

Anomalous diffusion schemes underlying the Cole–Cole relaxation: The role of the inverse-time α -stable subordinator

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Abstract

The paper presents the random-variable formalism of the anomalous diffusion processes. The emphasis is on a rigorous presentation of asymptotic behaviour of random walk processes with infinite mean random time intervals between jumps. We elucidate the role of the so-called inverse-time stochastic process, the main mathematical tool that allows us to modify the dynamics of standard relaxation processes and give rise to the nonexponential decay of modes. In particular, we show that the Brownian motion in combination with an appropriate inverse-time process may lead not only to exponential but also to the nonexponential relaxation responses.

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1. Introduction

Stochastic formulation of transport phenomena in terms of a continuous time random walk (CTRW) [1] was fundamental for the understanding of the diffusive behaviour of various complex systems (see e.g., photoconductivity in amorphous semiconductors [2], transport processes in heterogeneous rocks [3], hydrodynamic transport [4], self-diffusion in micelle systems [5], transport in heterogeneous catalysis [6], reactions and transport in polymer systems [7], motion of gold nanoclusters on graphite [8], etc.). Beginning with the work of Montroll and Weiss in Ref. [1], the physical community showed a steady interest in the anomalous diffusion, a term that describes diffusive behaviour in absence of the second moments of the spatio-temporal jump parameters and with scaling different than that of the classical Gaussian diffusion.

Usually, in applications of the CTRW ideology, the analysis of the properties of the diffusion front (the random walk propagator) is presented within the approach that is based on a formal expression for the Fourier–Laplace transform [1] of the asymptotic distribution, or otherwise, use of the fractional calculus is required [9] as a legitimate tool. In this case, the useful explicit formulas are provided only under some

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restrictive assumptions on spatio-temporal properties of the random walk. In this paper, we present an approach to the random walk analysis which is based directly on the definition of the cumulative stochastic process. We demonstrate the power of the mathematical tools underlying the CTRW concept by showing how they can be generalized to handle different diffusive situations in complex systems. Our aim is to show that despite the extensive studies on the CTRWs and their long history in physics, the power of limit theorems [10], hidden behind the derivation of limiting distributions, has not been fully explored yet. We provide a clear random walk scheme and rigorous analysis of the anomalous diffusion, and emphasize the possibilities of application of that scenario in stochastic modelling of the nonexponential relaxation phenomena. Our effort is directed toward bringing into light all stochastic conditions underlying the well-known frequency-domain Cole–Cole relaxation response. The proposed approach may serve as a basis for further developments of the nonexponential relaxation models, in particular, the one that can lead the Havriliak–Negami function, commonly used to fit the dielectric relaxation data.

2. CTRW and anomalous diffusion

We begin with recalling some basic facts concerning the notion of the CTRW, Fig. 1. The starting point is a sequence T_i , $i = 1, 2, \dots$, of nonnegative, independent, identically distributed (i.i.d.) random variables which represent the time intervals between successive jumps of a particle. The random time interval of n jumps is given by

$$T(n) = \sum_{i=1}^n T_i, \quad T(0) = 0 \quad (1)$$

and the number of the particle jumps performed up to time $t > 0$ has the form

$$N_t = \max\{n : T(n) \leq t\}. \quad (2)$$

The process N_t is often referred to as the renewal process or, alternatively, as the counting process.

The position of the particle after n jumps is

$$R(n) = \sum_{i=1}^n R_i, \quad R(0) = 0, \quad (3)$$

where R_i are i.i.d. random variables indicating both the length and the direction of the i th jump. R_i are assumed to be independent of the sequence T_i , $i = 1, 2, \dots$. Finally, the total distance reached by the particle

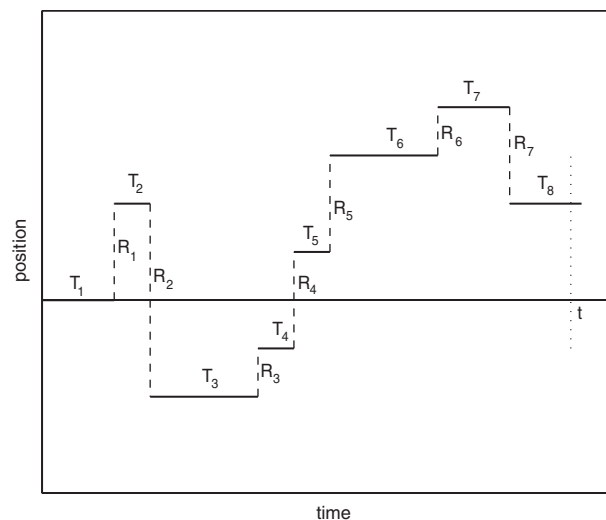


Fig. 1. A single realization of the one-dimensional CTRW process. In this case the number N_t of particle jumps (3) performed up to time t equals 7.

