

$$R(t) = \sum_{i=1}^{\nu(t)} R_i$$

with $\nu(t)$, random number of components, generated by the time steps by means of the following first-passage formula

$$\nu(t) = \min\left\{n : \sum_{i=1}^{n} T_i > t\right\}.$$

As a simple example of the coupled CTRW, we can consider a random walk around a regular spatio-temporal lattice where the walker's steps are random multiples of constant space and time unit steps, $\Delta R > 0$ and $\Delta T > 0$, respectively. Namely, let us take into account the jump parameters having the following form

$$R_i = M_i \Delta R, \quad T_i = M_i \Delta T\,, \tag{5}$$

where random multipliers M_1, $M_2,\ldots$ form a sequence of positive integer-valued i.i.d. random variables. In such a case coupling is provided by the multipliers M_i's; and it has, in fact, a strong form of the linear dependence between the space steps of the walker and the corresponding time steps since formulas (5) lead to $R_i = CT_i$ with C equal to the ratio of the space to the time units, $C = \Delta R/\Delta T$. The resulting biased linearly coupled CTRW has the following form

$$R(t) = M\frac{t}{\Delta T}\Delta R\,, \tag{6}$$

where the random multiplier

$$M\frac{t}{\Delta T} = \sum_{i=1}^{N(t/\Delta T)} M_i \tag{7}$$

is equal to the sum of positive integer-valued random variables M_i's with the random number of summands given by

$$N\frac{t}{\Delta T} = \min\left\{n : \sum_{i=1}^{n} M_i > \frac{t}{\Delta T}\right\}. \tag{8}$$

Let us observe that formulas (5) can be simply rewritten into random sums

$$R_i = \sum_{j=1}^{M_i} \Delta R\,, \quad T_i = \sum_{j=1}^{M_i} \Delta T\,, \tag{9}$$

and that the resulting CTRW (6) has the equivalent form

$$R(t) = \sum_{j=1}^{M(t/\Delta T)} \Delta R\,. \tag{10}$$

Following the above trick and generalizing formulas (5) for the CTRW jump parameters (R_i, T_i) by substituting the constant space/time units steps ΔR and ΔT in (9) by the corresponding random spans ΔR_{ij}, ΔT_{ij}, we can construct a class of the coupled memory CTRWs yielding the Havriliak–Negami response (1). Namely, let us consider the jump parameters of the following random-sum form

$$R_i = \sum_{j=1}^{M_i} \Delta R_{ij}\,, \quad T_i = \sum_{j=1}^{M_i} \Delta T_{ij}\,, \tag{11}$$

where $\Delta R_{ij} = \delta^R_{ij}\Delta R$ and $\Delta T_{ij} = \delta^T_{ij}\Delta T$ for positive dimensionless random perturbations δ^R_{ij}, δ^T_{ij} forming independent sequences $\{\delta^R_{ij}, i, j = 1, 2, \ldots\}$ and $\{\delta^T_{ij}, i, j = 1, 2, \ldots\}$, each consisting of i.i.d. random variables. As in the simpler case (9), the random numbers of summands in (11) form an i.i.d. sequence $\{M_i, i = 1, 2, \ldots\}$ that is additionally assumed to be independent of the perturbation sequences $\{\delta^R_{ij}\}$, $\{\delta^T_{ij}\}$. If the distribution of M_i is nondegenerate (*i.e.* random variable M_i takes at least two different values with positive probabilities), the former linear dependence $R_i = CT_i$, characterizing the lattice case (5), is here substituted by a weaker but more general stochastic dependence between time and space steps. As a consequence, the CTRW resulting from relations (11) is usually coupled, and coupling is provided by the random-number sequence $\{M_i\}$ as in the previous example. Moreover, the obtained coupled CTRW has an equivalent random-sum representation, similar to (10). Namely, the total distance $R(t)$ has the same distribution as the random sum over the space spans ΔR_{1j}'s where the random number of summands, $L(t/\Delta T)$, has the form resembling (7); namely,

$$L\frac{t}{\Delta T} = \sum_{i=1}^{N(K(t/\Delta T))} M_i$$

with the number of summands defined in a way parallel to (8) as

$$N\left(K\frac{t}{\Delta T}\right) = \min\left\{n : \sum_{i=1}^{n} M_i > K(t/\Delta T)\right\}$$

