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A GENERAL PROBABILISTIC APPROACH TO THE UNIVERSAL RELAXATION RESPONSE OF COMPLEX SYSTEMS

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Abstract: A new probabilistic representation of the multichannel relaxation mechanism, which generates the universal two power-law relaxation response with the stretched exponential and the classical exponential decays as special cases, is presented. The consideration of irreversible stochastic transitions of complex systems is based on a general probabilistic formalism applied to the analysis of the first passage of a system. By means of limit theorems the origins of the universality of relaxation responses are indicated. This approach, without referring to the conventional stochastic transition description, allows us to derive explicitly the intensity of transition from an initial state for a complex system in the most general case of parallel channel relaxation with a random number of transition channels, each characterized by an individual relaxation rate. The nonexponential relaxation is shown to result from general properties of transition channels only, namely, from the asymptotical self-similar behavior of their relaxation rate distributions. For the reader's convenience a survey of limit theorems of probability theory is included in the Appendix.

Key Words: Universal Relaxation Law, Intensity of Transition, Stable Schemes, Limit Theorems.

INTRODUCTION

The physical origin of the kinetic dispersion in complex systems like glasses, polymers and biomolecular objects has received much attention in recent decades. This is due to the surprising empirical observation that the following time-dependent form

$$k_o(t) = Bt^{\alpha-1}, \qquad 0 < \alpha < 1, \tag{1.1}$$

of the reaction rate coefficient describes adequately the experimental data (see eg. [1-9]). A convincing body of experimental evidences shows that in contrary to the classical concept of chemical kinetics, the reaction patterns for complex systems cannot be described in terms of the familiar time-independent rate constants; instead, the decay curves can be reproduced only by introducing the reaction rate (1.1) in the kinetic equation describing the bimolecular reaction

$$-\frac{dc_I}{dt} = -\frac{dc_{II}}{dt} = k_o(t)c_I c_{II}, \tag{1.2}$$

where c_I and c_{II} denote the concentration of particles of type *I* and *II*, respectively. In the absence of other processes, the conservation of particles implies that $c_I + c = c_{II}$, where c is a positive constant. Two limiting cases are of special interest [1,2]. If $c_{II}(0) >> c_I(0)$ then $c_I + c \sim c_{II}(0) = const$ and Eq.(1.2) yields the stretched exponential evolutionary law

$$c_I(t) = c_I(0)\exp\left(-cBt^{\alpha}/\alpha\right) \tag{1.3}$$

that is proper for a pseudo first-order kinetics. If $c_I(0) = c_{II}(0)$ then $c \to 0$, and Eq.(1.2) yields the second-order (equal concentration) kinetics

$$c_I(t) = c_I(0)\frac{1}{1 + c_I(0)Bt^{\alpha}/\alpha}. \tag{1.4}$$

If one considers the short- and long-time properties of the response function

$$f(t) = -\frac{1}{c(0)}\frac{dc(t)}{dt}$$

a remarkable difference between the above evolutionary laws can be observed. Namely, for the second-order kinetics (1.4) one gets

$$f(t) \propto \begin{cases} t^{\alpha-1} & \text{for} \quad t \to 0, \\ t^{-\alpha-1} & \text{for} \quad t \to \infty \end{cases}$$

while for the pseudo first-order kinetics (1.3) one has

$$f(t) \propto \begin{cases} t^{\alpha-1} & \text{for} \quad t \to 0 \\ \text{no power law} & \text{for} \quad t \to \infty. \end{cases} \tag{1.5}$$

The nonexponential regression to equilibrium is observed not only in reaction kinetics but also in the study of a variety of problems from condensed matter physics, nuclear physics, spectroscopy, rheology, seismology, radiochemistry, cell and population dynamics, etc. (see eg. [10-26]). Empirical data, exhibiting a great degree of universality, suggest the existence of a universal relaxation (decay) function $\phi(t)$ that the relaxations of nonequilibrium states obey. (For example, in the case of reaction kinetics $\phi(t) = c(t)/c(0)$). On the basis of linear dielectric response measurements, allowing one to follow relaxation processes over several decades of time, the existence of the two power-law response

$$f(t) = -\frac{d\phi(t)}{dt} \propto \begin{cases} t^{-n} & \text{for} \quad t << \frac{1}{A}, \\ t^{-m-1} & \text{for} \quad t >> \frac{1}{A}, \end{cases} \tag{1.6}$$

in relaxation dynamics of complex systems has been established unambiguously [20,21]. The power coefficients $0<n,m<1$ and $A>0$ are constants characteristic of the material.

Among different relaxation functions, suggested to fit data [10,11], the stretched exponential decay law (1.3) appears frequently. The wide occurrence of the stretched exponential decay (examples include the mechanical creep, the dielectric relaxation in polymers, the decay of remnant magnetization in spin glasses, the decay of luminescence, and the pseudo first-order reaction kinetics) has led in the physical literature to the assumption that this relaxation function corresponds to a kind of universal behavior which is independent of the details of individual systems; this idea has stimulated the proposal of several "universal" mechanisms based either on parallel relaxation or on hierarchically constrained dynamics (see eg. [20-30] and refs therein). In contrast, much less attention [31-35] has been paid to the origins of the universally valid two power-law response (1.6) and its relationship, if any, to the specific case of the stretched exponential decay (1.3).

The purpose of this paper is to present a general probabilistic approach to the irreversible stochastic transitions which the complex system undergoes as a whole due to the transitions of individual objects (atoms, molecules, etc.) forming the system. Using the main mathematical tool of the problem - the probability of transition from an initial nonequilibrium state for an object - we introduce a clear probabilistic scheme which relates the local random characteristics of complex systems to the deterministic and universal relaxation laws observed on the macroscopic level in the form of the two power-law response with the stretched exponential and the classical exponential decay laws as special cases. We derive the probability of transition of a system in an explicit form. We show that, in general, this form cannot be attributed to any particular object in the system. However, we specify conditions (imposed by limit theorems of probability theory) under which it is possible. The considerations carried out in the present work provide means to treat the nonexponential relaxation in a way that separates it from a particular physical context and hence to show that they are not limited to a particular type of random evolution. From the mathematical point of view the proposed formalism, used for the direct computation of dynamical averages, does not need assumptions concerning Markovian or non-Markovian, stationary or non-stationary characteristics of the transition process. This advantage, as well as the simplicity of the stochastic pattern leading to the universal relaxation response (1.6), makes the presented approach different from all other approaches which can be found in the literature. The presented formalism also points out why recent probabilistic attempts (see eg. [36-40]) to explain the irreversible stochastic transitions in complex systems do not fully succeed in deriving the universal relaxation response.

The origin of the intensity $r_i(t)$ of transition from an initial nonequilibrium state for an object is considered in chapter: "Transition Probability of an Object". We investigate properties of $r_i(t)$ using its relationship with the total survival probability of the state imposed at time t=0. The obtained results are used in chapter: "Probability of Transition from an Initial State for the Entire System" to derive the effective intensity $r(t)$ of transition for an entire system with objects undergoing irreversible transitions from an initial state. In this paper we emphasize the importance of the so-called first passage of the system in which the relaxation is due to events occurring through a fixed or random collection of independent transition channels characterized by individual relaxation rates β_i. The main conclusions following from our investigations are, for convenience, summarized in Tables 1 and 2. The survey of mathematical tools used in the presented probabilistic formalism is given in the Appendix.

