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Anomalous transport and diffusion versus extreme value theory

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Abstract

In the present work we match the biased hierarchical continuous-time random flight (HCTRF) on a regular lattice (based on hierarchical waiting-time distribution) and the extreme event theory (EVT). This approach extends the understanding of the anomalous transport and diffusion (for example, found in some amorphous, vitreous solids as well as in conducting and light-emitting organic polymers). Both independent approaches were developed in terms of random-trap or valley model where the disorder of energy landscape is exponentially distributed while the corresponding mean residence times in traps obey the power-law. This type of disorder characterizes several amorphous (even used commercially) materials which makes it possible to apply the HCTRF formalism. By using the EVT we additionally show that the rare (stochastic) events are indeed responsible for the transport and diffusion in these materials.

Keywords: Biased hierarchical continuous-time random flight; Extreme value theory; Rare event; Random-trap or valley model; Anomalous transport and diffusion; Amorphous materials; Vitreous solids; Conducting and light-emitting organic polymers

1. Introduction and motivation

The variety of observed relaxation phenomena in condensed and soft matter are related to transport and/or diffusion of atoms, particles, carriers, defects, excitons

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and complexes [1] (and references therein). In fact, the transport and diffusion are regarded as a paradigm of irreversible behaviour of many ordered and disordered systems. A universal feature of a disordered system is the temporal complex pattern, where the Debye-relaxation is no longer obeyed. The sentence which we quote after Scher and Montroll [2] characterizes well the straightforward link between physics of anomalous transient-time dispersion in an amorphous substance and its application. *The development of modern photocopying machines has motivated experimental work on amorphous materials, some of which display anomalous transport properties.*

The theory of carrier transport in some amorphous insulators (such as the commercially used vitreous As_2Se_3) and in some amorphous charge-transfer complexes of organic polymers (as the commercially used trinitrofluorenone mixed with polyvinylcarbazole, TNF-PVK) provides canonical examples of

(i) continuous-time random flights and walks, and
(ii) broad- or long-tailed waiting-time distribution between steps.

More precisely, the generic description of the dispersive transport and diffusion [3] found in the canonical experiments on transient current in an amorphous medium (induced by flash light [4–6,2,7] or voltage pulse [8] and references therein) is given indeed by the hierarchical continuous-time random flight (HCTRF) formalism[1] [9–15]. The principal aim of my lecture is to express this description in terms of the extreme value theory (EVT) [16–18]. Such an approach shows that rare (stochastic) events are indeed responsible for the transport and diffusion in these materials.

The paper consists of two parts. The first part (Section 2) includes remarks considering the basic elements of HCTRF and particularly, the averaged over disorder, hierarchical waiting-time distribution and its scale-invariance as the main property. In the second part (Section 3) we develop the EVT in the context of the random-trap or valley model where disorder is due to the energetic depth of the traps (which are exponentially distributed) and by the corresponding mean residence times (which obey then the power-law).

2. Basic elements of the biased hierarchical continuous-time random flight

The most spread models describing transport and diffusion in disordered substrates are based on the continuous-time random walk formalism. The major simplification in these models is that the disordered energetic landscape of the substrate can be described by an exponential distribution and incorporated into a regular lattice. In this work we consider single particle random instantaneous hops (flights) between regularly displaced valleys which have, however, different depths; the mountain peaks have all at the same energy level (which justifies the name of the model).

[1] We distinguish between particle flights and walks as the former are instantaneous while the latter ones need some time to move between the traps.

Waiting-time distribution. The pausing or residence time t in a given trap (between the successive hops) is a stochastic variable whose statistics is defined by the normalized waiting-time distribution $\psi_\varepsilon(t)$. This basic quantity here is the sharp probability density that the particle will perform its next hop exactly at time t after having waited until this instant in a trap of depth ε. The simplest but realistic example is provided by the exponential waiting-time distribution of a local in space Poisson process

$$\psi_\varepsilon(t) = \frac{1}{\tau(\varepsilon)} \exp\left(-\frac{t}{\tau(\varepsilon)}\right) , \tag{1}$$

where the factor $1/\tau(\varepsilon)$ is the probability density per unit time or rate of transition to a neigbouring site; the second factor is the probability that no hop has occurs until time t.

As we consider here only thermally activated over-barrier hops in the presence of a constant external bias, we can use asymmetric transition rates in the form

$$\Gamma_\pm(\varepsilon) = \Gamma_0 \exp(-\beta'(\varepsilon \mp \tfrac{1}{2}Fa)) , \tag{2}$$

where

$$\beta' = \begin{cases} (k_B T)^{-1} & \text{for the Hopf}-\text{Arrhenius (HA) law} , \\ (k_B \Theta)^{-1} & \text{for the Vogel}-\text{Tamm}-\text{Vulcher (VTF) law} , \end{cases} \tag{3}$$

where k_B is the Boltzmann constant, T is the absolute temperature, and $\Theta = T - T_g > 0$, where T_g is the transition temperature to the glass phase. Note that in expression (2) the external force is denoted by F, the lattice constant by a and Γ_+ is the transition rate along the direction of external force while Γ_- is the one in the opposite direction. Hence, the approximate equality (in the second line) in expression

$$\begin{aligned} \frac{1}{\tau(\varepsilon)} &= \Gamma_-(\varepsilon) + \Gamma_+(\varepsilon) = 2\Gamma_0 \exp(-\beta'\varepsilon)\cosh(\beta' Fa) \\ &\approx 2\Gamma_0 \exp(-\beta'\varepsilon)[1 + \tfrac{1}{8}(\beta' Fa)^2] , \end{aligned} \tag{4}$$

gives the second-order effect in the applied field, i.e., quadratically depends on the small quantity $\beta' Fa$. Fortunately, in all our discussions we have $\beta' Fa \ll 1$ as this is an obvious experimental constraint justifying the restriction only to the first-order effect in the applied field in all our considerations.

Sojourn probability. It is useful to introduce the sojourn probability $\Psi_\varepsilon(t)$ that the particle remains at a lattice site at least until time t without any hop; and is defined by using the waiting-time distribution

$$\Psi_\varepsilon(t) = \int_t^\infty \mathrm{d}t' \psi_\varepsilon(t') \tag{5}$$

which in the case of a local Poisson process described by (1) assumes the simple exponential form

$$\Psi_{\varepsilon}(t) = \exp\left(-\frac{t}{\tau(\varepsilon)}\right) . \tag{6}$$

In our model the averaging of this distribution over disorder is required to calculate the full propagator. How to perform this averaging is the essential problem considered below.

The structure factor of the biased random walk. Before we calculate the propagator we need to define the structure factor of the biased random walk. This definition requires the knowledge of the (stationary) spatial (single hop) transition probabilities, $p_{\pm}$, along and against the applied force, respectively, and includes here (for simplicity) the transitions only to the nearest neighbours. Then

$$p_{\pm} = \frac{\Gamma_{\pm}(\varepsilon)}{\Gamma_{-}(\varepsilon) + \Gamma_{+}(\varepsilon)} \approx \tfrac{1}{2}(1 \pm \tfrac{1}{2}\beta' Fa) , \tag{7}$$

and the corresponding spatial probability density

$$p(x) = p_{+}\delta(x-a) + p_{-}\delta(x+a) . \tag{8}$$

Hence, the structure factor of the biased random walk is defined as the Fourier transform of $p(x)$

$$\tilde{p}(k) = \cos(ak) - \mathrm{i}(p_{+} - p_{-})\sin(ak) \approx \cos(ak) - \frac{\mathrm{i}}{2}\beta' Fa \sin(ak) ; \tag{9}$$

here again only the first-order effect in the applied field was taken into account.

