Subordination model of anomalous diffusion leading to the two-power-law relaxation responses

A. Stanislavsky¹(a), K. Weron² and J. Trzmiel²

¹ Institute of Radio Astronomy - 4 Chervonopraporna St., 61002 Kharkov, Ukraine
² Institute of Physics, Wrocław University of Technology - Wyspiańskiego 27, 50-370 Wrocław, Poland, EU

received 24 May 2010; accepted in final form 5 August 2010
published online 3 September 2010

PACS 05.40.Fb – Random walks and Levy flights
PACS 77.22.Gm – Dielectric loss and and relaxation
PACS 02.50.Ey – Stochastic processes

Abstract – We derive a general pattern of the nonexponential, two-power-law relaxation from the compound subordination theory of random processes applied to anomalous diffusion. The subordination approach is based on a coupling between the very large jumps in physical and operational times. It allows one to govern a scaling for small and large times independently. Here we obtain explicitly the relaxation function, the kinetic equation and the susceptibility expression applicable to the range of experimentally observed power-law exponents which cannot be interpreted by means of the commonly known Havriliak-Negami fitting function. We present a novel two-power relaxation law for this range in a convenient frequency-domain form and show its relationship to the Havriliak-Negami one.

Copyright © EPLA, 2010

Introduction. – Many studies have been reported on the phenomenon of nonexponential, power-law relaxation which is typically observed in complex systems such as dielectrics, ferroelectrics, polymers and so on (see [1,2] and references therein). The main feature of such systems is a strong (in general, random) interaction between their components in the passage to a state of equilibrium. Therefore, theoretical construction of an “averaged” object representing the entire relaxing system is not a simple problem; it requires application of advanced probabilistic tools. One of them uses a randomization in the parameters of distributions that describes the relaxation rates in disordered systems. With regard to the dielectric relaxation, each individual dipole in a dielectric system relaxes exponentially, but their relaxation rates are different and obey a probability distribution (continuous function) [3]. This method is successive for getting many empirical response laws and their classification, but it sometimes becomes enough complicated to interpret their interrelations and to derive kinetic/diffusion equations. An alternative approach, applied to analysis of diffusion processes underlying the macroscopic dynamics, is based on subordination of random processes (see, for example, [4] and references therein). The anomalous diffusion process \( Y(U(t)) \) is obtained by the time clock randomization of a random (parent) process \( Y(t) \) by means of another random process \( U(t) \) called the directing process. The latter process is also often referred to as the randomized or operational time [5]. As it has been shown in [6,7], the subordination method is also useful for analysis of the relaxation processes. However, up to now the approach had some difficulties in interpretation of the Havriliak-Negami (HN) law, one of the most general description of relaxation data. Only recently the effective picture of the HN relaxation, based on subordination, has been found in [8]. It requires introduction of compound subordinators to the study of the anomalous diffusion. The compound subordination procedure relates one subordinator to another in such a way that the temporal evolution of the parent random process has a different scaling on short and long times.

Coupling between the \( \alpha \)-stable process as the real time and its inverse as an operational time. – The inverse \( \alpha \)-stable process is actually the left-inverse process of the \( \alpha \)-stable process (see fig. 1). This means that the \( \alpha \)-stable process \( T(\tau) \) and its inverse \( S_t = \inf \{ \tau \geq 0 \mid T(\tau) > t \} \) fulfill the relation \( S_T(\tau) = \tau \), while \( T(S_t) > t \) holds. The random variable \( S_t \) corresponds to the first passage time of the strictly increasing process

\[(a)\text{E-mail: astex@ukr.net}\]
T(\tau) above t. To find the probability density distribution (pdf) of the compound process T(S_t), we start with a sum of independent and identically distributed heavy-tailed random variables T_i, namely \( U_n = \sum_{i=0}^{\infty} T_i \) with \( T_0 = 0 \). The process \( N_t = \max\{n \in N \mid U_n \leq t\} \) is inverse to \( U_n \). From this definition it follows directly the inequality

\[
U_{N_t} \leq t < U_{N_{t+1}} \quad \text{for } t \geq 0. \tag{1}
\]