for $K\frac{t}{\Delta T} = \min\{k : \sum_{j=1}^{k} \Delta T_{1j} > t\} = \min\{k : \sum_{j=1}^{k} \delta_{1j}^{T} > t/\Delta T\}$. More precisely, we have

$$R(t) \stackrel{d}{=} \sum_{j=1}^{L(t/\Delta T)} \Delta R_{1j} = \sum_{j=1}^{L(t/\Delta T)} \delta_{1j}^{R} \Delta R\,, \qquad (12)$$

where equality $\stackrel{d}{=}$ refers to the distributions of the considered random variables (and it means that the random variables on the left and right-hand sides have the same distributions). Let us stress that the total distance $R(t)$ is not simply equal to the random sum in (12) but only has the same distribution. However, representation (12) allows us to examine statistical and asymptotic properties of $R(t)$ and of the diffusion front $\widetilde{R}(t)$, being a total-distance limit in distribution approached as the characteristic time and space scales ΔT and ΔR tend to 0 (with ΔR related somehow to ΔT). Information on the diffusion-front distribution can be provided by nonstandard limit theorems of probability theory [18, 22]. The statistical properties of $\widetilde{R}(t)$ depend on assumptions set on the distributions of the variables ΔR_{ij}, ΔT_{ij}, and M_i, basic for the considered construction of the coupled CTRW.

The proposed procedure, applied here for the case of biased walk with the positive space steps R_i only, reminds the well-known approximation of the Brownian motion based on limiting properties of the simplest unbiased random walk on the spatio-temporal lattice given under the following assumptions $\Pr(R_i = \Delta R) = \Pr(R_i = -\Delta R) = 1/2$ and $T_i = \Delta T$ (implying equally probable up and down jumps). Such a random walk approaches (in distribution) the Brownian motion if ΔT and ΔR both tend to 0 while the ratio $(\Delta R)^2/\Delta T$ remains constant [20, 21]. Following this classical idea for the unbiased decoupled random walk, in the model of the biased coupled CTRW introduced above, the new type of diffusion processes can be derived. In the next section we present detailed analysis of two important cases connected with the Debye and the Havriliak–Negami responses.

3. The Havriliak–Negami relaxation response

In the framework of the biased CTRW approach the relaxation function can be expressed by means of the diffusion front $\widetilde{R}(t)$ as an average

$$\phi(t) = \left\langle e^{-\mathrm{k}\widetilde{R}(t)} \right\rangle ,$$

where k is an appropriate positive constant [14, 17, 23]. According to the assumed detailed statistical properties of the space and time spans ΔR_{ij}, ΔT_{ij} (or equivalently, of the perturbations δ_{ij}^R, δ_{ij}^T) and of the random numbers M_i of summands in formulas (11), the obtained coupled CTRW and the resulting diffusion front may yield responses of different types.

In order to obtain the classical exponential response we have to consider the case when the mean values of both, space and time spans are finite. It is reasonable to assume that these mean values determine the space and time units, *i.e.* that $\langle \Delta R_{ij} \rangle = \Delta R$, $\langle \Delta T_{ij} \rangle = \Delta T$ (or equivalently, that $\langle \delta_{ij}^R \rangle = \langle \delta_{ij}^T \rangle = 1$). If the number M_i of the random-sum components in (11) also has a finite mean value, then for any $t > 0$ the total distance $R(t)$ tends with probability 1 to the diffusion front of the form linear in time

$$\widetilde{R}(t) = Ct$$

as ΔT and ΔR decrease to 0 with the ratio $C = \Delta R/\Delta T$ being retained [7, 18]. The resulting relaxation function $\phi(t)$ has then the Debye form (2) with $\omega_{\mathrm{p}} = C\mathrm{k}$.