TRANSITION PROBABILITY OF AN OBJECT

Let us consider a complex physical system containing identical objects undergoing irreversible transitions from state A, imposed at time t=0, to state B at random instants of time. States A and B differ in some physical parameter, so that the transition $A \rightarrow B$ is defined as the change of this particular parameter (changes in all other parameters may also have an influence on the transition). Let us choose one of the objects. Consider the conditional probability $p_i(t, dt)$ that the ith object will undergo the transition during the time interval $(t, t+dt)$ if the transition has not occurred before time t, i.e.

$$p_i(t,dt) = \Pr(t \le \theta_i < t + dt \mid \theta_i \ge t), \tag{2.1}$$

where θ_i is the random waiting time for the transition of the chosen object. The conditional probability defined in (2.1) can be expressed in a more useful for further considerations form. Namely,

$$p_i(t,dt) = -\frac{\Pr(\theta_i \ge t + dt) - \Pr(\theta_i \ge t)}{\Pr(\theta_i \ge t)}, \tag{2.2}$$

where $\Pr(\theta_i \ge t + dt)$ and $\Pr(\theta_i \ge t)$ are the survival probabilities, i.e. the probabilities that the ith object will remain in state A until time $t+dt$ and t, respectively. Moreover, the right-hand side of (2.1) for $dt \rightarrow 0$ can be written as

$$p_i(t,dt) = -d \ln \Pr(\theta_i \ge t). \tag{2.3}$$

On the other hand the survival probability of the ith object can be expressed as

$$\Pr(\theta_i \ge t) = 1 - p_i(t)$$

where

$$p_i(t) = F_{\theta_i}(t) = \Pr(\theta_i < t)$$

is the waiting time distribution of the ith object, i.e. the total probability of transition $A \rightarrow B$ of the ith object until time t. Letting

$$\lambda_i(t) = -\ln \Pr(\theta_i \ge t)$$

and observing that $\lambda_i(t)$ is an increasing function satisfying $\lambda_i(0)=0$, one can rewrite the survival probability in the form

$$\Pr(\theta_i \geq t) = \exp(-\lambda_i(t)) = \exp\left(-\int_0^t r_i(s)ds\right) \qquad (2.4)$$

which is dependent on a non-negative quantity $r_i(s)$ called the intensity of transition [41]. In general, this quantity is time-dependent and because of random impacts affecting each object it is not necessarily the same for all objects in the system [36].

The survival probability $\Pr(\theta_i \geq t)$ can be derived if one knows the explicit form of the intensity $r_i(s)$. For the time independent intensity $r_i(s) = b_0 = const$ one gets

$$\Pr(\theta_i \geq t) = \exp(-b_0 t)$$

what recovers the classical exponential evolutionary law for each object. The value b_0 determines the relaxation rate of the transition process. If the intensity of transition is time-dependent then $\lambda_i(t)$ is a nonlinear function of time and the evolutionary law for the object

$$\Pr(\theta_i \geq t) = \exp(-\lambda_i(t))$$

is of the nonexponential form. In this case the relaxation rate is not directly given by the intensity of transition as it is in the exponential case. In order to find the relationship between these two quantities describing the transition process of the object one can consider that the relaxation rate of the *i*th object is the random variable β_i such that

$$\Pr(\theta_i \geq t | \beta_i = b) = \exp(-bt).$$

Then the total survival probability has the form of a mean value with respect to the relaxation rate distribution (in general, of an unknown form)

$$\Pr(\theta_i \geq t) = \langle \exp(-\beta_i t) \rangle . \qquad (2.5)$$

The randomness of the relaxation rates $\beta_i (1 \leq i \leq N)$ is motivated by the fact that in a complex system an object does not have a single conformational state, but a set of substates [9]. There may even be a whole hierarchy of states within states (in fact, this will be the necessary condition to obtain the universal, macroscopic

relaxation laws, see Sec.3.3). Each of the objects is locked into a substate and a distribution of relaxation rates occurs as a result of having many substates, hence the total survival probability (2.5) expresses the average behavior of an individual object in a complex system.
Eq.(2.5) can be rewritten as

$$\Pr(\theta_i \geq t) = \int_0^\infty \exp(-bt) dF_{\beta_i}(b) \tag{2.6}$$

where $b \in [0, \infty)$ denotes the value of the relaxation rate β_i for the ith object. The probability that this value is in the range (b, $b+db$) is equal to $dF_{\beta_i}(b)$. From Eq.(2.4) the intensity of transition from an initial state is related to the total survival probability $\Pr(\theta_i \geq t)$ of the ith object as follows

$$r_i(t) = -\frac{d}{dt} \ln \Pr(\theta_i \geq t). \tag{2.7}$$

Comparing (2.6) and (2.7) we obtain the relationship between the time-dependent intensity of transition and the relaxation rate distribution

$$r_i(t) = -\frac{d}{dt} \ln \int_0^\infty \exp(-bt) dF_{\beta_i}(b). \tag{2.8}$$

In general there is a lack of information about the relaxation rate distribution $F_{\beta_i}(b)$ and hence the corresponding intensity $r_i(t)$ is of an unknown form. The explicit form of $r_i(t)$ depends on the characteristics of the random environment around the ith object and the rules for calculation needed to specify the sets of deterministic and stochastic parameters. But, as we shall show below, it is not necessary to know the explicit form of $r_i(t)$ in order to derive the intensity $r(t)$ of transition from the initial state for the system as a whole. Existence of the effective intensity $r(t)$ determines, however, some properties of $r_i(t)$ (see Sec. 3.3). Notice that the classical exponential case can be also expressed in the form (2.5) with the relaxation rate β_i taking only one value (b_0) with probability 1. In this case $\frac{dF_{\beta_i}(b)}{db} = \delta(b_0)$, i.e. the corresponding probability density takes the Dirac-delta form, and relation (2.8) gives $r_i(t)=b_0=const.$

In order to proceed with the probabilistic analysis the impact of the size of the system on the behavior of each individual object has to be taken into account. It seems physically plausible to consider that in a complex system the intensity $r_i(t)$ for one object (also $\lambda_i(t)$ and $p_i(t)$) depends directly on the number N of objects undergoing transition $A\rightarrow B$ (i.e. $r_i(t)= r_{iN}(t)$) in such a way that the total probability of transition until time t tends to zero as N tends to infinity, i.e.

$$\begin{aligned} p_{iN}(t) &= \Pr(\theta_{iN} < t) = 1 - \exp(-\lambda_{iN}(t)) \\ &= 1 - \exp\left(-\int_0^t r_{iN}(s)ds\right) \rightarrow 0 \text{ as } N \rightarrow \infty \end{aligned} \tag{2.9}$$

Notice that the dependence on N, assumed for $r_{iN}(t)$, affects also the individual waiting time, i.e. $\theta_i = \theta_{iN}$.

PROBABILITY OF TRANSITION FROM AN INITIAL STATE FOR THE ENTIRE SYSTEM

Fraction of objects not transformed at t>0

Consider (as in preceding chapter) a system of N objects, each waiting for transition $A\rightarrow B$ for a random time θ_{iN}, $1\leq i \leq N$. For each N the non-negative waiting-times $\theta_{1N},\ldots,\theta_{NN}$ form a sequence of independent, identically distributed random variables. The waiting time distribution $F_{\theta_i N}(t) = p_{iN}(t)$ is hence the same for each θ_{iN} and is equal to some function $F_\theta(t)$ that may depend on N.

The objects undergo transition in a certain order that can be reflected in the notion of order statistics $\theta_{(1)} \leq \ldots \leq \theta_{(N)}$ [43], which is simply a nondecreasing rearangement of times $\theta_{1N},\ldots,\theta_{NN}$. Traditionally, $\theta_{(n)}$ is called the nth order statistics of sample $\theta_{1N},\ldots,\theta_{NN}$. Note that $\theta_{(1)} = \min(\theta_{1N},\ldots,\theta_{NN})$ and $\theta_{(N)} = \max(\theta_{1N},\ldots,\theta_{NN})$.