According to the Feller’s book [5], the renewal theory tells us how the pdfs of \( U_{N_t} \) and \( U_{N_{t+1}} \) behave in the long time limit. The random variable \( U_{N_t} / t \) tends (in distribution) to \( Y \) with the pdf equal

\[
p^Y(x) = \frac{\sin(\pi \alpha)}{\pi} x^{\alpha-1}(1-x)^{-\alpha}, \quad 0 < x < 1, \tag{2}
\]

and \( U_{N_{t+1}} / t \) tends to \( Z \) which pdf reads

\[
p^Z(x) = \frac{\sin(\pi \alpha)}{\pi} x^{-1}(x-1)^{-\alpha}, \quad x > 1. \tag{3}
\]

The functions \( p^Y(x) \) and \( p^Z(x) \) correspond to special cases of the well-known beta density [5]. We note that the pdf of \( p^Y(x) \) concentrates near 0 and 1, whereas \( p^Z(x) \) concentrates near 1, where both tend to infinity. The moments of the random value \( Y \) are finite and can be calculated directly from the pdf (2). However, even the first moment of \( Z \) is infinite.

A passage from the discrete process \( T_i \) to the continuous limit \( T(\tau) \) allows one to rewrite the inequality (1) into a form

\[
T(S_t^-) \leq t < T(S_t^+) \quad \text{for } t \geq 0, \tag{4}
\]

underestimating or overestimating the real time \( t \). In this case we obtain an analogous to (2) and (3) result. In the long limit the pdfs of \( T(S_t^-) \) and \( T(S_t^+) \) read

\[
p^-(t, y) = \frac{\sin(\pi \alpha)}{\pi} y^{\alpha-1}(1-y)^{-\alpha}, \quad 0 < y < t, \tag{5}
\]

\[
p^+(t, z) = \frac{\sin(\pi \alpha)}{\pi} y^{-1}(y-t)^{-\alpha}, \quad y > t. \tag{6}
\]

Their moments are computed directly from the moments of \( Y \) and \( Z \) due to the relations \( T(S_t^-) \leq tY \) and \( T(S_t^+) \leq tZ \), where \( \leq \) denotes the equality in distribution. Thus, the process \( T(S_t^-) \) has finite moments of any order, while \( T(S_t^+) \) gives us even no finite the first moment. It should be noticed that the processes \( T(S_t^-) \) and \( T(S_t^+) \) evolve to infinity with growing \( t \). They show a coupling between the very large jumps in physical and operational times.

**Universality of relaxation in two-state systems.** – The simplest interpretation of relaxation processes uses the concept of a system of independent exponentially relaxing objects (for example, dipoles) with different (independent) relaxation rates [9]. The systems, following this law (called Debye’s), can easily be described as a two-state system. Let \( N \) be the common number of dipoles in a dielectric system. If \( N_\uparrow \) is the number of dipoles in the state \( \uparrow \), \( N_\downarrow \) is the number of dipoles in the state \( \downarrow \) so that \( N = N_\uparrow + N_\downarrow \). Assume that for \( t = 0 \) the system is stated in order so that the states \( \uparrow \) dominate, namely

\[
\frac{N_\uparrow(t=0)}{N} = n_\uparrow(0) = 1, \quad \frac{N_\downarrow(t=0)}{N} = n_\downarrow(0) = 0,
\]

where \( n_\uparrow(t) \) is the ratio of dipoles in the state \( \uparrow \) and \( n_\downarrow(t) \) in the state \( \downarrow \). Denote the transition rate by \( w \) defined from microscopic properties of the system (for instance, according to given Hamiltonian of interaction and the Fermi’s golden rule). In this case the kinetic equation is of the form

\[
\begin{cases}
\dot{n}_\uparrow(t) - w \{n_\downarrow(t) - n_\uparrow(t)\} = 0, \\
\dot{n}_\downarrow(t) - w \{n_\uparrow(t) - n_\downarrow(t)\} = 0,
\end{cases} \tag{7}
\]

where the dotted symbol means the first-order time derivative. The relaxation function for the two-state system reads then \( \phi_D(t) = 1 - 2n_\downarrow(t) = 2n_\uparrow(t) - 1 = \exp(-2wt) \). It is easy see that the steady state of the system corresponds to equilibrium with \( n_\uparrow(\infty) = n_\downarrow(\infty) = 1/2 \). However, if the dipoles interact with their environment, and the interaction is complex (random), their contribution in relaxation already will not result in any exponential decay.