To pass from the Debye to the power-law Havriliak–Negami relaxation response, we have to assume that — instead of the finite mean values — both ΔR_{ij} and ΔT_{ij} (or equivalently, the perturbations δ_{ij}^R, δ_{ij}^T) have heavy-tailed distributions with the same exponent α where $0 < \alpha < 1$, *i.e.* that the distributions of the random variables ΔR_{ij} and ΔT_{ij} satisfy conditions

$$\lim_{x\to\infty} \frac{\Pr(\Delta R_{ij} > x)}{(x/\Delta R)^{-\alpha}} = 1 \tag{13}$$

and

$$\lim_{x\to\infty} \frac{\Pr(\Delta T_{ij} > x)}{(x/\Delta T)^{-\alpha}} = 1 \,, \tag{14}$$

where the space and time units are determined by the scale parameters of the corresponding heavy tails. (Equivalently, one can assume that the dimensionless perturbations δ_{ij}^R, δ_{ij}^T satisfy conditions $\lim_{x\to\infty} \frac{\Pr(\delta_{ij}^R > x)}{x^{-\alpha}} = 1$ and $\lim_{x\to\infty} \frac{\Pr(\delta_{ij}^T > x)}{x^{-\alpha}} = 1$.) Moreover, it has to be assumed that the distribution of the random number M_i (that provides coupling) has also a heavy tail with exponent γ where $0 < \gamma < 1$, *i.e.*, the distribution of M_i fulfils the condition

$$\lim_{x\to\infty} \frac{\Pr(M_i > x)}{(x/c)^{-\gamma}} = 1 \tag{15}$$

for some $c > 0$. Then for any $t > 0$ the total distance $R(t)$ tends in distribution to

$$\widetilde{R}(t) \overset{d}{=} Ct\, \frac{\mathcal{S}'_\alpha}{\mathcal{S}_\alpha} \left(\frac{1}{\mathcal{B}_\gamma}\right)^{1/\alpha} \tag{16}$$

as $\Delta T \to 0$ and $\Delta R \to 0$ but with constant ratio $C = \Delta R/\Delta T$ [7,18]. The random variables $\mathcal{B}_\gamma$, $\mathcal{S}_\alpha$, and $\mathcal{S}'_\alpha$ in (16) are independent. Moreover, $\mathcal{S}_\alpha$ and $\mathcal{S}'_\alpha$ are identically distributed according to the completely asymmetric Lévy-stable law such that

$$\langle e^{-\mathrm{k}\mathcal{S}_\alpha} \rangle = \langle e^{-\mathrm{k}\mathcal{S}'_\alpha} \rangle = e^{-\mathrm{k}^\alpha}\,; \tag{17}$$

and $\mathcal{B}_\gamma$ is distributed according to the generalized arcsine distribution with parameter γ (*i.e.*, the beta distribution with parameters $p = \gamma$ and $q = 1-\gamma$) defined by the density function

$$f_\gamma(x) = \begin{cases} \frac{1}{\Gamma(\gamma)\Gamma(1-\gamma)} x^{\gamma-1}(1-x)^{-\gamma} & \text{for} \quad 0 < x < 1\,, \\ 0 & \text{otherwise}\,. \end{cases}$$

Let us notice that the limiting law (16) represents a mixture of a generalized arcsine distribution, corresponding to $\mathcal{B}_\gamma$, and a fractional stable distribution of the ratio of independent Lévy-stable random variables $\mathcal{S}'_\alpha$ and $\mathcal{S}_\alpha$. The assumptions set on the distributions of the variables ΔR_{ij}, ΔT_{ij}, and M_i, given by (13)–(15), can be interpreted as scaling properties of a large-value asymptotic behaviour of the respective quantity.

Now we show that the relaxation function $\phi(t)$ corresponding to the diffusion front (16) is related to the Havriliak–Negami function (1) with $\omega_{\mathrm{p}} = C\mathrm{k}$. For any $0 < \gamma < 1$ we have [7]

$$\langle e^{-\mathrm{k}\cdot 1/\mathcal{B}_\gamma} \rangle = \Pr(\mathcal{G}_\gamma \geq \mathrm{k})\,, \tag{18}$$

where random variable $\mathcal{G}_\gamma$ is distributed according to the gamma distribution with scale parameter 1 and shape parameter γ and independent of $\mathcal{S}_\alpha$. Using the conditional-expected-value tools, one obtains from (17) and (18) that [7]

$$\left\langle e^{-\mathrm{k}\left(\frac{\mathcal{S}'_\alpha}{\mathcal{S}_\alpha}\left(\frac{1}{\mathcal{B}_\gamma}\right)^{1/\alpha}\right)} \right\rangle = \Pr(\mathcal{G}_\gamma^{1/\alpha}\mathcal{S}_\alpha \geq \mathrm{k}).$$

As a consequence, for the diffusion front $\widetilde{R}(t)$ given by (16), the corresponding relaxation function $\phi(t)$ has the form

$$\phi(t) = \left\langle e^{-(C\mathrm{k})t\left(\frac{\mathcal{S}'_\alpha}{\mathcal{S}_\alpha}\left(\frac{1}{\mathcal{B}_\gamma}\right)^{1/\alpha}\right)} \right\rangle = \Pr(1/(C\mathrm{k})\mathcal{G}_\gamma^{1/\alpha}\mathcal{S}_\alpha \geq t)\,.$$

From (4) the spectral representation of such a function coincides with (1) if we take $\omega_\mathrm{p} = C\mathrm{k}$.