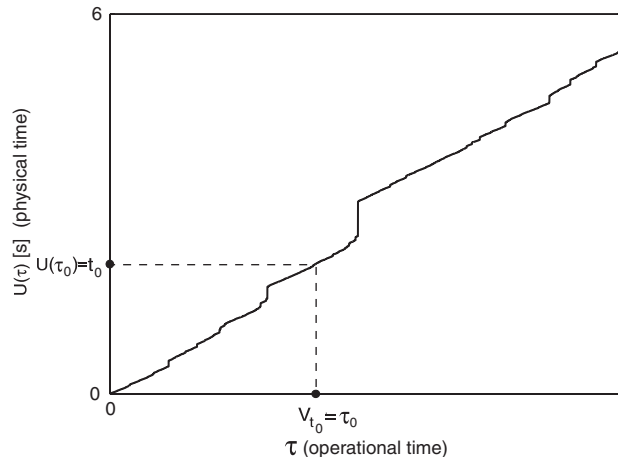


Fig. 2. A realization of the continuous limit $U(\tau)$ of the random sum (1) and its relationship to the inverse-time α -stable subordinator V_t ($\alpha = 0.8$). For the details of simulation see Ref. [23].

by time $t \geq 0$ defines the cumulative stochastic process

$$W(t) = R(N_t) = \sum_{i=1}^{N_t} R_i \tag{4}$$

known as the CTRW.

Assuming that the time intervals T_i belong to the domain of attraction of a completely asymmetric stable distribution $S_{\alpha,1}(t)$ ¹ (see Refs. [11,12]), i.e., $P(T_i > t) \propto t^{-\alpha}$ as $t \rightarrow \infty$ for some $0 < \alpha < 1$, then the generalization of the central limit theorem [12] yields the continuous limit of the random sum (1)

$$s^{-1/\alpha} T([s\tau]) \xrightarrow{d} U(\tau) \quad \text{as } s \rightarrow \infty, \tag{5}$$

where $U(\tau)$ is a strictly increasing α -stable Lévy process. Here “[x]” denotes the integer part of x and “ \xrightarrow{d} ” reads “tends in distribution”. Similarly, if the jumps R_i belong to the domain of attraction of a γ -stable distribution $S_{\gamma,\beta}(x)$, $0 < \gamma \leq 2$, $|\beta| \leq 1$, then

$$s^{-1/\gamma} R([s\tau]) \xrightarrow{d} X(\tau) \quad \text{as } s \rightarrow \infty, \tag{6}$$

where $X(\tau)$ is a γ -stable Lévy process, a continuous limit of (3). In particular, for $\gamma = 2$, $X(\tau)$ is the classical Brownian motion.

Taking advantage of the fact that $T(n)$, the random time interval of n jumps, and N_t , the number of jumps performed up to time $t > 0$, are related by the following formula

$$\{T([x]) \leq t\} = \{N_t \geq x\},$$

and applying (5) we get

$$s^{-\alpha} N_{st} \xrightarrow{d} V_t \quad \text{as } s \rightarrow \infty, \tag{7}$$

where V_t is the so-called inverse-time α -stable subordinator (or inverse-time α -stable process) defined as

$$V_t = \inf\{\tau : U(\tau) > t\}.$$

An example of realization of the continuous limit $U(\tau)$ of the random sum (1) and its relationship to the inverse-time α -stable subordinator V_t is shown in Fig. 2.

¹Here, for a stable distribution we use the notation $S_{\alpha,\beta}(t)$, where $0 < \alpha \leq 2$ denotes the index of stability and $|\beta| \leq 1$ denotes the skewness parameter.

Using (6) and (7) we derive the continuous limit of the CTRW process (4)

$$s^{-\alpha/\gamma} W(st) = s^{-\alpha/\gamma} R(N_{st}) \approx (s^\alpha)^{-1/\gamma} R([s^\alpha V_t]) \xrightarrow{d} X(V_t) \quad (8)$$

as $s \rightarrow \infty$. Thus the scaling limit of $W(t)$ leads to the subordinate process $X(V_t)$ with the random discrete-time jumps $R(n)$ replaced by the process $X(\tau)$, where τ denotes the operational time [13] (replacing the number of steps n), and the counting process N_t replaced by the inverse-time α -stable subordinator V_t . Following the idea of the recent paper of Piryatinska et al. [14], we can call process $X(V_t)$ the *anomalous diffusion*.