Assume that the interaction of dipoles with environment is taken into account with a help of subordination in time. Take the process \( S_t \) as a subordinator. It accounts for the amount of time when a dipole does not participate in motion. The ratio of dipoles in the state \( \uparrow \) and another in the state \( \downarrow \) is subordinated by the process \( S_t \). The
Subordination model of anomalous diffusion etc.

equation describing the two-state system takes the form similar to eq. (7), but the derivatives of first order become fractional of order \( 0 < \alpha < 1 \) determined by the index of the process \( S_t \) inverse to the \( \alpha \)-stable process \( T(\tau) \). This leads to the Cole-Cole (CC) relaxation (see [6,7] for details). The relaxation function for the two-state system satisfies now the following equation:

\[
\frac{d^\alpha}{dt^\alpha} \phi_{CC}(t) - \frac{t^{-\alpha}}{\Gamma(1-\alpha)} = -\omega_p^\alpha \phi_{CC}(t),
\]

with the initial condition \( \phi_{CC}(0) = 1 \). Here we use the Riemann-Liouville definition of fractional derivative [10], namely

\[
\frac{d^\alpha}{dt^\alpha} x(t) = \frac{d^n}{dt^n} \left[ \frac{1}{\Gamma(n-\alpha)} \int_0^t \frac{x(\tau)}{(t-\tau)^{\alpha+1-n}} d\tau \right],
\]

where \( n-1 < \alpha < n \). The constant \( \omega_p^\alpha \) characterizes the transition rate from microscopic properties of the system. The relaxation function reads \( \phi_{CC}(t) = E_\alpha(-\omega_p^\alpha t^\alpha) \), where \( E_\alpha(z) = \sum_{n=0}^{\infty} z^n/\Gamma(1+n\alpha) \) is the one-parameter Mittag-Leffler function [11].

For the experimental study the frequency-domain representation of the latter function

\[
\varphi^*(\omega) \propto \int_0^\infty e^{-i\omega t} \left(-\frac{d\phi(t)}{dt} \right) dt \quad (8)
\]

is of interest. It is well known that the complex dielectric susceptibility \( \chi(\omega) = \chi'(\omega) - i\chi''(\omega) \propto \varphi^*(\omega) \) of most dipolar substances demonstrates a peak in the loss component \( \chi''(\omega) \) at a characteristic frequency \( \omega_p \). The CC susceptibility is

\[
\chi_{CC}(\omega) = \frac{1}{1 + (i\omega/\omega_p)^\alpha}, \quad 0 < \alpha < 1. \quad (9)
\]

With reference to the theory of subordination the CC law shows that the dipoles tend to equilibrium via motion alternating with stops so that the temporal intervals between them are random. However, there are other well-known laws of relaxation, in particular, the Cole-Davidson (CD) and Havriliak-Negami (HN) ones. The description of the laws requires a modification in the theory of subordination.

It should be noticed that the physical mechanism underlying the nonexponential relaxation can be described as a diffusive limit of continuous-time random walks. The resulting relaxation patterns are connected not only with stochastic features of the jumps and the inter-jump times themselves, but also with a stochastic dependence between them. In the framework of the linear response theory the temporal decay of a given mode \( k \), representing excitation undergoing diffusion in the system under consideration, is given by the inverse Fourier transform of the diffusion front [12].

**Subordination by the process \( T(S_t^\gamma) \).** – The subordinator \( T(S_t^\gamma) \) results in stretching of the real time \( t \). It will underline scaling properties in short and long times, respectively. The useful feature is just observed in CD and HN relaxation. Consider the process \( T(S_t^\gamma) \) as a subordinator to exponentially decreasing states. Let it be indexed by \( \gamma \), i.e. the process is obtained from a \( \gamma \)-stable random process. The relaxation function for the two-state system takes the form

\[
\phi_{CD}(t) = \int_1^\infty e^{-\omega_p t z} \frac{z^{-1}(z-1)^{-\gamma}}{\Gamma(\gamma)\Gamma(1-\gamma)} \, dz. \quad (10)
\]

Here the subscript CD is not by chance. It shows a direct connection of the relaxation function with the Cole-Davidson law [1]. In fact, the one-sided Fourier transform (8) gives

\[
\chi_{CD}(\omega) = \frac{1}{(1+i\omega/\omega_p)^\gamma}, \quad 0 < \gamma < 1.
\]

It should be mentioned that the theory of subordination suggests also one more scenario leading to the CD relaxation. It is based on the inverse tempered \( \alpha \)-stable process (see [13] in more detail).