Let us add that considering other sets of conditions imposed on the distributions of the space and time spans ΔR_{ij} and ΔT_{ij} and on the random number M_i of summands one can repeat the above scheme getting other types of relaxation responses.

4. Kinetic equation

As it has been recently shown [19, 24], the turnover from the classical exponential to the inverse power-law relaxation pattern associated with the empirical Cole–Cole function (the special case of function (1) with $\gamma = 1$) involves modification of the Brownian dynamics to the fractional one represented in terms of the fractional Fokker–Planck or the fractional kinetic equations. The fractional calculus appears hence as a useful approach for description of transport dynamics in complex systems that are governed by anomalous diffusion and nonexponential relaxation [19].

Below, in connection with this problem, we discuss the fractional equation which is satisfied by the response function $f(t) = -\frac{d\phi}{dt}(t)$ of the relaxing system for which the relaxation function $\phi(t)$ is given by (3). Our aim is to find the role of the exponent γ by means of which the Havriliak–Negami response differs from the Cole–Cole case ($\gamma = 1$) discussed already by Metzler and Klafter in [19].

The fractional kinetic equation underlying the Cole–Cole response with the parameters $0 < \alpha < 1$, $\omega_\mathrm{p} > 0$ has been shown to have the form [19, 24]

$$\frac{d\phi}{dt}(t) = -\omega_\mathrm{p}^\alpha D^{1-\alpha}\phi(t)\,, \tag{19}$$

where the fractional derivative $D^{1-\alpha}$ is defined as $D^{1-\alpha} = \frac{d}{dt}(D^{-\alpha})$ for $D^{-\alpha}$ denoting the fractional Riemann–Liouville integral operator [25]

$$D^{-\alpha}h(t) = \frac{1}{\Gamma(\alpha)}\int_0^t (t-s)^{\alpha-1}h(s)ds\,.$$

Let us observe that equation (19) for the relaxation function $\phi(t)$ yields the following equation for $f(t)$, the response function of the system

$$(1+\omega_{\mathrm{p}}^{-\alpha}D^{\alpha})f(t)=\delta(t)\,, \tag{20}$$

where $\delta(t)$ is the Dirac delta function and $D^{\alpha}=\frac{d}{dt}(D^{-(1-\alpha)})$. The solutions of equations (19) and (20) are given by the tail function of the Mittag–Leffler distribution [26] (a special case of the generalized Mittag–Leffler distribution for $\gamma=1$) and by its probability density, respectively. Now, following the relationship of the Bessel operators to the fractional derivatives discussed by Samko *et al.* in [27] we propose such a modification of the Bessel operator that leads to a fractional equation satisfied by the probability density of the generalized Mittag–Leffler distribution (3).

For constant parameters $0<\alpha<1$, $\gamma>0$, $\omega_{\mathrm{p}}=C\mathrm{k}>0$ we define operator $\mathcal{G}_{\gamma}^{\alpha}$ via its one-sided Fourier transform as

$$\mathcal{F}_t\{\mathcal{G}_{\gamma}^{\alpha}h\ (t)\}=\frac{1}{(1+(i\omega/\omega_{\mathrm{p}})^{\alpha})^{\gamma}}h(\omega)$$

for any function $h:\mathbb{R}_+\to\mathbb{R}_+$. Here $h(\omega)$ denotes the one-sided Fourier transform of the function h, *i.e.* $\mathcal{F}_t\ h(t)=h(\omega)=\int_0^{\infty}e^{-i\omega t}h(t)dt$. From the properties of the Fourier transform we get the following representation for $\mathcal{G}_{\gamma}^{\alpha}$:

$$\mathcal{G}_{\gamma}^{\alpha}h(x)=\int_0^x f(t)h(x-t)dt$$

which is a convolution of function h and the Riesz function

$$f(t)=\sum_{k=0}^{\infty}\frac{(-1)^k\Gamma(\gamma+k)}{\Gamma(\gamma)\Gamma(\alpha(\gamma+k))k!}\omega_{\mathrm{p}}(\omega_{\mathrm{p}}t)^{\alpha(\gamma+k)-1}\,. \tag{21}$$