The propagator. The waiting-time distribution and sojourn probability averaged over disorder are, together with the structure factor, the relevant quantities to construct the full propagator considered in this paragraph.

The motion of the particle consists of a sequence of alternative events defined by the waiting in a given trap and next the hop to the neighbouring one. Correspondingly, the propagator consists of an unrestricted superposition of the n-step partial propagators

$$P_{\varepsilon_0,\varepsilon_1,\varepsilon_2,\ldots,\varepsilon}(X,t) = P_{\varepsilon=\varepsilon_0}(X,t;n=0) + \sum_{n=1}^{\infty} P_{\varepsilon_0,\varepsilon_1,\varepsilon_2,\ldots,\varepsilon_{n-1},\varepsilon}(X,t;n) , \tag{10}$$

where the multi-step propagators (defined as the probability density of finding a particle at position X at time t within n steps over a sequence of traps which have depths $\varepsilon_0, \varepsilon_1, \varepsilon_2, \ldots, \varepsilon_{n-1}, \varepsilon$) can be expressed as follows:

$$P_{\varepsilon_0=\varepsilon}(X,t;n=0) = \delta(X)\Psi_{\varepsilon_0=\varepsilon}(t) ,$$

$$P_{\varepsilon_0,\varepsilon_1,\varepsilon_2,\ldots,\varepsilon_{n-1},\varepsilon}(X,t;n) = \int_0^t \mathrm{d}t_n \int_0^{t_n} \mathrm{d}t_{n-1} \ldots \int_0^{t_3} \mathrm{d}t_2 \int_0^{t_2} \mathrm{d}t_1 \times \int_{-\infty}^{\infty} \mathrm{d}x_n \int_{-\infty}^{\infty} \mathrm{d}x_{n-1} \ldots \int_{-\infty}^{\infty} \mathrm{d}x_2 \int_{-\infty}^{\infty} \mathrm{d}x_1 \times \psi_{\varepsilon_0}(x_1,t_1)\psi_{\varepsilon_1}(x_2-x_1,t_2-t_1)\ldots \times \psi_{\varepsilon_{n-1}}(x_n-x_{n-1},t_n-t_{n-1})\delta(X-x_n)\Psi_\varepsilon(t-t_n)\,, \quad n=1,2,3,\ldots\ . \tag{11}$$

where the full waiting-time distribution, $\psi_\varepsilon(x,t) \stackrel{\text{def.}}{=} p(x)\,\psi_\varepsilon(t)$, means the sharp probability density of a single displacement x just at time t when the particle stayed whole the time (from 0 to t) at a given trap. As it is seen, the terms with $n\geqslant 1$ are n-fold convolutions. That is, for the n-step partial propagator the walker performs exactly n single steps while the last nth one is just under way (in general it is not finished). It should be admitted that the initial condition is not visible here because it is the same for each partial propagator. This condition has a non-stationary character and says that initially the particle was surely at the origin.

The average propagator. Now, to obtain the average propagator we should average the above expression by using the distribution $\rho_{\varepsilon_0,\varepsilon_1,\varepsilon_2,\ldots,\varepsilon_{n-1},\varepsilon}$ in the factorized form, i.e., $\rho(\varepsilon_0,\varepsilon_1,\varepsilon_2,\ldots,\varepsilon_{n-1},\varepsilon)=\rho(\varepsilon_0)\rho(\varepsilon_1)\ldots\rho(\varepsilon_{n-1})\rho(\varepsilon)$, as the depths of traps are, by definition, statistically independent. The key point of our consideration is given by the exponential form of the single-trap distribution

$$\rho(\varepsilon) = \frac{1}{\langle\varepsilon\rangle}\exp\left(-\frac{\varepsilon}{\langle\varepsilon\rangle}\right)\,. \tag{12}$$

By applying waiting-time distribution ψ_ε and $\rho_{\varepsilon_0,\varepsilon_1,\varepsilon_2,\ldots,\varepsilon_{n-1},\varepsilon}$ in the factorized form together with expression (12) into (11) we get the average propagator in the form

$$P(X,t) = \sum_{n=0}^{\infty} P(X,t;n)\,, \tag{13}$$

where the partial, average n-step propagators are

$$P(X,t;n=0) = \delta(X)\Psi(t)\,,$$

$$P(X,t;n) = \int_0^t \mathrm{d}t_n \int_0^{t_n} \mathrm{d}t_{n-1} \ldots \int_0^{t_3} \mathrm{d}t_2 \int_0^{t_2} \mathrm{d}t_1 \times \int_{-\infty}^{\infty} \mathrm{d}x_n \int_{-\infty}^{\infty} \mathrm{d}x_{n-1} \ldots \int_{-\infty}^{\infty} \mathrm{d}x_2 \int_{-\infty}^{\infty} \mathrm{d}x_1 \times \psi(x_1,t_1)\psi(x_2-x_1,t_2-t_1)\ldots \times \psi(x_n-x_{n-1},t_n-t_{n-1})\delta(X-x_n)\Psi(t-t_n)\,, \quad n=1,2,3,\ldots \tag{14}$$

and the average waiting-time distributions and sojourn probability are given by

$$\psi(x,t) = p(x)\psi(t), \quad \psi(t) = \int_0^\infty \mathrm{d}\varepsilon \rho(\varepsilon)\psi_\varepsilon(t)\,,$$

$$\Psi(t) = \int_0^\infty \mathrm{d}\varepsilon \rho(\varepsilon)\Psi_\varepsilon(t)\,. \tag{15}$$

After the Fourier and Laplace transformations of the convolutions (14) we get the geometric series which can be written in a simple, closed form

$$\tilde{P}(k,s) = \frac{\tilde{\Psi}(s)}{1-\psi(\tilde{k},s)}\,,$$

$$\tilde{\psi}(k,s) = \tilde{p}(k)\,\tilde{\psi}(s), \quad \tilde{\Psi}(s) = \frac{1-\tilde{\psi}(s)}{s}\,, \tag{16}$$

where $\tilde{f}(\ldots)$ means the Fourier and/or Laplace transform of function $f(\ldots)$. We should find now an explicit asymptotic form of the waiting-time distribution.

2.1. Scaling relation obeyed by the waiting-time distribution

It can be easily found that the average waiting-time distribution, given by the second relation in (15) combined with (1), has an approximate form

$$\psi(t) \approx \left(1-\frac{1}{N}\right)\int_0^\infty \mathrm{d}\xi \frac{1}{N^\xi}\frac{1}{\tau_0(\tau')^\xi}\exp\left(-\frac{t}{\tau_0(\tau')^\xi}\right) \tag{17}$$

or

$$\tilde{\psi}(s) \approx \left(1-\frac{1}{N}\right)\int_0^\infty \mathrm{d}\xi \frac{1}{N^\xi}\frac{1}{1+\tau_0(\tau')^\xi s}\,, \tag{18}$$

where we introduced a convenient notation

$$\xi \stackrel{\text{def.}}{=} \frac{\varepsilon}{\Delta}, \quad N \stackrel{\text{def.}}{=} \exp\left(\frac{\Delta}{\langle\varepsilon\rangle}\right), \quad 1-\frac{1}{N} \approx \frac{\Delta}{\langle\varepsilon\rangle}, \quad \tau' = \exp(\beta'\Delta)\,, \tag{19}$$

and assumed (for simplicity) $\Delta \ll \langle\varepsilon\rangle$.