**Relaxation from compound subordinators.** – The CC and CD relaxations are only special cases of the more general HN law. To get that law, the operational time \( S_t = S_{\alpha}(t) \) of the CC diffusion mechanism has to be modified [8] by means of coupling between jumps and inter-jump times in the underlying continuous-time random-walk scheme. In other words, the temporal decay of a given mode, representing excitation undergoing diffusion in the relaxing system, will be characterized by short- and long-time power laws with different fractional exponents (as in the HN case) only if the anomalous diffusion scenario is based on a compound operational time. To construct such an operational time, denote conveniently the processes \( T(S_t^\gamma) \) and \( T(S_t^\gamma) \) as \( X_t^U \) and \( X_t^O \), respectively. They corresponds to the under- and overshooting subordination scenarios [8]. Next, we can write \( Z_{\alpha,\gamma}(t) \leq S_{\alpha}(t) \leq Z_{\alpha,\gamma}(t) \) for \( t \geq 0 \), where \( Z_{\alpha,\gamma}(t) = X_t^U(S_{\alpha}(t)) \), \( Z_{\alpha,\gamma}(t) = X_t^O(S_{\alpha}(t)) \). The overshooting subordinator leads (stretching the operational time \( S_{\alpha}(t) \)) to the HN relaxation in the form

\[
\phi_{HN}(t) = \int_1^\infty E_\alpha\left(-(\omega_p t)^\alpha z \right) \frac{z^{-1}(z-1)^{-\gamma}}{\Gamma(\gamma)\Gamma(1-\gamma)} \, dz. \quad (11)
\]

By direct calculations of the Fourier transformation (8) the susceptibility reads

\[
\chi_{HN}(\omega) = \frac{1}{(1+i\omega/\omega_p)^\gamma}, \quad 0 < \alpha, \gamma < 1.
\]

The above approach demonstrates clearly a success in the probabilistic treatment of the observed relaxation laws. Therefore, we continue our analysis as applied to the undershooting (compressing \( S_{\alpha}(t) \)) subordinator \( X_t^U(S_{\alpha}(t)) \).
In this case we obtain a new relaxation function
\[ \phi(t) = \int_0^1 E_\alpha \left( - (\omega_p t)^\alpha z \right) \frac{z^{\gamma-1}}{\Gamma(\gamma) \Gamma(1-\gamma)} \, dz, \quad (12) \]
which can be identified as a special case of the generalized Mittag-Leffler function [14]
\[ E_{\alpha,\beta}(x) = \sum_{k=0}^{\infty} \frac{(\gamma, k)}{\Gamma(\alpha + \beta) n!} x^n, \quad \alpha, \beta > 0, \]
where \((\gamma, n) = \gamma(\gamma + 1)(\gamma + 2) \ldots (\gamma + n - 1)\) is the Appell’s symbol with \((\gamma, 0) = 1, \gamma \neq 0\). To avoid any confusion, it should be mentioned that the two-parameter Mittag-Leffler function \(E_{\alpha,\beta}(z) = \sum z^n/\Gamma(n\alpha + \beta)\), more common in the literature [11], is a special case of the function \(E_{\alpha,\beta}(z)\) with \(\gamma = 1\). From the series expansion of the ordinary Mittag-Leffler function \(E_{\alpha}(z)\), it is easy to check by direct calculations of eq. (12) that \(\phi(t) = E_{\alpha,1}(1(-\omega_p t)^\alpha)\). This type of the relaxation function has been derived in the continuous-time random-walk framework by Jurlewicz and Weron in [8]. Using relation with the Mittag-Leffler function we may write now the kinetic equation for (12) in the pseudodifferential equation form
\[ \left( \frac{d^n}{dt^n} + \omega_p^\alpha \right)^\gamma \phi(t) = \frac{t^{-\alpha \gamma}}{\Gamma(1-\alpha \gamma)}, \]
where \(d^n/dt^n\) is the Riemann-Liouville fractional derivative [10], and \(\phi(0) = 1\) the initial condition. Taking the Fourier transform (8), we get the susceptibility corresponding to (12) in the form useful for fitting the dielectric spectroscopy data
\[ \chi^*(\omega) = 1 - \frac{1}{(1 + (i \omega/\omega_p)^-\alpha \gamma)}, \quad 0 < \alpha, \gamma \leq 1. \quad (13) \]
for $\text{Cd}_{0.99}\text{Mn}_{0.01}\text{Te}:\text{Ga}$ at 77 K is fitted with the function (13)). This material belongs to semiconductor of group II–VI possessing deep metastable recombination centers. Formation of such centers in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}:\text{Ga}$ results from the bistability of Ga dopant which makes this mixed crystal as an attractive material for holography and high-density data storage (optical memories).