For $n\in\mathbb{N}$ such that $n\alpha\le 1$ the following identity:

$$(1+\omega_{\mathrm{p}}^{-\alpha}D^{\alpha})^n\ \mathcal{G}_n^{\alpha}h(t)=h(t) \tag{22}$$

holds for any $h:\mathbb{R}_+\to\mathbb{R}_+$. Namely, Newton's binominal formula and the one-sided Fourier transform of the left-hand side of equation (22) give the result

$$\begin{aligned}\sum_{k=0}^{n}\binom{n}{k}\left(\frac{i\omega}{\omega_{\mathrm{p}}}\right)^{\alpha k}\mathcal{F}_t\{\mathcal{G}_n^{\alpha}h(t)\} &= \sum_{k=0}^{n}\binom{n}{k}\left(\frac{i\omega}{\omega_{\mathrm{p}}}\right)^{\alpha k}\frac{1}{(1+(i\omega/\omega_{\mathrm{p}})^{\alpha})^n}h(\omega)\\ &= \frac{1}{(1+(i\omega/\omega_{\mathrm{p}})^{\alpha})^n}h(\omega)\sum_{k=0}^{n}\binom{n}{k}\left(\frac{i\omega}{\omega_{\mathrm{p}}}\right)^{\alpha k}\\ &= \frac{1}{(1+(i\omega/\omega_{\mathrm{p}})^{\alpha})^n}h(\omega)\left(1+\left(\frac{i\omega}{\omega_{\mathrm{p}}}\right)^{\alpha}\right)^n=h(\omega)\end{aligned}$$

which yields (22). Thus for fixed α and $n \in \mathbb{N}$ such that $n\alpha \leq 1$ the operator $(1+\omega_{\rm p}^{-\alpha}D^{\alpha})^n$ is inverse to $\mathcal{G}_n^{\alpha}$. Following the above idea, for fixed $\alpha \in (0,1)$ and any $\gamma > 0$ such that $\alpha\gamma \in (0,1)$ let us define operator $(1+\omega_{\rm p}^{-\alpha}D^{\alpha})^{\gamma}$ as the inverse operator to $\mathcal{G}_{\gamma}^{\alpha}$, *i.e.*

$$(1+\omega_{\rm p}^{-\alpha}D^{\alpha})^{\gamma}h(t) = (\mathcal{G}_{\gamma}^{\alpha})^{-1}h(t)\,.$$

For any probability density function (pdf) $g(x,t)$, in particular for the pdf of the process $\widetilde{R}(t)$ obtained in formula (16), we have

$$\mathcal{F}_t\{(\mathcal{G}_{\gamma}^{\alpha})^{-1}\mathcal{L}_x g(x,t)\} = (1+(i\omega/\omega_{\rm p})^{\alpha})^{\gamma}\; g({\rm k},\omega) = \frac{[(C{\rm k})^{\alpha}+(i\omega)^{\alpha}]^{\gamma} g({\rm k},\omega)}{(C{\rm k})^{\alpha}}\,, \tag{23}$$

where $\mathcal{L}_x\; g(x,t) = \int_0^{\infty} e^{-{\rm k}x} g(x,t)dx$ and $g({\rm k},\omega)$ is the Fourier–Laplace $\mathcal{F}_t\mathcal{L}_x$ transform of $g(x,t)$. The last equation shows that the operator $(1+\omega_{\rm p}^{-\alpha}D^{\alpha})^{\gamma}$ is closely related to the fractional material derivative defined by Sokolov and Metzler in [28]. However, the exact relationship between both fractional operators is not obvious and will be the subject of our further research.