Expression (18) obeys the convenient scaling relation

$$\begin{aligned}\tilde{\psi}(\tau's) &= N\tilde{\psi}(s) - (N-1)\int_0^1 \mathrm{d}\xi \frac{1}{N^\xi}\frac{1}{1+\tau_0(\tau')^\xi s} \\ &\approx N\tilde{\psi}(s) - (N-1)(1-\tau_0 s)\,,\end{aligned} \tag{20}$$

which can be solved by assuming, as usual for an equation of this type, that the solution is composed of the sum of two essentially different terms, i.e.,

$\tilde{\psi}(s) = \tilde{\psi}_s(s) + \tilde{\psi}_r(s)$, where the singular (general) term $\tilde{\psi}_s(s)$ obeys the homogeneous part of Eq. (20), and the regular (particular) one $\tilde{\psi}_r(s)$ obeys the (full) homogeneous Eq. (20).

2.2. Explicit asymptotic form of the waiting-time distribution

For $|s| \ll 1$ we obtain the singular term

$$\tilde{\psi}_s(s) \approx -Q\left(\frac{\ln(s)}{\ln(\tau')}\right)(\tau_0 s)^{\alpha} , \tag{21}$$

where the exponent $\alpha = \ln(N)/\ln(\tau') = (\beta'\langle\varepsilon\rangle)^{-1}$ and the *log-periodic* function (whose period is equal to 1) reduces, in the lowest approximation (or zero-order in s-variable), to the form[2]

$$Q\left(\frac{\ln(s)}{\ln(\tau')}\right) \approx C_s^0 = \frac{1-\dfrac{1}{N}}{\ln(N)}\frac{\pi\alpha}{\sin(\pi\alpha)} . \tag{22}$$

The regular term (controlled by an approximate form of the inhomogeneouity in Eq. (20)) reduces, within the linear approximation in s-variable, into the form

$$\tilde{\psi}_r(s) \approx 1 - C_r^1\tau_0 s, \quad C_r^1 = \frac{1-\dfrac{1}{N}}{1-\dfrac{\tau'}{N}} . \tag{23}$$

Finally, we obtain the seeked waiting-time distribution in the Laplace domain for $|s| \ll 1$

$$\begin{aligned}\tilde{\psi}(s) &\approx 1 - C_s^0(\tau_0 s)^{\alpha} - C_r^1\tau_0\, s \\ &\approx \begin{cases} 1 - C_s^0(\tau_0 s)^{\alpha} & \text{for } \alpha < 1 , \\ 1 - C_r^1\tau_0 s & \text{for } \alpha > 1 \end{cases}\end{aligned} \tag{24}$$

and in the asymptotic-time domain

$$\psi(t) \approx \begin{cases} \dfrac{1}{\tau_0}\dfrac{1-\dfrac{1}{N}}{\ln(N)}\alpha\mathbf{\Gamma}_{Euler}(1+\alpha)\left(\dfrac{t}{\tau_0}\right)^{-1-\alpha} & \text{for } \alpha < 1 , \\ \langle t\rangle^{-1}\exp\left(-\dfrac{t}{\langle t\rangle}\right) & \text{for } \alpha > 1 \end{cases} \tag{25}$$

(here $\langle t\rangle = \tau_0 C_r^1$) which makes it possible to consider the propagator and hence the asymptotic mean- as well as mean-square displacement in an explicit form.[3] (Note

[2]The derivation of the detailed form of coefficient C_s^0 by using the Mellin transformation, is given, e.g., in Ref. [12].

[3]In the paper we do not consider the marginal case defined by the threshold $\alpha = 1$.

that for the derivation of the first expression in (25) for $\alpha < 1$ we used relations (16), (15), (5) and (22).)

2.3. Asymptotic form of the propagator

For $|\tau_0 s| \ll 1$ and $|ka| \ll 1$ the propagator (given by (16)) can assume the following explicit form:

$$\tilde{P}(k,s) = \frac{1}{s + [1-\tilde{p}(k)]\dfrac{s\tilde{\psi}(s)}{1-\tilde{\psi}(s)}} \approx \begin{cases} \dfrac{1}{s + [1-p(k)]\dfrac{s}{C_s^0(\tau_0 s)^\alpha}} & \text{for } \alpha < 1\,, \\ \dfrac{1}{s + [1-p(k)]\dfrac{1}{\langle t\rangle}} & \text{for } \alpha > 1\,, \end{cases} \tag{26}$$

where we used the explicit asymptotic form of the waiting-time distribution (24). In the Fourier and time domain the above relation transforms still into the relatively simple form

$$\tilde{P}(k,t) \approx \begin{cases} E_\alpha\left(-\dfrac{[1-p(k)]}{C_s^0}\left(\dfrac{t}{\tau_0}\right)^\alpha\right) & \text{for } \alpha < 1\,, \\ \exp\left(-[1-p(k)]\dfrac{t}{\langle t\rangle}\right) & \text{for } \alpha > 1\,, \end{cases} \tag{27}$$

where $E_\alpha(\ldots)$ is the well-known Mittag–Leffler function [3]. The Fourier transformation of the second relation in (27) into the real space gives the well-known shifted Gaussian. The analogous transformation for $\alpha < 1$ is unknown in a closed form although it can be expressed in the integral form in terms of the (non-shifted) Gaussian and the weight given by the corresponding Fox H-function as the integrand (for details see Ref. [3] and references therein).

2.4. Explicit asymptotic form of the first and second moments

The mean displacement. Now, we are able to obtain the general formula for the average time-dependent displacement of the particle along the direction of the external field. This is the essential quantity which characterizes the drift of each particle. From (16) we obtain in the Laplace domain

$$\langle \tilde{X}\rangle(s) = \mathrm{i}\,\frac{\mathrm{d}}{\mathrm{d}k}\tilde{P}(k,s)|_{k=0} = \langle x\rangle \frac{1}{s}\frac{\tilde{\psi}(s)}{1-\tilde{\psi}(s)}\,, \tag{28}$$

where the single-hop mean displacement $\langle x \rangle = a(p_+ - p_-)$. From (28) and (24) we obtain for $|s| \ll 1$

$$\langle \tilde{X} \rangle(s) \approx \langle x \rangle \frac{1}{s} \frac{1}{C_s^0 (\tau_0 s)^\alpha + C_r^1 \tau_0 s}$$
$$\approx \begin{cases} \dfrac{\langle x \rangle}{C_s^0} \dfrac{1}{\tau_0^\alpha} \dfrac{1}{s^{\alpha+1}} & \text{for } \alpha < 1 , \\ \dfrac{\langle x \rangle}{C_r^1} \dfrac{1}{\tau_0} \dfrac{1}{s^2} & \text{for } \alpha > 1 . \end{cases} \quad (29)$$

From the above relation we easily obtain for the asymptotic time, i.e., for $t_0 \gg \tau_0$,

$$\langle X \rangle(t) \approx \begin{cases} \dfrac{\langle x \rangle}{C_s^0} \dfrac{1}{\mathbf{\Gamma}_{Euler}(1+\alpha)} \left(\dfrac{t}{\tau_0} \right)^\alpha & \text{for } \alpha < 1 , \\ \dfrac{\langle x \rangle}{\langle t \rangle} t & \text{for } \alpha > 1 . \end{cases} \quad (30)$$

where $\mathbf{\Gamma}_{Euler}(\dots)$ denotes the well-known Gamma–Euler function. Although the time-dependence of the drift below and above the threshold $\alpha = 1$ differ essentially the transition between both cases is smooth; nevertheless, we obtain for these cases essentially different drift velocities

$$V(t) = \frac{\mathrm{d}}{\mathrm{d}t} \langle X \rangle(t) \approx \begin{cases} \dfrac{\langle x \rangle}{C_s^0} \dfrac{1}{\mathbf{\Gamma}_{Euler}(\alpha)} \dfrac{1}{\tau_0} \dfrac{1}{(t/\tau_0)^{1-\alpha}} & \text{for } \alpha < 1 , \\ \dfrac{\langle x \rangle}{\langle t \rangle} & \text{for } \alpha > 1 . \end{cases} \quad (31)$$

Indeed, this quantity is proportional to the transient photocurrent measured in experiments made on amorphous materials mentioned in Section 1.