For a fixed size N of the system, the ratio of objects not transformed up to time t is equal to

$$1 - \frac{\eta_N(t)}{N} \tag{3.1}$$

where $\eta_N(t)$ denotes an unknown (random!) number of objects already transformed at time $t>0$. For $n=0,1,\ldots,N$ the events $\{\eta_N(t)=n\}$ can be expressed via order statistics in the following way:

$$\begin{aligned}
&\{\eta_N(t)=0\}=\{\theta_{(1)}>t\},\\
&\{\eta_N(t)=n\}=\{\theta_{(n)}\le t,\theta_{(n+1)}>t\} \quad \text{for} \quad n=1,\ldots,N-1,\\
&\{\eta_N(t)=N\}=\{\theta_{(N)}\le t\},
\end{aligned} \tag{3.2}$$

and the probability that exactly n transitions take place in the system until time t is given (see Appendix) by the Bernoulli distribution

$$\Pr(\eta_N(t)=n)=\binom{N}{n}[p_{iN}(t)]^n[1-p_{iN}(t)]^{N-n}, n=0,1,\ldots,N \tag{3.3}$$

Thus the random number $\eta_N(t)$ has the Bernoulli (binomial) distribution $B(N, p)$, with the parameter $p=p_{iN}(t)$. Consequently, the fraction in (3.1) is a random variable. However, it follows from the strong law of large numbers [41] that for N large enough

$$\frac{\eta_N(t)}{N}\approx\left\langle\frac{\eta_N(t)}{N}\right\rangle=p_{iN}(t)=F_\theta(t), \tag{3.4}$$

i.e. the random nature of the fraction in (3.1) vanishes for large N. Hence (3.1) is asymptotically equal to $(1-p_{iN}(t))$ which is the survival probability $\Pr(\theta_{iN}\ge t)$ of any single object. The basic property of the relaxation function $\phi(t)$ is its monotonic decrease from 1 at $t=0$ to 0 as $t\to\infty$. This is in fact a property of the survival probability and therefore (3.1) has been used as a definition of the relaxation function in several models. The relation (3.4) holds for any arbitrarily chosen form of the waiting time distribution (e.g. $F_\theta(t)=0$ for $t<0$, $=t$ for $0\le t\le 1$, and $=1$ for $t>1$). Yet empirical results indicate strictly limiting properties (1.6) of the survival probability of the initial state of a complex system. Since the ratio in (3.4) is not uniquely determined, the attempts [36, 37] leaving the probabilistic analysis of the irreversible stochastic transitions in complex systems at this stage can only propose the form of distribution $F_\theta(t)$ fitting the data most exactly, they do not explain the observed universality (1.6). Let us also observe that for $N\to\infty$ the ratio in (3.4) keeps the properties of a proper probability distribution ($F_\theta(0)=0$ and $F_\theta(\infty)=1$) only if the intensity $r_i(t)$ of an object does not depend on the total number N of objects undergoing the transition. Otherwise, the ratio in (3.4) asymptotically is zero for any instant of time.

Summing up the results obtained in this chapter we observe that if the considered complex system consists of a fixed, large number N of objects undergoing irreversible transitions from state A (imposed at $t = 0$) to state B with random waiting times $\{\theta_{iN}\}$ then the fraction of objects not transformed at $t > 0$ is given by

$$1-\frac{\eta_N(t)}{N}\approx \Pr(\theta_{iN}\geq t)=1-p_{iN}(t). \tag{3.5}$$

If the intensity $r_i(t)$ of an object does not depend on the number N of objects in the system, then

$$1-\frac{\eta_N(t)}{N}\approx 1-p_i(t)$$

has the sense of the survival probability for large N. However, in this case (3.1) can be used to describe the evolution of the entire system only if the behavior of the system can be represented by any individual object (from those forming the system). Unfortunately, this strict condition seems to contradict the idea of complexity of the investigated systems and hence models defining the survival probability of a complex system as in (3.5) do not capture the nature of relaxation phenomena.

If the dependence (2.9) is assumed, then for large N

$$1-\frac{\eta_N(t)}{N}\approx 1$$

for any instant of time t. In this case (3.1) differs strongly from the functions used to fit experimental relaxation data.

Survival probability of the system

The consideration of irreversible stochastic transitions in complex systems shows that the behavior of the system as a whole, in general, cannot be attributed to any chosen object forming the system [31-37]. Crucially relevant to this statement is the question of a proper mathematical construction of an "averaged" object representing the entire system. In general, such an object does not exist in reality. It is, however, reasonable to ask under what conditions the properties of such an imaginary object coincide with the properties of any chosen, real object.

As it follows from (2.7) the intensity of transition from an initial state for any real or imaginary object depends on its survival probability. Let us denote the survival probability of an imaginary object representing the system as a whole by $\Pr(\widetilde{\theta} \geq t)$ and by $\widetilde{\theta}$ the effective waiting time for the entire system. Repeating the arguments of chapter: "Transition Probability of an Object" for the system as a whole, the effective intensity $r(t)$ has to be of the form

$$r(t) = -\frac{d}{dt} \ln \Pr(\widetilde{\theta} \geq t) = \frac{d}{dt} \lambda(t). \tag{3.6}$$

where $\lambda(t) = -\ln \Pr(\widetilde{\theta} \geq t)$

The survival probability $\Pr(\widetilde{\theta} \geq t)$ is the probability that the transition of the system as a whole from its initial state (imposed by external constraints at $t = 0$) has not happened prior to a time instant t. This mathematical quantity is defined as the probability that there is no transition occurring in the system up to time t, i.e.

$$\Pr(\widetilde{\theta} \geq t) = \Pr(\eta_N(t) = 0). \tag{3.7}$$

By means of the Bernoulli scheme (3.3) we have that the survival probability of the system

$$\Pr(\widetilde{\theta} \geq t) = \Pr(\eta_N(t) = 0) = (1 - p_{iN}(t))^N \tag{3.8}$$

is the product of N factors, each asymptotically equal to (3.1), see Eq. (3.5). On the other hand, by means of order statistics, see Eq. (3.2), the survival probability of the entire system

$$\Pr(\widetilde{\theta} \geq t) = \Pr(\eta_N(t) = 0) = \Pr(\theta_{(1)} \geq t) = \Pr(\min(\theta_{1N}, \ldots, \theta_{NN}) \geq t) \tag{3.9}$$

is just the probability of the first passage of the system. As we shall show below the probabilistic analysis of both forms (3.8) and (3.9) is necessary to obtain the complete description of the irreversible stochastic transition of a complex system. Let us first discuss the survival probability of the system in the form given by Eq. (3.8). It follows from assumption (2.9) that:

$$\Pr(\widetilde{\theta} \geq t) = (1 - p_{iN}(t))^N = \exp(-N\lambda_{iN}(t)) \to \exp(-\lambda(t)) \text{ as } N \to \infty \tag{3.10}$$

if only

$$N\lambda_{iN}(t) \to \lambda(t) \tag{3.11}$$

or equivalently,

$$Np_{iN}(t) \to \lambda(t). \tag{3.12}$$

For those t for which $\lambda(t) > 0$, Eq. (3.12) together with (2.9) indicates that the transitions in large complex systems follow the Poisson rather than the Bernoulli scheme (see Appendix), namely, the probability that exactly n transitions take place in the system until time t equals:

$$\Pr(\eta_N(t) = n) = \frac{(\lambda(t))^n}{n!}\exp(-\lambda(t)), n = 0,1,\ldots.$$

Because there is not enough detailed information about $\lambda_{iN}(t)$, at this stage of the analysis the explicit form of $\lambda(t)$, and consequently of $r(t)$, cannot be derived.
In the presented approach the survival probability $\Pr(\tilde{\theta} \geq t)$ of an imaginary object representing the system is used as a definition of the relaxation function $\phi(t)$ describing decay of the nonequilibrium state of the system. Let us observe that here the limiting exponential form in (3.10), being in agreement with the form of the relaxation function assumed in models involving the dispersive transport of defects [42], is a consequence of assumption (2.9). In this case, taking into account (3.7) and (3.10), for large N we have

$$\Pr(\eta_N(t) = 0) \approx \exp(-\lambda(t))$$

which has properties of the survival probability only if the limit $\lambda(t)$ in (3.11) (or equivalently in (3.12)) is positive for any $t > 0$. Let us note that if the intensity for an individual object did not depend on N, then for large N

$$\Pr(\eta_N(t) = 0) \approx 0$$

for each instant of time and the random variable $\tilde{\theta}$ (defined by (3.7)) could not represent the time evolution of the system.