In the language of subordinators this means that the process $X^U(t)$ makes a rescaling for small times, and the process $X^O(t)$ turns on a similar rescaling for long times. As for $0 < \alpha, \gamma < 1$, in the case of HN relaxation the declination of the imaginary susceptibility $\chi''(\omega)$ for low frequencies will be greater than for high frequencies, whereas the less typical relaxation shows an opposite relation.

The original HN relaxation [1,2] with exponents $0 < \alpha, \gamma \leq 1$ satisfies $m \geq 1 - n$. Its modified version [15], proposed to fit relaxation data with power-law exponents satisfying $m < 1 - n$, assumes $0 < \alpha, \alpha \gamma \leq 1$. Unfortunately, the HN function with $\gamma > 1$ cannot be derived within the framework of diffusive relaxation mechanisms. Only for $\gamma \leq 1$ the origins of the HN function can be found within the fractional Fokker-Planck [17] and continuous-time random-walk [8] approaches. The approach considered above includes all the data in one, mathematically unified approach.

Conclusions. – We have discovered a novel law of relaxation accompanied by the well-known Havriliak-Negami function. Earlier the development of the theory of nonexponential relaxation went behind the fitting of experimental data. Now the subordination approach allows one to explain not only the well-known experimental laws of relaxation, but it makes a prediction of other adequate models useful for experimentalists.

***

AS is grateful to the Institute of Physics and the Hugo Steinhaus Center for Stochastic Methods for pleasant hospitality during his visit in Wroclaw University of Technology.

REFERENCES

[1] Jonscher A. K., *Dielectric Relaxation in Solids* (Chelsea Dielectrics Press, London) 1983.
[2] Jonscher A. K., *Universal Relaxation Law* (Chelsea Dielectrics Press, London) 1996.
[3] Jurlewicz A., Weron K. and Jonscher A. K., *IEEE Trans. Dielectr. Electr. Insul.*, 8 (2001) 352; Jurlewicz A. and Weron K., *J. Non-Cryst. Solids*, 305 (2002) 112; Jonscher A. K., Jurlewicz A. and Weron K., *Contemp. Phys.*, 44 (2003) 329.
[4] Metzler R. and Klafter J., *J. Phys. A*, 37 (2004) R161.
[5] Feller W., *An Introduction to Probability and Its Applications* (Wiley, New York) 1996.
[6] Mainardi F., *Fractional calculus: integral and differential equations of fractional order, in Fractals and Fractional Calculus in Continuum Mechanics*, edited by Carpinteri A. and Mainardi F. (Springer-Verlag, New York) 1997, pp. 223–276.
[7] Erdélyi A. (Editor), *Higher Transcendental Functions*, Vol. 3 (McGraw-Hill, New York) 1955, sect. 18.
[8] Klafter J., *Phys. Rep.*, 51 (2000) 1.
[9] Stanislavsky A. A., Weron K. and Teuerle M., *Phys. Rev. E*, 78 (2008) 011103; Weron K., Jurlewicz A., Magdziarz M., Weron A. and Trzmiel J., *Phys. Rev. E*, 81 (2010) 041123.
[10] Böttcher C. J. F. and Borzwik P., *Theory of Electronic Polarization* (Elsevier, Amsterdam) 1978.
[11] Jonscher A. K., *Universal Relaxation Law*, 70 (2004) 041103.
[12] Stanislavsky A. A. and Weron K., *Phys. Rev. E*, 78 (2008) 051106; Stanislavsky A. A. and Weron K., *Phys. Lett.*, 373 (2009) 2520.
[13] Mathai A. M., Saxena R. K. and Haubold H. J., *The H-Function. Theory and Applications* (Springer, Amsterdam) 2009.
[14] Havriliak S. jr. and Havriliak S. J., *J. Non-Cryst. Solids*, 172–174 (1994) 297.
[15] Trzmiel J., Pilszachek-Popko E., Zielony E. and Gumiaryn Z., *Acta Phys. Pol. A*, 116 (2009) 956; Trzmiel J., Jurlewicz A. and Weron K., *J. Phys.: Condens. Matter*, 22 (2010) 095802.
[16] Kalmykov Y. P., Coffey W. T., Crotgers D. S. F. and Titov S. V., *Phys. Rev. E*, 70 (2004) 041103.