The mean-square displacement. The mean-square displacement, involving infintely many steps of the walker or a time-dependent variance of displacement, is the main stochastic characteristics of the diffusion process. At first, we derive this quantity in the Laplace domain

$$\langle \tilde{X}^2 \rangle(s) = -\frac{\mathrm{d}^2 \tilde{P}(k,s)}{\mathrm{d}k^2}\bigg|_{k=0} = \frac{1}{s} \frac{\tilde{\psi}(s)}{1 - \tilde{\psi}(s)} \left(\langle x^2 \rangle + \langle x \rangle^2 \frac{\tilde{\psi}(s)}{1 - \tilde{\psi}(s)} \right)$$
$$\approx \langle x^2 \rangle \frac{1}{s} \frac{1}{C_s^0 (\tau_0 s)^\alpha + C_r^1 \tau_0 s}$$
$$+ \langle x \rangle^2 \frac{2}{s} \left(\frac{1}{C_s^0 (\tau_0 s)^\alpha + C_r^1 \tau_0 s} \right)^2$$
$$\approx \begin{cases} \dfrac{\langle x^2 \rangle}{C_s^0} \dfrac{1}{\tau_0^\alpha} \dfrac{1}{s^{\alpha+1}} + \left(\dfrac{\langle x \rangle}{C_s^0} \right)^2 \dfrac{2}{\tau_0^{2\alpha}} \dfrac{1}{s^{2\alpha+1}} & \text{for } \alpha < 1 , \\ \dfrac{\langle x^2 \rangle}{C_r^1} \dfrac{1}{\tau_0} \dfrac{1}{s^2} + \left(\dfrac{\langle x \rangle}{C_r^1} \right)^2 \dfrac{2}{\tau_0} \dfrac{1}{s^3} & \text{for } \alpha > 1 . \end{cases} \quad (32)$$

Next, from (32) and (30) we obtain for the asymptotic time (i.e., for $t_0 \gg \tau_0$)

$$\langle \tilde{X}^2 \rangle(t) - [\langle X \rangle(t)]^2 \approx \begin{cases} \dfrac{\langle x^2 \rangle}{C_s^0} \dfrac{1}{\alpha} \dfrac{1}{\mathbf{\Gamma}_{Euler}(\alpha)} \left(\dfrac{t}{\tau_0}\right)^{\alpha} \\ + \left(\dfrac{\langle x \rangle}{C_s^0}\right)^2 \dfrac{1}{\alpha} \left\{ \dfrac{2}{\mathbf{\Gamma}_{Euler}(2\alpha)} - \dfrac{1}{\alpha [\mathbf{\Gamma}_{Euler}(\alpha)]^2} \right\} \left(\dfrac{t}{\tau_0}\right)^{2\alpha} & \text{for } \alpha < 1 , \\ \dfrac{\langle x^2 \rangle}{\langle t \rangle} t & \text{for } \alpha > 1 . \end{cases} \tag{33}$$

As it is seen, the time-dependence of the mean-square displacement below and above the threshold $\alpha = 1$ differ essentially. For $\alpha < 1$ the diffusion is controlled by the drift while for the opposite case it is not.

3. Statistics of extremes

The central values and typical fluctuations are not sufficient to characterize natural systems which exhibit rare but extreme events often dominating the long-term behaviour. Therefore, the statistics of extrema is a classical subject of great interest in mathematics, physics and economical and social sciences [16–18]. In physics, extreme events have been studied in a number of fields [19] (and references therein) including self-organized fluctuations and critical phenomena, material fracture, disordered systems at low temperatures, and turbulence. Knowledge of extreme event statistics is of fundamental importance to predict and estimate the risk in a variety of natural and man-made phenomena such as earthquakes, changes in climate conditions, floods and large movement in financial markets. A new field where extreme statistics is of interest are complex networks [19].

3.1. General derivation

If one observes a series of L independent realizations of the same random phenomenon (or its stochastic replica), the central question of the EVT imposes how to characterize the maximum observed value of random variables[4] $x_{max} \stackrel{\text{def.}}{=} max\{x_l\}_{l=1,\dots,L}$. For example, the maximum value could be the deepest trap encountered by the walker in a disordered medium (then we would have $x \equiv \varepsilon$, where ε is the energetic depth of the trap) or the longest mean residence time (called also the sojourn time of the walker) in such a trap (then we would have $x \equiv \tau$, where τ is the mean residence time).

The main goal of the EVT is to characterize x_{max} by determination of the probability distribution, $P(x_{max} = \Lambda)$, of the maximal value x_{max}, where Λ is an

[4] We developed the EVT by considering continuous variables.

arbitrary threshold. In the case of dispersive transport and diffusion we apply the EVT to characterize, the two above-mentioned related, stochastic variables (ε and τ).

First, we calculate the cumulative probability distribution $P(x_{max} < \Lambda)$ of the random variable x_{max} by noting that if the maximum x_{max} is smaller than Λ then all x_l's are also smaller than this threshold and vice versa. As these random variables are independent and identically distributed (iid), we can put

$$P(x_{max} < \Lambda) = [\rho_<(\Lambda)]^L = [1 - \rho_>(\Lambda)]^L \, , \tag{34}$$

by assuming the cumulative probability distribution of random variable x

$$\rho_<(\Lambda) = \int_{x_{down}}^{\Lambda} \rho(x)\mathrm{d}x \, , \tag{35}$$

where $\rho(x)\,\mathrm{d}x$ is the probability that the random variable x can be found in the interval $x, x + \mathrm{d}x$, and x_{down} is the lowest value which this variable can assume. Of course, the second equality in expression (34) comes from the normalization of the probability density (or distribution) $\rho(\ldots)$ where

$$\rho_>(\Lambda) = \int_{\Lambda}^{x_{up}} \rho(x)\,\mathrm{d}x \, , \tag{36}$$

here x_{up} is the largest value which the variable x can assume. We set here $x_{down} \ll \Lambda \leqslant x_{up}$ so that the strong inequality $\rho_>(\Lambda) \ll 1$ is obeyed. Therefore, the second equality in expression (34) takes, with a good approximation, the useful form

$$P(x_{max} < \Lambda) \approx \exp(-L\rho_>(\Lambda)) \, . \tag{37}$$

In this way, we reached our second step, namely the intermediate formula useful for further transformations

$$P(x_{max} = \Lambda) = \frac{\mathrm{d}P(x_{max} < \Lambda)}{\mathrm{d}\Lambda} \approx L\rho(\Lambda)\exp(-L\rho_>(\Lambda)) \, , \tag{38}$$

where the notation $\rho(\Lambda) = \rho(x = \Lambda)$ and definition (36) have been introduced.