First passage of a system with a fixed number of transition channels

In order to find an explicit form of the effective intensity $r(t)$ of transition from an initial state for the entire system consider Eq. (3.9). Let θ_i denote the waiting time for the ith object undergoing transition $A \rightarrow B$ in a "system" consisting only of this one object, i.e. a one-particle system. For simplicity assume that statistical properties of a single object in a system of N objects depend on N in a way such that the waiting time θ_i is simply stretched out to θ_{iN} by means of a sequence of normalizing constants A_N tending to infinity as the size N of the system increases, namely

$$\theta_{iN} = A_N \theta_i \,. \tag{3.13}$$

In this case the waiting time distribution $F_\theta(t) = F_{\theta_i}(t / A_N)$ where $F_{\theta_i}(t) = p_i(t)$ is the distribution of the random variable θ_i. According to the assumptions of Sec. (3.1) concerning the sequence $\{\theta_{iN}\}$, random variables $\theta_1, \theta_2, \ldots$ are independent and identically distributed. Straightforwardly, by means of extreme value theory (see Appendix), we obtain that for large N the only possible form of the survival probability $\Pr(\tilde{\theta} \geq t)$ defined by (3.9) is the function $\exp(-(At)^\alpha)$ with $\alpha > 0$. If $0 < \alpha \leq 1$, the above result coincides with the stretched exponential function (1.3), used to fit experimental data,. Let us note that $\tilde{\theta}$ is distributed according to the Weibull law that is widely used in the reliability theory.
In order to derive the range (0, 1] for α let us recall relation (2.5) between the waiting time θ_i and the relaxation rate β_i for the object. If (3.13) is assumed, Eq. (3.9) can be rewritten as

$$\Pr(\tilde{\theta} \geq t) = \Pr\left(\theta_1 \geq \frac{t}{A_N}\right) \cdot \ldots \cdot \Pr\left(\theta_N \geq \frac{t}{A_N}\right) = \left(\Pr\left(\theta_1 \geq \frac{t}{A_N}\right)\right)^N .$$

Hence, using (2.5), the survival probability of the system can be derived in the form of an expected value of the random variable $\exp(-t\tilde{\beta})$ with respect to the distribution of the effective relaxation rate $\tilde{\beta}$ representing the entire system:

$$\Pr(\tilde{\theta} \geq t) = \left\langle \exp\left(-t \sum_{i=1}^{N} \beta_i / A_N\right) \right\rangle = \left\langle \exp(-t\tilde{\beta}) \right\rangle \tag{3.14}$$

where

$$\widetilde{\beta} = \sum_{i=1}^{N} \beta_i / A_N, \tag{3.15}$$

and non-negative random relaxation rates β_i, i=1,2,..., are assumed to form a sequence of independent and identically distributed random variables. Note that $\widetilde{\beta}$ depends on N.

It has been shown [31-33] that asymptotically for large N the only possible probability distributions for the effective relaxation rate $\widetilde{\beta}$ are the completely asymmetric Lévy-stable laws with $0<\alpha<1$. When $\alpha\to 1$ the effective relaxation rate $\widetilde{\beta}$ takes a constant value with probability 1 and its distribution becomes degenerate. Consequently, for large enough systems with a fixed number of objects undergoing transitions the only possible formula for the survival probability of the entire system is given by

$$\Pr\left(\widetilde{\theta} \geq t\right) = \exp\left(-(At)^{\alpha}\right) \text{ with } 0 < \alpha \leq 1, \tag{3.16}$$

so that the presented stochastic scheme directly leads to the specific case of the stretched exponential relaxation law (1.3). It includes the classical exponential decay as a limiting case (when $\alpha\to 1$) which corresponds to the absence of stochastic characteristics in considered systems ($\widetilde{\beta}$ = *const*) moreover. The effective intensity $r(t)$, see (3.6), has the form of the power function

$$r(t) = \alpha A (At)^{\alpha - 1}.$$

It is worth noting that to obtain the limiting stretched exponential relaxation law on the macroscopic level it is not necessary to know the detailed nature of the distribution of relaxation rates β_i and consequently, the detailed nature of the intensity $r_i(t)$ of an object. The necessary and sufficient condition for the existence of an asymptotical effective relaxation rate $\widetilde{\beta}$ with the one-sided Lévy-stable distribution is that the distribution of individual relaxation rates β_i belongs to the domain of attraction of the Lévy-stable distribution of $\widetilde{\beta}$ (see Appendix). This condition is equivalent to the self-similar property of $\Pr(\beta_i \geq b)$ for large b expressed as

$$\Pr(\beta_i \geq xb) \approx x^{-\alpha} \Pr(\beta_i \geq b) \text{ as } b \to \infty \tag{3.17}$$

for each x>0. The above scaling property corresponds to the power-law behavior of the waiting time distribution $F_{\theta_i}(t)$ in the short-time regime

$$p_i(t) = F_{\theta_i}(t) \propto t^{\alpha} \quad \text{for small } t \quad (t \to 0),$$

or, equivalently, to the short-time behavior of the intensity $r_i(t)$ of an object:

$$r_i(t) \propto t^{\alpha-1} \quad \text{for} \quad t \to 0 .$$

Among commonly used one-sided distribution functions (see Appendix) only the long-tailed Pareto-like or the Lévy-stable distribution functions satisfy condition (3.17). In the case when β_i in (3.15) are Lévy-stable distributed then $\tilde{\beta}$ (with $A_N = N^{1/\alpha}$) has the same Lévy-stable distribution for any N and consequently $\Pr(\tilde{\theta} \geq t) = \Pr(\theta_i \geq t)$, so that the entire system may be simply represented by any single object from those making up the system.

First passage of a system with a random number of transition channels

The analysis of experimental data [20, 21] has shown that the stretched exponential relaxation law (1.3), although appears frequently, is not universally valid (compare the response functions (1.5) and (1.6)). As it has been unambiguously established, the relaxation dynamics in majority of complex systems follow the two power-law response (1.6). A detailed study of stochastic irreversible transitions (see preceding sections of this chapter) has shown that the only reason for the short-time power-law

$$f(t) = -\frac{d\phi(t)}{dt} = -\frac{d \Pr(\tilde{\theta} \geq t)}{dt} \propto (At)^{-n}, \quad 0 < n = 1 - \alpha < 1,$$

to appear is the self-similar property (3.17) of individual relaxation rates β_i (equivalent to the hierarchy of corresponding random conformational states). However, this condition leads only to the stretched exponential relaxation law, expressed as a weighted average (3.14) of an exponential decay with the Lévy-stable effective relaxation rate $\tilde{\beta}$ (3.15). For the stretched exponential law (3.16), the connection with the Lévy-stable distribution has been known for over a decade [22,29,30], but without a direct relation to the underlying stochastic mechanism. This deficiency is removed by the probabilistic analysis presented above (see Eqs. (3.14) and (3.15)).