The anomalous diffusion $X(V_t)$ displays some interesting properties, which deserve to be mentioned. First, it is self-similar with Hurst index $H = \alpha/\gamma$, in particular, for $\gamma = 2$ (i.e., when the second moment of $X(V_t)$ exists) we have $H = \alpha/2 < 1/2$ and the process is subdiffusive. Since $X(\tau)$ and V_t are assumed to be statistically independent, the probability density function (p.d.f.) $p(x, t)$ of $X(V_t)$ obtained with the help of the generalized total probability formula has the form

$$p(x, t) = \int_0^\infty f(x, \tau)g(\tau, t) d\tau, \quad (9)$$

where $f(x, \tau)$ and $g(\tau, t)$ are the p.d.f.s of $X(\tau)$ and V_t , respectively. Further, the Fourier transform $\tilde{p}(k, t) = \langle \exp(ikX(V_t)) \rangle$ and the Laplace transform $\hat{p}(k, t) = \langle \exp(-kX(V_t)) \rangle$ are given by

$$\begin{aligned} \tilde{p}(k, t) &= \int_0^\infty \tilde{f}(k, \tau)g(\tau, t) d\tau, \\ \hat{p}(k, t) &= \int_0^\infty \hat{f}(k, \tau)g(\tau, t) d\tau, \end{aligned} \quad (10)$$

where $k > 0$ has the physical sense of a wave number.

Taking into account that the inverse-time stable subordinator V_t is self-similar with index $H = \alpha$ and computing moments of the random variable V_1 , one can show [14] that the Laplace transform $\hat{g}(u, t) = \langle \exp(-uV_t) \rangle$ of V_t has the form

$$\hat{g}(u, t) = E_\alpha(-c_\alpha u t^\alpha), \quad c_\alpha > 0, \quad (11)$$

where

$$E_\alpha(z) = \sum_{n=0}^{\infty} \frac{z^n}{\Gamma(n\alpha + 1)} \quad (12)$$

is the Mittag–Leffler function [15]. The latter property plays a significant role in analyzing the relaxation of physical systems in the framework of the diffusion mechanism.

3. Cole–Cole response and anomalous diffusion

Broad, time- and frequency-domain experimental investigations confirmed that the classical Debye pattern of exponential relaxation

$$\phi(t) = e^{-\omega_p t},$$

where ω_p is the loss-peak frequency (a characteristic material constant), hardly ever fits the dielectric relaxation spectroscopy data [16,17]. Instead, it has been found that many physical systems exhibit nonexponential relaxation well fitted in the frequency-domain with the Cole–Cole function

$$\phi^*(\omega) = \frac{1}{1 + (i\omega/\omega_p)^\alpha}, \quad 0 < \alpha < 1. \quad (13)$$

By definition, the frequency-domain response $\phi^*(\omega)$ is connected to the temporal relaxation function $\phi(t)$ through the relation

$$\phi^*(\omega) = \int_0^\infty e^{-i\omega t} d(-\phi(t)).$$

The temporal counterpart of the Cole–Cole function can be hence expressed in terms of the Mittag–Leffler function (12)

$$\phi(t) = E_\alpha(-(\omega_p t)^\alpha). \tag{14}$$

Note that for $\alpha = 1$, formula (14) takes the form of the exponential relaxation function.

In a rather general perspective, the theoretical attempt to model nonexponential relaxation phenomena can be based on the idea of relaxation of an excitation undergoing diffusion in the system under consideration [18–22]. Consequently, the relaxation function is connected to the temporal decay of a given mode k and, in the framework of the one-dimensional CTRWs, can be defined through the following Fourier Transform

$$\phi(t) = \langle e^{ikR(t)} \rangle,$$

where $R(t)$ denotes the diffusion front, i.e., the scaling limit of the CTRW. If $R(t)$ is supported on positive half-line only, its Fourier transform in the foregoing definition has to be replaced by the Laplace transform [19]. We have hence

$$\phi(t) = \langle e^{-kR(t)} \rangle$$

for the biased walk. As experimental techniques probe the behaviour of the system for a given mode, the above formulas give the temporal relaxation of a makroscopic excitation.