In the third step, we relate the number of observations (L) to the rare event. The law of large numbers tells us that one can expect to observe (typically) such events which have a probability at least equal to $1/L$. Hence, it would be surprising to encounter an event which has a probability much smaller than $1/L$. The largest event Λ_{max}, observed in a series of $L \gg 1$ iid random variables (which we call indeed the rare one), is thus given by relation

$$\rho_\geqslant(\Lambda_{max}) = \frac{1}{L} \, . \tag{39}$$

We can call the above definition of the rare event the weak one; the stronger definition (which seems to be even easier to interpret) could have the form

$$\rho(\Lambda_{max}) = \frac{1}{L} \, , \tag{40}$$

which is, however, less convenient (from the technical point of view of the general approach).[5] Since now we operate with two types of max-variables our aim is to find the probabilistic relation between them.

By combining Eqs. (37), (38) and (39) we finally find the general formula for the searched distribution

$$P(x_{max} = \Lambda) \approx \frac{\rho(\Lambda)}{\rho_{\geqslant}(\Lambda_{max})} \exp\left(-\frac{\rho_{>}(\Lambda)}{\rho_{\geqslant}(\Lambda_{max})}\right) . \tag{41}$$

It is just the above formula that we use to get the Gumbel and Fréchet distributions as well as to find a relation between them.

3.2. The Gumbel distribution versus the Fréchet one

We assume that disordered substrate (medium) is characterized by the random-trap or valley model defined on a regular lattice. Therefore, all valleys are equally spaced but have different (energetic) depths, $\{\varepsilon > 0\}$, while the mountain peaks are all at the same energy level. It is assumed that the distribution of depths is exponential

$$\rho(\varepsilon) = \frac{1}{\langle\varepsilon\rangle} \exp\left(-\frac{\varepsilon}{\langle\varepsilon\rangle}\right) \tag{42}$$

which was done by many authors. The visible aspect of the random-trap model is its symmetry where (in absence of a bias) there is no tendency for the carrier to drift from any configuration of traps. Hence, the carrier hops in any possible direction have an equal probability and the different hops between valleys are, of course, uncorrelated. We use the above-given distribution as a basis for further considerations.

The Gumbel distribution. As we already mentioned in Section 3.1, we can identify the random variables $x \equiv \varepsilon$. Moreover, from expression (42) we find

$$\rho(\Lambda) = \frac{1}{\langle\varepsilon\rangle} \exp\left(-\frac{\Lambda}{\langle\varepsilon\rangle}\right) ,$$

$$\rho_{>}(\Lambda) = \exp\left(-\frac{\Lambda}{\langle\varepsilon\rangle}\right), \quad \rho_{\geqslant}(\Lambda_{max}) = \exp\left(-\frac{\Lambda_{max}}{\langle\varepsilon\rangle}\right) , \tag{43}$$

required to express formula (41) in an explicit form. Note that the third expression (43) together with (40) gives an explicit, unique relation between the value of the rare event Λ_{max} and the number of observations L

$$\frac{\Lambda_{max}}{\langle\varepsilon\rangle} = \ln(L) , \tag{44}$$

which points to a slow (logarithmic) growth[6] with increasing L.

[5]Note that for most cases analytically solvable both definitions give identical shapes of distributions of random variables which require only rescaling by additive and/or multiplicative constants.

[6]For the stronger definition of the rare event (40) we obtain $\Lambda_{max}/\langle\varepsilon\rangle = \ln(L/\langle\varepsilon\rangle)$ while the Gumbel distribution (47) of variable u defined by (46) is unaffected.

By using (43), formula (41) takes an intermediate form

$$P(\varepsilon_{max} = \Lambda) \approx \frac{1}{\langle\varepsilon\rangle} \exp\left(-\frac{\Lambda - \Lambda_{max}}{\langle\varepsilon\rangle}\right) \exp\left(-\exp\left(-\frac{\Lambda - \Lambda_{max}}{\langle\varepsilon\rangle}\right)\right) . \tag{45}$$

To obtain the searched distribution in a closed, explicit form the following transformation of variable ε_{max} or Λ should be made:

$$u \overset{\text{def.}}{=} \frac{\varepsilon_{max} - \Lambda_{max}}{\langle\varepsilon\rangle} = \frac{\Lambda - \Lambda_{max}}{\langle\varepsilon\rangle} \Rightarrow \mathrm{d}u = \frac{\Lambda}{\langle\varepsilon\rangle} . \tag{46}$$

Hence, and by expression (45), we finally obtain the well-known Gumbel distribution

$$P(u) = \exp(-u) \exp(-\exp(-u)) \tag{47}$$

of the u random variable, where we tacitly use the invariance of the probability under the monotonic transformation of random variable (invariant measure); thus we used the equality

$$P(\varepsilon_{max} = \Lambda)\mathrm{d}\Lambda = P(u)\,\mathrm{d}u . \tag{48}$$

Note that the most probable value of this distribution is $u = 0$ which shows that, paradoxally, the rare event Λ_{max} is the most probable value among ε_{max}'s. On the other hand, when $u \to \infty$ the Gumbel distribution $P(u \to \infty) \to \exp(-u)$. Hence, the distribution of random variable ε and the analogous (although asymptotic) one of variable ε_{max} are exponential. We can say that the exponential distribution is asymptotically stable with respect to the 'max' operation.

The Fréchet distribution. Now, we are ready to answer the question concerning the distribution of sojourn times of the walker in traps and find (by using formula (41)) the distribution of its longest values present within a given series of observations. Then (as we mentioned at the beginning of Section 3.1) we assume that the random variable $x \equiv \tau$.

Accordingly, we perform as the first step the transformation

$$\varepsilon \Rightarrow \tau(\varepsilon) = \tau_0(\tau')^{\varepsilon/\Delta} ,$$

$$\rho(\varepsilon) \Rightarrow \rho'(\tau(\varepsilon)) = \frac{1}{\tau_0} \frac{\alpha}{(\tau/\tau_0)^{\alpha+1}} , \tag{49}$$

where we set $\tau' = \exp(\beta'\Delta)$, as we consider over-barrier jumps of a carrier (here Δ denotes the energy unit), and the exponent

$$\alpha = \frac{\ln(N)}{\ln(\tau')} = \frac{1}{\beta'\langle\varepsilon\rangle} . \tag{50}$$

To derive of the second equality in (49) we used again the invariance of the probability under the monotonic transformation of random variable (as given by the first equation of (49)), i.e., we used the equality

$$\rho'(\tau)\mathrm{d}\tau = \rho(\varepsilon)\mathrm{d}\varepsilon . \tag{51}$$

Note that the *exponential transformation of the random variable leads to the transformation of its* (*invariant*) *probability distribution from the exponential one to the* *power-law*. Conversely, *the logarithmic transformation of random variable leads to the transformation of its probability distribution from the power-law to exponential ones.*

From the second relation in (49) and definition (36) we can easily calculate the probability

$$\rho'_{>}(\Lambda) = \frac{1}{(\Lambda/\tau_0)^{\alpha}} \; . \tag{52}$$

and hence

$$\rho'_{\geqslant}(\Lambda_{max}) = \frac{1}{(\Lambda_{max}/\tau_0)^{\alpha}} \; . \tag{53}$$

necessary to obtain probability distribution (41) in an explicit form.[7] Note that by using Eq. (39) we obtain Λ_{max} as a power-law function of L[8]

$$\frac{\Lambda_{max}}{\tau_0} = L^{1/\alpha} \; . \tag{54}$$

It should be noted that the same result is obtained if we use the rare event of energy depth of traps (44) as a power (divided by Δ) of τ' which gives self-consistency of the approach.