In order to derive the long-time power-law response a slowing-down stochastic mechanism has to be incorporated [32-35] in the scheme of the first passage of a complex system. Following the idea of two basic relaxation mechanisms, i.e. the parallel channel and the hierarchically constrained dynamics, two natural stochastic ways to achieve the "goal" can be found [35]. In the correlated cluster relaxation model the conditionally exponential decay (CED) property, introduced and studied in [32, 34], provides a well defined class of all empirically observed two power-law responses (1.6) with the stretched exponential and the exponential decays as special cases. Unfortunately, in general, the relaxation function derived in this model is given only in an integral form

$$\phi(t) = \exp\left\{ -\frac{1}{k} \int_0^{k(At)^{\alpha}} \left(1 - \exp\left(-s^{-1}\right)\right) ds \right\},$$

where $0<\alpha\leq 1$, $k\geq\alpha$, $A>0$.

In the parallel channel relaxation model [35] it is assumed that the number of objects taking part in the relaxation process is not necessarily fixed at time $t = 0$, but can be randomly chosen from all N objects forming the system so that the relaxation process starts with a random initial number ν_N of objects and then runs due to the transitions of those objects occurring at random instants of time $\theta_{1N},...\theta_{NN}$. The number ν_N is an integer-valued random variable (including the degenerate deterministic case $\nu_N = N$ with probability 1) depending on the size N of the system. In this case, assuming (3.13) and that the random initial number ν_N of objects is stochastically independent of the random waiting times $\theta_1,\theta_2,...$, the survival probability of the entire system takes form (3.14). It is a weighted average of an exponential decay with the effective relaxation rate given by

$$\tilde{\beta} = \tilde{\beta}^* = \sum_{i=1}^{\nu_N} \beta_i / A_N$$

instead of (3.15). The effective relaxation rate $\tilde{\beta}^*$ is obtained by a random summation of individual rates β_i over all ν_N possible routes for its realization. The main question in this approach is: what types of integer-valued distributions describe the randomness of ν_N adequately, i.e. in agreement with the nature of the relaxation phenomenon. Still it is an open question, however, it has been shown [35] that assuming ν_N to be distributed geometrically [44], i.e.

$$\Pr(\nu_N = n) = \frac{1}{N}\left(1 - \frac{1}{N}\right)^{n-1}, n = 1,2,...$$

under the condition (3.17) for the distribution of relaxation rates β_i, one obtains that for large N the effective relaxation rate $\tilde{\beta}^*$ is asymptotically distributed according to the so-called geo-stable law that corresponds to the Pareto distribution of the effective waiting time $\tilde{\theta}$ with $0<\alpha\leq 1$. This leads to the evolutionary law in the form of the second-order kinetics (1.4). It is worth noting that the law of the effective relaxation rate can be represented in this case by a mixture of one-sided Lévy-stable and exponential distributions. Namely,

$$\tilde{\beta}^* = E^{1/\alpha}\tilde{\beta},$$

where E is an exponentially distributed random variable [44] (with the probability density function $g(x) = \exp(-x)$ for $x > 0$) which is independent of the Lévy-stable effective relaxation rate $\tilde{\beta}$ obtained for $\nu_N = N$. The probability distribution $F_{\tilde{\beta}^*}(b)$ of the effective relaxation rate $\tilde{\beta}^*$ takes then the integral form

$$F_{\tilde{\beta}^*}(b) = \int_0^\infty S_\alpha\left(\frac{b}{x^{1/\alpha}}\right)g(x)dx,$$

where $S_\alpha(\cdot)$ denotes the probability distribution of the one-sided Lévy-stable random variable $\tilde{\beta}$. This type of mixture has been shown to produce the Mittag-Leffler law [45] and hence

$$F_{\tilde{\beta}^*}(b) = \sum_{i=0}^\infty \frac{(-1)^i}{\Gamma(1+\alpha(i+1))}\left(\frac{b}{A}\right)^{\alpha(i+1)}.$$

As a generalization of the geometrical law let us consider the class of negative binomial [44] distributions for ν_N:

$$\Pr(\nu_N = n) = \frac{\Gamma(1/k + n - 1)}{\Gamma(1/k)(n-1)!}\left(\frac{1}{N}\right)^{1/k}\left(1 - \frac{1}{N}\right)^{n-1}, n = 1,2,... .$$

For this type of distributions, again under (3.17), one can get [35, 45, 46]

$$\Pr\left(\tilde{\theta} \geq t\right) = \frac{1}{\left(1 + k(At)^{\alpha}\right)^{1/k}}, \tag{3.18}$$

where $0 < \alpha \leq 1$ and $k > 0$. When $k \geq \alpha$, formula (3.18) gives us the class of relaxation functions possessing two power-law (1.6) with $n = 1-\alpha$, $m = \alpha/k$. The distribution of the effective waiting time $\tilde{\theta}$ is then a generalized Pareto law (Burr of type XII) [44].

In this case the effective relaxation rate $\tilde{\beta}^*$ is distributed according to the negative-binomial-stable law [46] that can be recognized as a generalized Mittag-Leffler distribution [45]

$$F_{\tilde{\beta}^*}(b) = \sum_{i=0}^{\infty} \frac{(-1)^i \Gamma(i + 1/k)}{i!\,\Gamma(1/k)\Gamma(1 + \alpha(i + 1/k))} \left(\frac{b}{Ak^{1/\alpha}}\right)^{\alpha(i+1/k)}.$$

Thus it can be represented as

$$\tilde{\beta}^* = (\Gamma_k k)^{1/\alpha} \tilde{\beta},$$

where Γ_k is a random variable distributed according to the gamma law (with the probability density function $g_k(x) = \frac{1}{\Gamma(1/k)} x^{1/k-1} \exp(-x)$ $x>0$) [44] which is independent of the Lévy-stable effective relaxation rate $\tilde{\beta}$ obtained in the case of a fixed number of transition channels. Hence

$$F_{\tilde{\beta}^*}(b) = \int_0^{\infty} S_{\alpha}\left(\frac{b}{(kx)^{1/\alpha}}\right) g_k(x)\,dx.$$

The effective intensity of transition, resulting from (3.18), is of the form

$$r(t) = \frac{\alpha A (At)^{\alpha-1}}{1 + k(At)^{\alpha}}. \tag{3.19}$$

The specific form $r(t) = \alpha A (At)^{\alpha-1}$ of (3.19) (obtained as $k \to 0$) leads to the stretched exponential relaxation function (1.3), while for $k = 1$ the intensity $r(t) = \frac{\alpha A (At)^{\alpha-1}}{1 + (At)^{\alpha}}$ corresponds to the second-order law (1.4) of reaction kinetics.

CONCLUSIONS

We have considered the irreversible stochastic transitions of complex systems using the notion of the first passage of a system to express its survival probability in the nonequilibrium state imposed at $t=0$. We have introduced a clear probabilistic scheme, based on the formalism of limit theorems of probability theory, that relates the local random characteristics to the deterministic and universal relaxation laws established empirically for the complex systems. In the framework of the proposed probabilistic representation of relaxation mechanism we have obtained a class of universal two power-law responses, including the stretched exponential and the classical exponential decays as special cases. The formalism of limit theorems has allowed us to find the origins of the nonexponential relaxation responses without specifying the details of the microscopic irreversible transitions of individual objects. We have shown that the nonexponential relaxation follows from the asymptotical self-similar behavior of the individual relaxation rate distributions.

We have discussed also the main differences between the proposed representation of the relaxation phenomenon and the approaches based on the assumption that the survival probability of the system as a whole is equal to the fraction of objects not transformed at $t>0$. (For convenience the comparison is presented in Tables 1 and 2.) We have found that the latter does not reflect the complexity of relaxing systems and, moreover, it does not point out the origins of the universal relaxation law.