Let us now consider the problem of finding the function $\phi(t)$ for the anomalous diffusion $X(V_t)$ defined in (8). Recall that V_t is the inverse-time α -stable subordinator with the property (11) and $X(\tau)$ belongs to the class of γ -stable Lévy processes. In the case of the nonbiased random walk, i.e., when the symmetric process $X(\tau)$ has the following characteristic function

$$\langle e^{ikX(\tau)} \rangle = e^{-c_\gamma k^\gamma \tau}, \quad c_\gamma > 0,$$

formulas (10) and (11) imply that the relaxation function takes the form

$$\phi(t) = \langle e^{ikX(V_t)} \rangle = \int_0^\infty e^{-c_\gamma k^\gamma \tau} g(\tau, t) d\tau = E_\alpha(-c_{\alpha,\gamma} k^\gamma t^\alpha),$$

where $c_{\alpha,\gamma} = c_\alpha c_\gamma$. Thus for $\omega_p = (c_{\alpha,\gamma} k^\gamma)^{1/\alpha}$ we obtain the Cole–Cole relaxation function (13). In particular, for $\gamma = 2$, i.e., when $X(\tau)$ is the standard Brownian motion parametrized by the operational time τ , we get the following relaxation function

$$\phi(t) = E_\alpha(-c_{\alpha,2} k^2 t^\alpha).$$

The above formula clearly shows that in this special case we obtain the nonexponential relaxation pattern as well. Additionally, it can be proved that p.d.f. of $X(V_t)$ in this particular example is the solution of the celebrated fractional diffusion equation [20]

$$\frac{\partial p(x, t)}{\partial t} = {}_0D_t^{1-\alpha} c_{\alpha,2} \frac{\partial^2}{\partial x^2} p(x, t).$$

In the case of the biased random walk, for asymmetric $X(\tau)$ having the Laplace transform

$$\langle e^{-kX(\tau)} \rangle = e^{-c_\gamma k^\gamma \tau}, \quad 0 < \gamma \leq 1$$

analogous arguments show that

$$\phi(t) = \langle e^{-kX(V_t)} \rangle = \int_0^\infty e^{-c_\gamma k^\gamma \tau} g(\tau, t) d\tau = E_\alpha(-c_{\alpha,\gamma} k^\gamma t^\alpha)$$

and once again we obtain the Cole–Cole relaxation function with $\omega_p = (c_{\alpha,\gamma} k^\gamma)^{1/\alpha}$. In particular for $\gamma = 1$ we obtain the result discussed in Ref. [19] and for $\gamma = \alpha$ the one derived in Ref. [10]. In an even more general case studied in Ref. [14], when $X(\tau)$ belongs to the wide family of Lévy processes with characteristic function

$$\langle e^{ikX(\tau)} \rangle = e^{C\psi(k)\tau},$$

where $\psi(k)$ is the logarithm of the characteristic function of the random variable $X(1)$, similar calculations lead to the response function described by the Cole–Cole expression as well.

Table 1

Stochastic schemes of the Cole–Cole response with inverse-time α -stable subordinator V_t

$X(\tau), 0 < \gamma \leq 2, \beta \leq 1$	$\phi(t)$	$\phi^*(\omega) = 1/(1 + (i\omega/\omega_p)^z)$
Symmetric γ -stable Lévy processes ($0 < \gamma < 2, \beta = 0$)	$E_\alpha(-c_{\alpha,\gamma} k^\gamma t^\alpha)$	$\omega_p = (c_{\alpha,\gamma} k^\gamma)^{1/\alpha}$
Strictly increasing α -stable Lévy processes ($0 < \gamma < 1, \beta = 1$)	$E_\alpha(-c_{\alpha,\gamma} k^\gamma t^\alpha)$	$\omega_p = (c_{\alpha,\gamma} k^\gamma)^{1/\alpha}$
Brownian motion ($\gamma = 2, \beta = 0$)	$E_\alpha(-c_{\alpha,2} k^2 t^\alpha)$	$\omega_p = (c_{\alpha,2} k^2)^{1/\alpha}$
Deterministic process linear in operational time ($\gamma = 1, \beta = 1$)	$E_\alpha(-c_{\alpha,1} k t^\alpha)$	$\omega_p = (c_{\alpha,1} k)^{1/\alpha}$

4. Conclusions

We have demonstrated how the empirical Cole–Cole function can be derived from a diffusion model based on the CTRW ideology. We have brought into light the role of the inverse-time α -stable subordinator V_t , which in turn originates from the heavy-tailed distributions of the waiting times T_i . The key observation is that the Laplace transform of V_t given in the formula (11) is equal to the temporal counterpart (up to a constant ω_p) of the Cole–Cole function. As the carried out calculations show, the γ -stable process $X(\tau)$, parametrized by the operational time τ , does not change the type of the relaxation response. It only affects the material constant ω_p by determining the spatial properties of the anomalous diffusion $X(V_t)$. Since $X(\tau)$ belongs to the broad family of stable processes, the presented probabilistic formalism creates a possibility to derive a broad class of stochastic processes underlying the Cole–Cole relaxation pattern (see Table 1). In particular, the proposed scheme includes also the Debye relaxation, as $\alpha \rightarrow 1$. This classical response is related to the inverse-time deterministic subordinator which originates from the waiting-time distributions with finite first moment.

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