By introducing formulae (52) and (53) into (41) we obtain after straightforward calculations

$$P(\tau_{max} = \Lambda) = \frac{1}{\Lambda_{max}} \frac{\alpha}{(\Lambda/\Lambda_{max})^{\alpha+1}} \exp(-1/(\Lambda/\Lambda_{max})^{\alpha}) \; . \tag{55}$$

Hence, we finally obtain the Fréchet distribution

$$P(u) = \frac{\alpha}{u^{\alpha+1}} \exp\left(-\frac{1}{u^{\alpha}}\right) \tag{56}$$

of $u \stackrel{\text{def.}}{=} \Lambda/\Lambda_{max}$ variable, where as usual we used the invariance of the probability under the monotonic transformation of random variable, i.e., we used the equality

$$P(\tau_{max} = \Lambda)\, \mathrm{d}\Lambda = P(u)\, \mathrm{d}u \; . \tag{57}$$

It can be easily found that the most probable value of τ_{max} is proportional to the value of the rare event Λ_{max}.[9]

As it is seen, for $u \gg 1$ the Fréchet distribution is the power-law of exponent $1 + \alpha$ with the power-law correction to the scaling of exponent α since

$$P(u) \approx \frac{\alpha}{u^{\alpha+1}} \left(1 - \frac{1}{u^{\alpha}}\right) \; . \tag{58}$$

Analogously to the Gumbel distribution, we can again say that the power-law tail is asymptotically stable with respect to the 'max' operation.

[7]The Λ variable used here relates to τ and not ε one.

[8]By using the stronger definition (40) of the rare event one gets a related scaling law $\Lambda_{max}/\tau_0 = (L/(\tau_0\alpha))^{1/(\alpha+1)}$.

[9]More precisely, $\tau_{max} = (\alpha/(1+\alpha))^{1/\alpha}\Lambda_{max}$ and only for $\alpha \to \infty$ variable $\tau_{max} = \Lambda_{max}$.

Relation between the Gumbel and Fréchet distributions. The above cosiderations show that, when we made the transformation from the random variable ε to its exponential representation $\tau(\varepsilon)$ (cf. the first relation in (49)) as a result we transformed the Gumbel to the Fréchet distributions. In other words, the Gumbel distribution characterizes an additive stochastic process while the multiplicative one is characterized by the Fréchet distribution (where relation between both processes is given by the *log* operation).

3.3. Pictorial analysis of rank ordering

The main goal of this section is to show the decisive role of rare events in hierarchical continuous-time random walk (HCTRW) for asymptotic many time steps. To make our analysis more convenient we treat variable ε/Δ as a discrete one which is possible as Δ can be always assumed to be sufficiently small (i.e., by assuming $\Delta \ll \langle\varepsilon\rangle$). Again, we assume that $x \equiv \tau$ is our random variable distributed according to the power-law defined by the second expression in (49). Now, we introduce the discrete notation $j = \varepsilon/\Delta$, $j = 0, 1, 2, \ldots$, and define $N = \exp(\Delta/\langle\varepsilon\rangle)$; hence, with a good approximation, $\Delta/\langle\varepsilon\rangle \approx 1 - (1/N)$, which makes the transformation to the discrete distribution

$$\rho(\varepsilon) \Rightarrow \rho''(j) = \left(1 - \frac{1}{N}\right)\frac{1}{N^j}\,, \quad j = 0, 1, 2, \ldots\,, \tag{59}$$

and the definition of the rare event

$$\rho''(j_{max}) = \left(1 - \frac{1}{N}\right)\frac{1}{N^{j_{max}}}\,, \tag{60}$$

clear.[10]

Hierarchical waiting-time distribution in a discrete representation. Note that our hierarchical waiting-time distribution, $\psi(t)$ (which is the basic function of the HCTRW) assumes, within the above-introduced discrete representation, the following useful form:

$$\psi(t) = \sum_{j=0}^{\infty} \rho''(j)\psi_j(t)\,, \tag{61}$$

where the conditional Poisson waiting-time distribution

$$\psi_j(t) = \frac{1}{\tau_0(\tau')^j}\exp\left(-\frac{t}{\tau_0(\tau')^j}\right)\,, \tag{62}$$

and $\rho''(j)$ is the weight which plays a fundamental role in these considerations. (Of course, this discretized $\psi(t)$ conserves the normalization and scaling). For example,

[10] In the above derivation we simply exchanged $d(\varepsilon/\Delta)$ for 1. Note that the distribution has still an exponential form and its normalization is conserved, as it should be.

the sojourn time can be easily calculated by using the weight

$$\langle t\rangle = \sum_{j=0}^{\infty} \rho''(j)\langle t\rangle_j, \quad \langle t\rangle_j = \tau(j) = \int_0^{\infty} t\psi_j(t)\,\mathrm{d}t = \tau_0(\tau')^j \, . \tag{63}$$

Note that the partial residence time $\langle t\rangle_j,\ j = 0, 1, 2, \ldots$, is always finite but the total residence time is finite only when $\alpha > 1$ and equal to

$$\langle t\rangle = \tau_0 \frac{1 - \dfrac{1}{N}}{1 - \dfrac{\tau}{N}} \, ; \tag{64}$$

otherwise it diverges which fully agrees with the result shown in Section 2.2. Hence, to obtain $\langle t\rangle$ finite the weight $\rho''(j)$ must converge sufficiently quickly with the increase of variable j.

It is decisive for our present considerations that the ratio of successive weights

$$\frac{\rho''(j+1)}{\rho''(j)} = \frac{1}{N} \, , \tag{65}$$

be already j independent. This means that in each single step the residence of a carrier in a trap with sojourn time $\tau_0(\tau')^j$ or in state (or hierarchy level) j is N times more likely than those of the next larger order $j + 1$. Hence, one expects (on the average) that the walker will visit N^j traps having the shortest sojourn time τ_0 before he encounters a sufficiently deep trap with a mean residence time $\tau(j) = \tau_0(\tau')^j,\ j = 1, 2, \ldots$.

Practical aims. In Fig. 1 the schematic illustration of this essential observation is given in the form of one-dimensional hierarchically ordered time-intervals or mean residence (sojourn) times in the corresponding traps. Here,

(i) we neglect (due to the Bernoulli law of large numbers) the fluctuation of the number of hierarchy levels as well as their succession (as we calculate the summarized quantities), and
(ii) plot only the length of the average time-intervals $\langle t\rangle_j,\ j = 0, 1, 2, \ldots$.

As it is seen, we made the transformation from the stochastic hierarchy to its deterministic representation. This makes it easier to realize our practical aims, namely, to discuss

(1) the rank ordering of residence times, and
(2) the finite-size effect as scaling of characteristic quantities with the size of the hierarchy.