Tab.1. Characteristics of the number $\eta_N(t)$ of transitions occurring at $t\geq 0$ in a complex system with a fixed, large number N of transition channels

	Intensity $r_i(t)$ of transition from an initial state for the ith object, does not depend on N	Intensity $r_i(t)$ of transition from an initial state for the ith object, depends on N
$\frac{\eta_N(t)}{N} \underset{N\to\infty}{\approx}$	survival probability of one object	0
$\Pr(\eta_N(t)=0) \underset{N\to\infty}{\approx}$	0	survival probability of a system (probability of the first passage)

Tab.2. Probability of the first passage of a complex system with ν_N transition channels. The intensity $r_i(t)$ of transition from an initial state for the ith object, $1 \le i \le N$, depends on N; $\tilde{\beta}$ represents the effective relaxation rate

	Fixed number $\nu_N = N$	Random number ν_N, distributed according to the negative binomial law
$\tilde{\beta}$ as $N \to \infty$	is distributed according to the one-sided Lévy-stable law, $0 < \alpha \le 1$	is distributed according to the generalized Mittag-Leffler law
$\Pr(n_N(t)=0) = \int_0^\infty e^{bt} dF_{\tilde{\beta}}(b) \underset{N\to\infty}{\approx}$	$\exp\left(-(At)^\alpha\right)$, $0 < \alpha \le 1$	$\left(1 + k(At)^\alpha\right)^{-1/k}$, $0 < \alpha \le 1$, $k \ge \alpha$

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APPENDIX.
LIMIT THEOREMS OF PROBABILITY THEORY. A SURVEY

Probability theory has its origins in regularities observed for the events considered to be random. Such regularities appear in multiple repeating random experiments; and so, for example, in a series of throws of a coin one can observe that the frequencies of the head and the tail both oscillate around ½, and the longer the series is the smaller the deviations are. This behavior, called *the stabilization of frequency of random events*, is the basis for the statistical concept of the notion of probability (understood as a chance of the occurrence of an event) [43, 47, 48].
In modeling of stochastic physical phenomena it is, in general, difficult to use directly the basic notion of probability theory, namely *the probability space* [47, 49, 50], since its elements usually are not abstract mathematical objects. The use of *random variables* [41, 43] allows us to avoid such problems in most of the cases. The notion of random variables transfers the considerations into the real line $\boldsymbol{R}$, well examined by real analysis. The random variable is defined [47-50] as *a measureable* function ξ defined on the probability space $(\Omega, \Sigma, \Pr)$ and taking

values in $\boldsymbol{R}$ so that the set of those elementary events $\omega\in\Omega$ for which $\xi(\omega)<t$, $t\in\boldsymbol{R}$, belongs to the σ-algebra Σ of events and hence the function

$$F(t)=\Pr(\xi<t) \tag{A.1}$$

called *the distribution function*, is well defined. This function fully characterizes the random variable ξ since it provides the information about the probability of taking a particular value by this variable. For example, the probability that ξ has taken the value between t and $t+dt$, $\Pr(t\leq\xi< t+dt)$, is equal to the difference $F(t+dt)-F(t)$. Any nondecreasing, continuous from the left function such that $F(-\infty)=0$ and $F(+\infty)=1$ is the distribution function of the form (A.1) of some random variable [47-49]. This allows us to define random variables - without specifying the probability space, modeling the considered stochastic phenomenon, and the random variable itself as a function on this space - by giving only its distribution function or, equivalently, *the characteristic function* (i.e. the Stieltjes-Fourier transform of the distribution function) [43, 51]. The full knowledge about the law of a random variable, given by the distribution function, in many issues is not necessarily needed. It is sufficient to have a general information about the variable provided by some characteristics of its distribution such as moments (among them the expected value and the variance), and the median [43, 44].
Although it is not difficult to describe the probabilistic space in the experiment with a coin, mentioned above, a more convenient description is given by the random variable ξ that takes value 1 if the result of the experiment is the head, and value 0 in the case of the tail; this random variable has *the zero-one distribution*:

$$\Pr(\xi=1)=p \quad\text{and}\quad \Pr(\xi=0)=1-p, \tag{A.2}$$

where $p\in(0, 1)$ is the probability of throwing the head. The series of throws is modeled by the sequence of random variables ξ_1, ξ_2,...where $\xi_i = 1$ if the result of the ith throw is the head, and $\xi_i=0$ in the case of the tail. It is the sequence of random variables with the same zero-one law as ξ has, and the assumed absence of influence of one separate throw on the others in the series is reflected in the theoretical notion of (stochastic) *independence* [47-51]. The number of the heads in n throws can be obtained by summing up the variables from the sequence and their sum $\zeta_n=\xi_1+...+\xi_n$ has *the binomial* (called also *Bernoulli*) *distribution* $B(n, p)$ with parameters n and p [44]:

$$\Pr(\zeta_n=k)=\binom{n}{k}p^k[1-p]^{n-k},(k=0,1,\ldots,n) \tag{A.3}$$

The frequency of occurrence of the head in the series of n throws corresponds in this description to the arithmetical mean ζ_n/n.

Already on the turn of the 17th century J. Bernoulli proved that ζ_n/n tends in probability to the number p, i.e. for any $\varepsilon>0$

$$\lim_{n\to\infty} \Pr\left(\left|\frac{\zeta_n}{n} - p\right| > \varepsilon\right) = 0 .$$

The above theorem, known as *the Bernoulli law of large numbers* [48, 50], can be applied not only to the series of throws of a coin but also to any sequence of the Bernoulli trials, i.e. the experiments in which there are possible only two results: "success" and "failure", p denotes then the probability of the success. The Bernoulli law of large numbers claims that in such experiments the frequency of the success should oscillate around the value p. It corresponds to the observed in nature stabilization of the frequency of the random event and it shows the conformity of the assumed model with the reality.

The Bernoulli law of large numbers can be interpreted also in another way, as a convergence of the distribution of the random variable ζ_n/n, where ζ_n has the binomial distribution (A.3), to the distribution of the random variable equal p with probability 1 (*the degenerate distribution*). This interpretation states then the limiting law for arithmetical means ζ_n/n, however it does not answer the important and interesting question about how to estimate the deviation $\left|\frac{\zeta_n}{n} - p\right|$. Studies of this problem led to the first central limit theorem, namely, in the 18th century de Moivre showed that if one uses another linear transformation of random variables ζ_n, one obtains the random variables with the distributions tending to *the normal distribution* [44]. More precisely, the sequence $F_n(t)$ of the distribution functions of random variables

$$\frac{\zeta_n - np}{\sqrt{np(1-p)}},$$

where ζ_n have the binomial distributions (A.3), tends to the distribution function of the standard normal law $\mathbf{N}(0,1)$, i.e. for any $t \in \boldsymbol{R}$ we have

$$\lim_{n\to\infty} F_n(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{t} \exp\left(-\frac{x^2}{2}\right) dx .$$

This theorem, known as *the Moivre-Laplace theorem* [43, 47, 48, 50], allows us to estimate not only the speed of the convergence in the Bernoulli law of large numbers but also (in the local version) the probabilities (A.3) of the binomial distribution by means of the normal one.

Although the above two limit theorems concern only the binomial distribution, i.e. the distribution of the sum of independent random variables distributed according to the same zero-one law, they can be generalized for a broader class of probability distributions. Namely, *the (weak) law of large numbers* [48, 50] holds for any sequence of independent and identically distributed random variables $\xi_1,\xi_2,\ldots$ with the distribution such that there exists the mean value $\mathbf{E}\xi_i=\mu<\infty$. It states that for any $\varepsilon>0$

$$\lim_{n\to\infty} \Pr\left(\left|\frac{\zeta_n}{n} - \mu\right| > \varepsilon\right) = 0,$$

(where $\zeta_n=\xi_1+\ldots+\xi_n$), i.e. the arithmetical mean ζ_n/n differs from the mean value μ less than an arbitrarily chosen fixed number $\varepsilon>0$ with probability tending to 1 as $n\to\infty$. Note that the Bernoulli law of large numbers is the special case of the above theorem since the zero-one random variable ξ given by (A.2) has a finite mean value equal p.