Let us consider the following fractional equation

$$(1+\omega_{\rm p}^{-\alpha}D^{\alpha})^{\gamma} f(t) = \delta(t) \tag{24}$$

being a generalization of (20). To solve equation (24) let us put the one-sided Fourier transform on both its sides. We get then

$$(1+(i\omega/\omega_{\rm p})^{\alpha})^{\gamma} f(\omega) = 1\,,$$

which implies

$$f(\omega) = \frac{1}{(1+(i\omega/\omega_{\rm p})^{\alpha})^{\gamma}}\,. \tag{25}$$

Thus we have established that the solution $f(t)$ of equation (24) is the response function related to the Havriliak–Negami function (1). Inverse Fourier transform of formula (25) yields the response function $f(t)$ having the form of the Riesz function (21). The time-domain relaxation function $\phi(t)$ corresponding to $f(t)$ is given by (3). Let us note that operator $(1+\omega_{\rm p}^{-\alpha}D^{\alpha})^{\gamma}$ can be informally considered in terms of series expansion; namely,

$$(1+\omega_{\rm p}^{-\alpha}D^{\alpha})^{\gamma} = \sum_{k=0}^{\infty}\binom{\gamma}{k}\omega_{\rm p}^{-\alpha k}D^{\alpha k}\,.$$

In this case, the heuristic solution of (24) is equivalent to (21), the one we have derived.

The classical kinetic equation

$$\frac{d\phi}{dt}(t) = -r(t)\phi(t) \tag{26}$$

with time-dependent transition rate $r(t)$ governs the Havriliak–Negami relaxations if

$$r(t) = \frac{\sum\limits_{k=0}^{\infty} \frac{(-1)^k \Gamma(\gamma+k)}{\Gamma(\gamma)\Gamma(\alpha(\gamma+k))k!} \omega_{\mathrm{p}} (\omega_{\mathrm{p}} t)^{\alpha(\gamma+k)-1}}{1 - \sum\limits_{k=0}^{\infty} \frac{(-1)^k \Gamma(\gamma+k)}{\Gamma(\gamma)\Gamma(1+\alpha(\gamma+k))k!} (\omega_{\mathrm{p}} t)^{\alpha(\gamma+k)}} . \tag{27}$$

This complicated formula for the transition rate exhibits power-law asymptotics [see Fig. 1(a)] of the form

$$r(t) \sim \begin{cases} (\omega_{\mathrm{p}} t)^{\alpha\gamma-1} , & \omega_{\mathrm{p}} t \ll 1 \\ (\omega_{\mathrm{p}} t)^{-1} , & \omega_{\mathrm{p}} t \gg 1 . \end{cases} \tag{28}$$

This corresponds, via the kinetic equation (26), to the power-law behaviour of the response function $f(t)$ [see Fig. 1(b)]

$$f(t) \sim \begin{cases} (\omega_{\mathrm{p}} t)^{\alpha\gamma-1} , & \omega_{\mathrm{p}} t \ll 1 \\ (\omega_{\mathrm{p}} t)^{-\alpha-1} , & \omega_{\mathrm{p}} t \gg 1 . \end{cases} \tag{29}$$

In general, the above properties are independent of the Havriliak–Negami response. It is easy to verify that for any response function $f(t)$ with property (29), the transition rate in equation (26) has to have property (28).

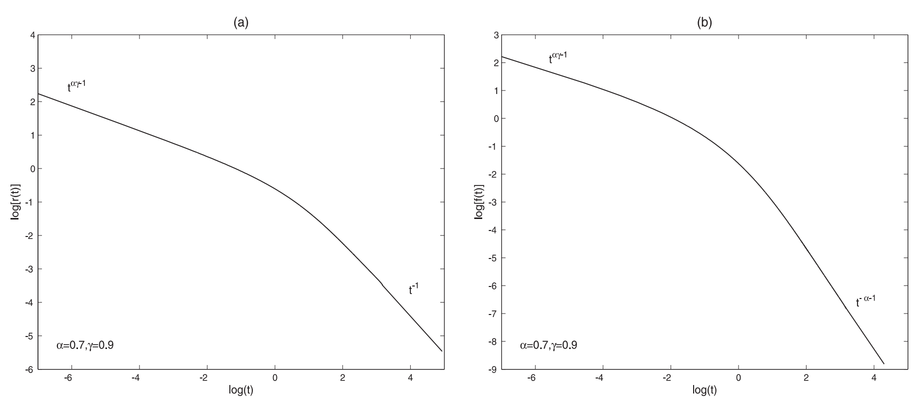

Fig. 1. The time-domain representation in the log–log scale of (a) transition rate and (b) response function corresponding to the Havriliak–Negami function. Parameters: $\alpha = 0.7$, $\gamma = 0.9$, $\omega_{\mathrm{p}} = 1$.