From Fig. 1 one gets the useful relation between the size of hierarchy L and the number of its levels $j(\geqslant 1$ and $\tau',\ N > 1)$,

$$L(j) = N^j + N^{j-1} + \cdots + N^1 + N^0 \approx \frac{1}{1 - 1/N} N^j \, . \tag{66}$$

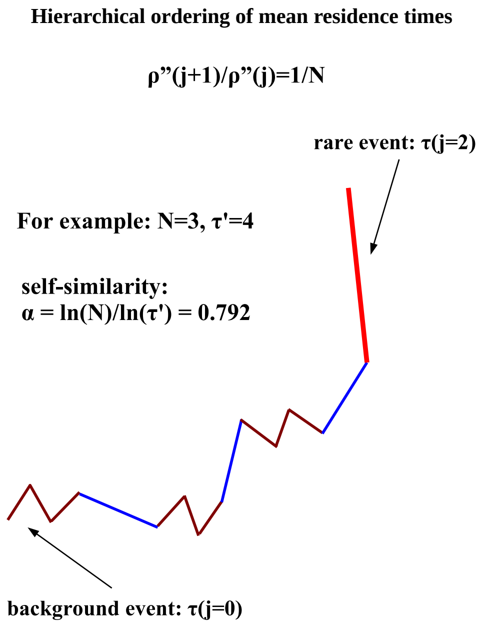

Fig. 1. The part of the stochastic hierarchy of the carrier residence times in random traps presented in the form of ordered two-dimensional zig-zag intervals (the art-view) where the length of each interval is given by $\tau(j) = \tau_0(\tau')^j,\ j = 0, 1, 2, \ldots$.

The quantity $L(j)$ is also the total number of steps after which the walker encountered the trap with sojourn time $\tau_0(\tau')^j$.

Now, we can set the rank $n = L(j)$ and look for the corresponding sojourn time as a function of n ranked according to its decreasing amplitude. Hence, we can write the one-to-one correspondence in the form: $n = L(j) \Leftrightarrow (\tau')^{j_{max}-j}$, where j_{max} is related to the total number of observations L; by using relation (66) we can write

$$L = L(j_{max}) \approx \frac{1}{1 - 1/N} N^{j_{max}} . \tag{67}$$

From expressions (66) and (67) we calculate exponent $j_{max} - j$ and by introducing it into the formula for n given the above, we finally find the searched rank dependence

$$\tau(n) = \tau_0(\tau')^{j_{max}-j} = \tau_0 \left(\frac{L}{n}\right)^{1/\alpha} , \tag{68}$$

which is (for large L) the power-law with exponent $-1/\alpha$. In Fig. 2 we presented this dependence, for example, for $\alpha = 0.792$ (or $N = 3$ and $\tau' = 4$) and $L = 9841$. Eq. (68) shows that hierarchically organized encountered random variables lead to the power-law rank of their amplitudes. Speaking more precisely, we obtained a kind of descending devil's staircase whose average slope is asymptotically given by exponent $-1/\alpha$.

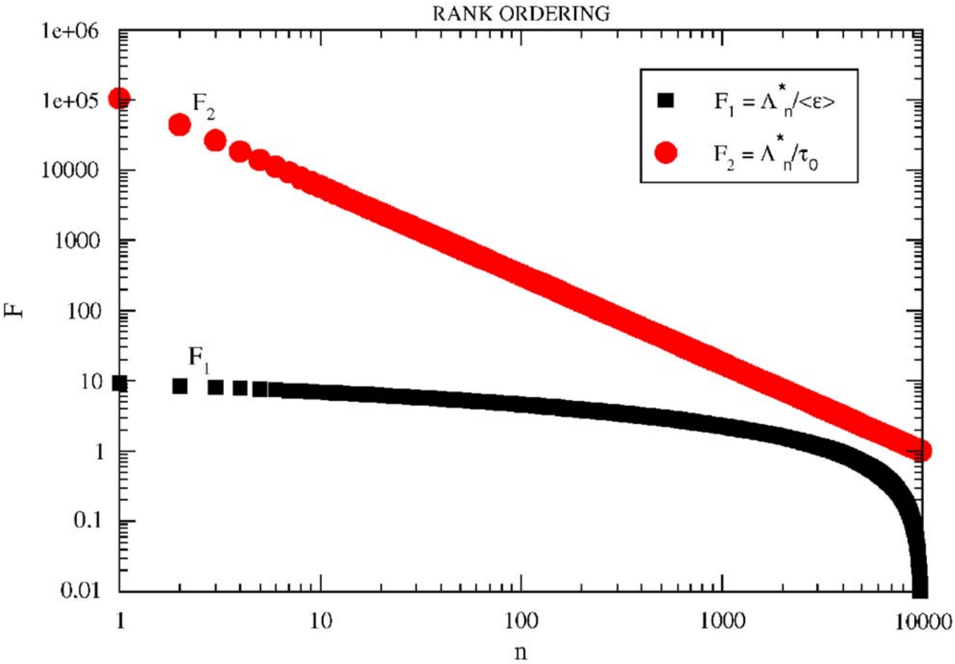

Fig. 2. The rank ordering of residence times and depths of traps described by the power-law (function F_1, where $\Lambda_n^\star$ is given by Eq. (83)) and logarithmic (F_2, where $\Lambda_n^\star$ is given by Eq. (82)) dependences, respectively.

Empirical verification of the tail. The rank relation (68) is very useful in identifying the nature of the tails of probability distributions. The single-step procedure is as follows: one sorts in decreasing order the series of observed random variables (for example, τ's) and one simply draws Λ_n (here equil to $\tau(n)$) as a function of n. If variables are power-law distributed, this graph should be a straight line in a log–log plot, with a slope given by exponent $-1/\alpha$ (as shown, e.g., by expression (68)).

Decisive role of rare events. Our second aim is realized in connection with rare events. Now, we can prove that the (average) total time for which carrier stays in the traps encountered during L steps obeys the same scaling law with L as a rare event.

First, from (59) and (60) we easily obtain

$$\rho''_{\geqslant}(\Lambda) = \sum_{j=\Lambda}^{\infty} \rho''(j) = \frac{1}{N^{\Lambda}} \Rightarrow \rho''_{\geqslant}(\Lambda_{max}) = \frac{1}{N^{\Lambda_{max}}} = \frac{1}{L} \equiv \Lambda_{max} = \frac{\ln(L)}{\ln(N)} \,, \tag{69}$$

where the second relation defines the rare event in agreement with weaker definition (40). Hence, we have

$$(\tau')^{\Lambda_{max}} = L^{1/\alpha} \,. \tag{70}$$

By using relations (67) and (60), we find that just j_{max} is the rare event in the stronger sense given by (40); thus,

$$(\tau')^{j_{max}} = \left[\left(1-\frac{1}{N}\right)L\right]^{1/\alpha}, \tag{71}$$

which means that the difference $\Lambda_{max} - j_{max} = \ln N/\ln(1-1/N)$ is an unimportant constant.

The total time mentioned above is given by the following sum:

$$\begin{aligned}\frac{t}{\tau_0} &\approx N^0(\tau')^{j_{max}} + N^1(\tau')^{j_{max}-1} + \cdots + N^{j_{max-1}}(\tau')^1 + N^{j_{max}}(\tau')^0 \\ &= N^{j_{max}}\,\frac{\left(\frac{\tau'}{N}\right)^{j_{max}+1} - 1}{\frac{\tau'}{N} - 1} \approx \begin{cases} \dfrac{1}{1-\dfrac{N}{\tau'}}\,(\tau')^{j_{max}} & \text{for } \alpha<1\,, \\ \dfrac{1}{1-\dfrac{\tau'}{N}}\,N^{j_{max}} & \text{for } \alpha>1\,. \end{cases}\end{aligned} \tag{72}$$

By introducing Eqs. (71) and (67) into (72) we obtain the important relations

$$\frac{t}{\tau_0} \approx \begin{cases} \dfrac{\left(1-\dfrac{1}{N}\right)^{1/\alpha}}{1-\dfrac{N}{\tau'}}\,L^{1/\alpha} & \text{for } \alpha<1\,, \\ \dfrac{1-\dfrac{1}{N}}{1-\dfrac{\tau'}{N}}\,L & \text{for } \alpha>1\,. \end{cases} \tag{73}$$

Note that both relations (72) and (73) distinguish two essentially different ranges of exponent α (the marginal case $\alpha = 1$ is not considered here). For the first range ($\alpha < 1$) we found t proportional to the rare event, i.e., it scales with the number of steps L in the same manner as the rare event; this is the main result of this section. The proportionality coefficient is called the (dimensionless) fractional residence time. For the opposite, regular case the analogous coefficient is simply the residence time given above (cf. Eq. (64) and second relation (33)).