According to the weak law of large numbers, the sequence ζ_n/n tends to μ in probability. In fact, it appears that the convergence is stronger - it holds for any point from some subset of Ω that has probability 1:

$$\Pr\left(\lim_{n\to\infty}\frac{\zeta_n}{n} = \mu\right) = 1.$$

This result, called *the strong law of large numbers* [48, 50], states that the random variable ζ_n/n loses its randomness as the number n of trials increases, and that the mean value of the sample (i.e. the arithmetical mean of the results obtained in experiments) well approximates for sufficiently large n the mean value μ of the variable modeling the studied stochastic phenomenon. This law is widely applied in empirical sciences. The special version of it is *the Borel theorem* [48, 50] proved by this French mathematician at the beginning of the 20th century under the assumptions of the Bernoulli law of large numbers. Let us stress that for the sequence of independent and identically distributed random variables the existence of a finite mean value of any single variable from the sequence is the necessary and sufficient condition to hold both, weak and strong laws of large numbers.

Let now a single random variable in the sequence $\xi_1,\xi_2,...$have finite not only the mean value but also the variance **Var**$\xi_i=\sigma^2<\infty$. Under that assumption there holds *the Lindeberg-Lévy central limit theorem* [43, 48] (the generalization of the Moivre-Laplace theorem) that states that the properly linearly normalized sequence of sums $\zeta_n=\xi_1+...+\xi_n$, namely

$$\frac{\zeta_n - n\mu}{\sigma\sqrt{n}}$$

tends in distribution to the random variable distributed according to the standard normal law **N**(0,1). Sum ζ_n for large enough n, independently of the distribution of a single component ξ_i, has hence the law close to the normal one with the mean value $n\mu$ and the variance $n\sigma^2$ (asymptotically normal), if only there exists finite variance of the variable ξ_i.

Central limit theorem explains why in so many applications (like the theory of errors, for example) one can find the probability distributions closely connected with the Gaussian one. Due to this theorem one can also, using the tables of the normal law **N**(0,1), calculate approximately the probability that the deviation

$$\left|\frac{\zeta_n}{n} - \mu\right|$$

is greater than $\varepsilon(\sigma/\sqrt{n})$, $\varepsilon > 0$, evaluating hence the speed of convergence in laws of large numbers.

Because of wide practical applications, limit theorems have been generalized in many different ways. One direction of studies is searching the conditions under which the law of large numbers and the central limit theorem hold in the case of a sequence of independent, however not identically distributed random variables (the examples can be the Lapunow and the Lindeberg-Feller central limits theorems and the Poisson, the Tchebyshev or the Kolmogorov laws of large numbers [43,48,50]). Other generalizations concern the limit theorems for those distributions of a single component ξ_i that have no finite variance or even no mean value so that it is impossible to formulate the central limit theorem for them. In this case the problem can be put as follows: What are the conditions that the distribution of ξ_i (in the sequence $\xi_1,\xi_2,...$ of independent and identically distributed random variables) has to fulfil to provide the existence of normalizing constants $a_n > 0$ and b_n for which the sequence

$$\frac{(\xi_1 + \ldots + \xi_n) - b_n}{a_n} \tag{A.4}$$

has the nondegenerate (i.e. taking more than one value) limit in distribution? Moreover, if such a limit exists what we know about its distribution?
It appears that the class of limiting distributions coincides with the family of *the Lévy-stable distributions*, defined by the following four-parameter characteristic function [52-54]

$$f(\theta) = \begin{cases} \exp\left[-\sigma^\alpha |\theta|^\alpha \left(1 - i\beta\,\mathrm{sgn}(\theta)\,\mathrm{tg}\frac{\alpha\pi}{2}\right) + i\mu\theta\right] & \text{for } \alpha \in (0,2], \alpha \neq 1 \\ \exp\left[-\sigma|\theta|\left(1 - i\beta\frac{2}{\pi}\mathrm{sgn}(\theta)\log|\theta|\right) + i\mu\theta\right] & \text{for } \alpha = 1 \end{cases}$$

with the normal law as a special case given when $\alpha = 2$. The characteristic exponent $\alpha \in (0,2]$, called also the index of stability, can be interpreted as the shape parameter; $\beta \in [-1,1]$, $\mu \in \boldsymbol{R}$, and $\sigma > 0$ are the skewness, the shift, and the scale parameters, respectively; function sgn(θ) takes the value -1 for $\theta < 0$, 0 for $\theta = 0$, and 1 for $\theta > 0$. It should be noted that the one-sided (completely asymmetric) Lévy-stable distributions, supported exactly on the whole non-negative half-line, one can get only for $\beta = 1$, $\mu = 0$ and $0 < \alpha < 1$. Then the Laplace transform, well defining the distributions from this class, has a simple stretched exponential form $\exp\left(-(\sigma t)^\alpha\right)$, $t \geq 0$ [43].
The Lévy-stable laws are defined also [52-54] by the condition that explains their name. Namely, a random variable ξ has the Lévy-stable distribution with parameter α, $0 < \alpha \leq 2$, if and only if

$$\forall a,b > 0 \quad a\xi_1 + b\xi_2 \overset{D}{\sim} c\xi + d \tag{A.5}$$

for some constants c and d, where ξ_1,ξ_2 are independent copies of ξ, and $\overset{D}{\sim}$ denotes the equality of distributions. It is known that then $c^\alpha = a^\alpha + b^\alpha$.
There are well-known the necessary and sufficient conditions for the distribution function $F(t)$ of a single component ξ_i to obtain the convergence of properly normalized sums (of those independent and identically distributed components) to the Lévy-stable random variable with the index of stability α. For case $\alpha = 2$, i.e. for the normal distribution, the condition has the form [53, 54]

$$\lim_{s\to\infty} \frac{s^2 \int\limits_{\{|t|>s\}} dF(t)}{\int\limits_{\{|t|<s\}} t^2 dF(t)} = 0 \tag{A.6}$$

and is fulfilled in particular when **Var**$\xi_i<\infty$. In case $\alpha\in(0,2)$, ($\alpha \neq 2$), one gets that the condition is [53, 54]

$$\lim_{t\to\infty} \frac{1-F(xt)+F(-xt)}{1-F(t)+F(-t)} = x^{-\alpha} \quad \text{for any} \quad x>0 \tag{A.7}$$

under the assumption that there exist limits

$$\lim_{t\to\infty} \frac{1-F(t)}{1-F(t)+F(-t)} \quad \text{and} \quad \lim_{t\to\infty} \frac{1-F(-t)}{1-F(t)+F(-t)}. \tag{A.8}$$

It is essential then the asymptotical behavior of the distribution function $F(t)$ in both $+\infty$ and $-\infty$, not its detailed form.

If for some constants $a_n>0$, b_n the sequence (A.4) tends in distribution to some nondegenerate random variable, then we say that the distribution $F(t)$ of random variables ξ_i belongs to *the domain of attraction* of the distribution of the limiting random variable. As it follows from the previous considerations, the Lévy-stable distributions with the normal law as a special case are the only ones that have the domain of attraction and the conditions (A.7) with (A.8), and (A.6), specify what kinds of distributions belong to this domain of attraction for $\alpha\in(0,2)$ and $\alpha=2$, respectively. Let us stress that a one-sided distribution $F(t)$ belongs to the domain of attraction of the one-sided Lévy-stable law if and only if for any $x>0$

$$\lim_{t\to\infty} \frac{1-F(xt)}{1-F(t)} = x^{-\alpha} \tag{A.9}$$

for some fixed α and this parameter is in the range $0<\alpha<1$. In other words, it is provided by the following self-similar property

$$\Pr(\xi_i \geq xt) \approx x^{-\alpha} \Pr(\xi_i \geq t) \quad \text{for} \quad t\to\infty.$$

The best known examples of the distributions satisfying condition (A.9) are the Pareto distribution $F(t) = 1 - \frac{1}{1+(At)^{\alpha}}$, $t\geq 0$ [44], and the Lévy-stable distributions themselves, in both cases when $\alpha<1$.