Equation (26) is equivalent to the following differential equation for the response function $f(t)$

$$\frac{df(t)}{dt} = -\left(r(t) - \frac{dr(t)}{dt}\frac{1}{r(t)}\right) f(t) \tag{30}$$

determined by the system's transition rate $r(t)$ given in (27). Thus the fractional equation (24) and the ordinary differential equation (30) with time-dependent transition rate (27) both correspond to the Havriliak–Negami relaxation response.

5. Conclusions

We have applied the random-variable formalism to the analysis of the CTRW as the one that allows us to omit the technical difficulties arising in the Fourier–Laplace technique commonly used to study this type of random walks. In the framework of the proposed attempt we have constructed a new class of coupled memory CTRWs underlying, in particular, the Havriliak–Negami relaxation response. We have shown that the turnover from the exponential Debye to the power-law Havriliak–Negami relaxation is associated with scaling properties of the defect diffusion process driving the fractional dynamics.

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REFERENCES

[1] A.K. Jonscher, *Nature* **267**, 673 (1977).

[2] C.J. Böttcher, P. Bordewijk, *Theory of Electronic Polarisation* Vol. 2, Elsevier, Amsterdam 1978.

[3] A.K. Jonscher, *Dielectric Relaxation in Solids* Chelsea Dielectrics Press, London 1983.

[4] R. Hilfer, *J. Non-Cryst. Solids* **305**, 122 (2002).

[5] K. Weron, M. Kotulski, *J. Stat. Phys.* **88**, 1241 (1997).

[6] A. Jurlewicz, K. Weron, *Acta Phys. Pol. B* **31**, 1077 (2000).

[7] A. Jurlewicz, *Appl. Math.* **30**, 325 (2003).

[8] C. Zener, *Phys. Rev.* **52**, 230 (1937).

[9] C. Zener, *Phys. Rev.* **53**, 90 (1938).

[10] S.H. Glarum, *J. Chem. Phys.* **33**, 639 (1960).

[11] M.F. Shlesinger, *J. Stat. Phys.* **10**, 421 (1984).

[12] A. Blumen, G. Zumofen, J. Klafter, *Phys. Rev.* **B30**, 5379 (1984).

[13] E.W. Montroll, G.H. Weiss, *J. Math. Phys.* **6**, 167 (1965).

[14] K. Weron, M. Kotulski, *Physica A* **232**, 180 (1996).

[15] M. Kotulski, *J. Stat. Phys.* **81**, 777 (1995).

[16] M. Kotulski, in *Chaos — The Interplay Between Stochastic and Deterministic Behaviour*, edited by P. Garbaczewski, M. Wolf, and A. Weron, *Lect. Notes Phys.* Vol. 457, Springer, Berlin 1995, p. 471.

[17] E. Gudowska-Nowak, K. Weron, *Phys. Rev.* **E65**, 011103 (2001).

[18] A. Jurlewicz, *Diss. Math.* **431**, 1 (2005).

[19] R. Metzler, J. Klafter, *Phys. Rep.* **339**, 1 (2000).

[20] W. Feller, *An Introduction to Probability Theory and Its Applications*, Vol. 1, Wiley, New York 1966.

[21] I. Karatzas, S.E. Shreve, *Brownian Motion and Stochastic Calculus*, Springer, New York 1991.

[22] M.M. Meerschaert, H-P. Scheffler, *Limit Theorems for Sums of Independent Random Vectors: Heavy Tails in Theory and Practice*, Wiley Interscience, New York 2001.

[23] S. Gomi, F. Yonezawa, *Phys. Rev. Lett.* **74**, 4125 (1995).

[24] R. Metzler, J. Klafter, *J. Non-Cryst. Solids* **305**, 81 (2002).

[25] K.S. Miller, B. Ross, *An Introduction to the Fractional Calculus and Fractional Differential Equations*, Wiley, New York 1993.

[26] R.N. Pillai, *Ann. Inst. Stat. Math.* **42**, 157 (1990).

[27] S.G. Samko, A.A. Kilbas, D.I. Maritchev, *Integrals and Derivatives of the Fractional Order and Some of Their Applications*, Gordon and Breach Science Publishers, 1993.

[28] I.M. Sokolov, R. Metzler, *Phys. Rev.* **67**, 010101(R) (2003).