Now, it is easy to calculate the dependence of the mean-time, $\langle t\rangle$, used by the walker for a single step, on L. For the asymptotic long L one can write the following average calculated along the L-step trajectory:

$$\frac{\langle t\rangle}{\tau_0} \approx \frac{N^{j_{max}}}{L}(\tau')^0 + \frac{N^{j_{max}-1}}{L}(\tau')^1 + \cdots + \frac{N^0}{L}(\tau')^{j_{max}}$$

$$
\approx \begin{cases} \dfrac{(1-\dfrac{1}{N})^{1/\alpha}}{1-\dfrac{N}{\tau'}} L^{(1/\alpha)-1} & \text{for } \alpha<1 \,, \\ \dfrac{1-\dfrac{1}{N}}{1-\dfrac{\tau'}{N}} & \text{for } \alpha>1 \,. \end{cases} \tag{74}
$$

Of course, this result can be obtained straightforward from expression (73) by deviding it simply by L.

Additional properties of rare events. It is useful to have a list of several simple properties of the rare events. The first question which we can easily answer is: how many potential rare events, l_{max}, typically appear within $L(\gg 1)$ events?[11] From (66) we immediately get (exchanging simply j for l_{max}): $l_{max} \approx \frac{\ln(L(l_{max}))}{\ln(N)}$.

The second question is: how the distance between the successive rare events increases with L? Again from (66) we obtain

$$
\Delta L(j) = L(j+1) - L(j) = N^{j+1} \approx (N-1)L(j) \,; \tag{75}
$$

i.e., this distance increases linearly with L.

The third question concerns the ratio of the value of the potential rare events and their difference. Directly from Fig. 1 we find that this ratio is simply equal to τ' independent of L while their difference

$$
\tau_0[(\tau')^{l_{max}+1} - (\tau')^{l_{max}}] \approx \tau_0(\tau'-1)L^{1/\alpha} \,, \tag{76}
$$

scales with L as a single rare event.

3.4. Rank ordering of random variables: general approach

In this section we ask a more general question than in Section 3.1 although we consider again a series of L independent observations of random, identically distributed phenomena. We can rank variables x_l, $l = 1, 2, \ldots, L$, in decreasing order of their amplitude. We denote by Λ_n the nth encountered value among these random variables. Hence, for example, $\Lambda_1 = x_{max}$ and $\Lambda_L = x_{min}$ (i.e., the minimal value of the variables x_l).

As the first step we are interested in the probability distribution $P_n(\Lambda_n)$ of the random variable Λ_n. We can write the exact formula

$$
P_n(\Lambda_n) = LC^{n-1}_{L-1}\rho(x=\Lambda_n)[\rho_>(\Lambda_n)]^{n-1}[\rho_<(\Lambda_n)]^{L-n} \,, \tag{77}
$$

[11] The potential rare event is such an event which is the maximal one but within the given number of steps smaller than L.

where C_{L-1}^{n-1} denotes the combinatorial (or Newton binomial) factor. The product LC_{L-1}^{n-1} gives the total number of ways to set Λ_n within all possible configurations of $L-1$ which remain random variables of the series. Note that for $n=1$ the above formula simplifies to expression (38), as it is expected to be.

In the second step we find the most probable value of $\Lambda_n^\star$ (for a given rank n). By differentiating probability distribution (77) and setting it equal to zero we obtain the formula

$$\frac{1}{L}\frac{d\rho(\Lambda_n)}{d\Lambda_n}\rho_>(\Lambda_n)\rho_<(\Lambda_n) - \frac{n-1}{L}[\rho(\Lambda_n)]^2\rho_<(\Lambda_n) + \left(1-\frac{n}{L}\right)[\rho(\Lambda_n)]^2\rho_>(\Lambda_n) = 0 \tag{78}$$

useful for further considerations particularly when $n,\ L\to\infty$ with fixed ratio n/L. Then the first term in (78) vanishes and we obtain the formula

$$\rho_>(\Lambda_n^\star) \approx \frac{n}{L} \tag{79}$$

which generalizes (39).[12]

To complete information about distribution $P_n(\Lambda_n)$ in the vicinity of $\Lambda_n^\star$ we calculate, as our third step, its width σ_n. We find σ_n by using the saddle-point (or Gaussian) approximation from the second derivative of $\ln P_n(\Lambda_n)$ calculated at $\Lambda_n^\star$ since in this approximation one can use

$$\left.\frac{d^2}{d\Lambda_n^2}\ln P_n(\Lambda_n)\right|_{\Lambda_n^\star} = -\frac{1}{\sigma_n^2}\,. \tag{80}$$

Hence, and from (77), we obtain immediately the width of the probability distribution $P_n(\Lambda_n)$ in the form

$$\sigma_n \approx \frac{1}{\sqrt{L}}\frac{\sqrt{\frac{n}{L}\left(1-\frac{n}{L}\right)}}{\rho(\Lambda_n^\star)}\,, \tag{81}$$

which is more and more sharply peaked around its most probable value $\Lambda_n^\star$ as L tends to infinity (with fixed ratio n/L).

Two useful cases. Let us assume the case of exponential tail (given in Section 3.2 by Eq. (42)). By applying the second relation of Eq. (43) to Eq. (78) we obtain that

$$\Lambda_n^\star \approx \langle\varepsilon\rangle \ln\left(\frac{L}{n}\right)\,. \tag{82}$$

[12]We used here the normalization condition $\rho_<(\Lambda_n) = 1-\rho_>(\Lambda_n)$ which is valid for the continuous random variable.

In the case of the power-law tail (given again in Section 3.2 by the second equation in (49)) we obtain

$$\Lambda_n^\star \approx \tau_0 \left(\frac{L}{n}\right)^{1/\alpha}, \tag{83}$$

which was already derived in Section 3.3 by the simplified approach (of course, $\Lambda_n^\star$ present in the above formula is equivalent to $\tau(n)$ in formula (68)).

In Fig. 2 we compare both the above-derived results in the log–log plot (where we used $L = 9841$ and $\alpha = 0.792$). For the exponential distribution we observe an effective slope which is smaller and smaller as the rank variable n increases, i.e., the remarkable difference between both rank plots is well seen.

3.5. Concluding remarks

In the paper we present, in the context of amorphous materials, two essentially different types of transport and diffusion: above the temperature threshold $1/\beta' = \langle\varepsilon\rangle$ they are regular (normal) while below they are anomalous (i.e., non-Gaussian). We discuss, for these two regions, the asymptotic form of the spatial–temporal propagator, the time-dependent drift and the variance emphasizing their subdiffusive character. Moreover, we were able to show the decisive role of rare events in these anomalous types of transport and diffusion by matching the biased hierarchical continuous-time random flight model and the extreme value theory. We hope that this approach makes possible a deeper understanding of the transport and diffusion phenomena.

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