Another group of limit theorems one obtains considering the operations on the sequence $\xi_1, \xi_2, \ldots$ different from the summation (A.4). In particular the minimum and maximum operations are taken into account in the extreme value theory [55]. As the limiting distributions for linearly normalized minima

$$a_n^{-1} \min(\xi_1, \ldots, \xi_n) - b_n \tag{A.10}$$

of independent and identically distributed random variables ξ_1, $\xi_2, \ldots$ one obtains *the min-stable distributions* with the distribution function $G(at+b)$, $a>0$, $b \in \boldsymbol{R}$, where $G(t)$ is one of the following three types:

Type I : $G(t) = 1 - \exp(-e^t), \quad -\infty < t < \infty$

Type II : $G(t) = \begin{cases} 1 - \exp(-(-t)^{-\gamma}), & \text{for some } \gamma > 0, \ t < 0, \\ 1, & t \geq 0, \end{cases}$

Type III : $G(t) = \begin{cases} 0, & t > 0, \\ 1 - \exp(-t^{\gamma}), & \text{for some } \gamma > 0, \ t \geq 0. \end{cases}$

Observe that the min-stable law of type III is the well-known *Weibull distribution* [44] often used in applications (e.g. in the reliability theory). It is the only type of the one-sided min-stable law supported on the non-negative half-line $[0,\infty)$.
If the sequence (A.10) tends in distribution to some nondegenerate random variable, then we say that the distribution $F(t)$ of random variables ξ_i belongs to the domain of attraction of the min-stable law of the type obtained as the limit. The covergence holds if and only if there are fulfiled the following conditions [55]:

Type I : there exists some strictly positive function $g(t)$ such that

$$\lim_{t \to t_F +} \frac{1 - F(t - xg(t))}{F(t)} = \exp(-x), \quad \text{for all real } x;$$

Type II : $t_F = -\infty$ and

$$\lim_{t \to -\infty} \frac{F(xt)}{F(t)} = x^{-\gamma}, \qquad \text{for any} \quad x > 0; \tag{A.11}$$

Type III : $t_F > -\infty$ and

$$\lim_{h\to 0+} \frac{F(t_F + xh)}{F(t_F + h)} = x^{\gamma}, \qquad \text{for any } x > 0$$

where $t_F = \inf\{t : F(t)>0\}$. As in the case of the Lévy-stable laws here is essential the asymptotical behavior of the distribution function $F(t)$ of a single factor ξ_i rather than its detailed form.

Let us note that for the one-sided distributions $F(t)$ supported on $[0,\infty)$ we have $t_F = 0$ so that F can belong to the domain of attraction of min-stable laws of types I and III only. Moreover, the condition (A.11) for obtaining the one-sided, supported on $[0,\infty)$ type III can be rewritten in this case as

$$\lim_{t\to 0+} \frac{F(xt)}{F(t)} = x^{\gamma}, \qquad \text{for any } x > 0$$

or equivalently,

$$\Pr(\xi_i < xt) \approx x^{\gamma} \Pr(\xi_i < t) \quad \text{for} \quad t \to 0_+.$$

Since $\max(\xi_1,\ldots,\xi_n) = -\min(-\xi_1,\ldots,-\xi_n)$ in case of maximum operation we obtain also three types of *the max-stable laws* with the distribution functions of the form $1-G(-t)$ and the conditions for the convergence can be found substituting $F(t)$ by $1-F(-t)$.

Going further in generalizing the scheme of limit theorems, one assumes [46] that the number of factors of the sum (A.4) is an integer-valued positive random variable ν_p with the distribution (e.g. the geometrical or the negative binomial one) depending on the parameter p, and then the convergence in distribution of random variables

$$\frac{\zeta_{\nu_p} - b(p)}{a(p)}$$

is studied as p tends to some limiting value. The obtained limiting distributions are called *the ν-stable laws* and they include the Lévy-stable distributions. Similarly, the classes of the ν-min- and ν-max-stable distributions are defined.

As we can see from the above considerations the Moivre-Laplace theorem, proved for the simple model of the Bernoulli trials, initiated a great development of the theory of limit theorems and more, the obtained limiting distributions are interesting from the point of view of mathematics as well as other sciences. Similarly, another one historical result for the Bernoulli scheme, namely *the Poisson theorem* [43, 50], strongly influenced the probability theory. This theorem states that if the parameter p of the binomial distribution depends on its parameter n such that

$$\lim_{n\to\infty} np_n = \lambda > 0$$

then

$$\lim_{n\to\infty} \Pr(\zeta_n = k) = \frac{\lambda^k}{k!}\exp(-\lambda), \quad k = 0,1,\ldots$$

i.e. the sums ζ_n tend in distribution to the Poisson law [44]. We can say therefore that for the series of n independent trials with the probability p of the success

$$\Pr(\zeta_n = k) \approx \frac{\lambda^k}{k!}\exp(-\lambda), \quad k = 0,1,\ldots, \quad \text{for} \quad \lambda = np \qquad \text{(A.12)}$$

if only n is sufficiently large while p sufficiently small (for example, $n \approx 10^2$ and $p \approx 10^{-2}$). The above result allows us to evaluate the probabilities (A.3) for the binomial distribution by means of (A.12) and it appears that for small p, $p < 0.1$, this approximation is much more precise than that obtained from the Moivre-Laplace local theorem. It is worth noting that recently - in view of a widespread use of computers to numerical calculations - practical meaning of the two mentioned above methods of approximation of the binomial distributions decreases.

The Poisson theorem concerns a particular case of a triangle system of random variables, i.e. the system

$$\begin{array}{lllll} \xi_{11} & & & & \\ \xi_{21} & \xi_{22} & & & \\ \vdots & \vdots & \ddots & & \\ \xi_{n1} & \xi_{n2} & \cdots & \xi_{nn} & \\ \vdots & \vdots & \cdots & \vdots & \ddots \end{array}$$

where in each separate row the random variables are independent and identically distributed, however the distributions can change from one row to another. In the

Poisson theorem the distribution of the random variables in the nth row is the zero-one law with the parameter p_n depending on n. In general case, examining the convergence of sums $\zeta_n=\xi_{n1}+...+\xi_{nn}$ of the variables in the nth row as $n\to\infty$ one obtains the next class of limiting laws - the family of *the infinitely divisible distributions* [43, 51].

The random variable X has the infinitely divisible distribution if and only if for any $n\geq 1$ there exist random variables $\xi_{n1},...,\xi_{nn}$, independent and identically distributed, such that

$$X \overset{D}{\sim} \xi_{n1} + ... + \xi_{nn}. \tag{A.13}$$

It follows from the above definition that to the class of infinitely divisible distributions - except for the Poisson one - there belong the normal law with another Lévy-stable distributions, *the gamma laws* [44] with the special case of *the exponential law* [44] - all of them often applied in probabilistic models.

Let us stress that all of the Lévy-stable and the infinitely divisible laws defined by the conditions (A.5) and (A.13), respectively, can be obtained as the limiting distribution of some limit theorem. It holds also in case of the stable distributions of other types (min-, max-stable, ν-stable etc.).

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