Anomalous statistics of random relaxations in random environments

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We comprehensively analyze the emergence of anomalous statistics in the context of the random relaxation (RARE) model [Eliazar and Metzler, J. Chem. Phys. 137, 234106 (2012)], a recently introduced versatile model of random relaxations in random environments. The RARE model considers excitations scattered randomly across a metric space around a reaction center. The excitations react randomly with the center, the reaction rates depending on the excitations' distances from this center. Relaxation occurs upon the first reaction between an excitation and the center. Addressing both the relaxation time and the relaxation range, we explore when these random variables display anomalous statistics, namely, heavy tails at zero and at infinity that manifest, respectively, exceptionally high occurrence probabilities of very small and very large outliers. A cohesive set of closed-form analytic results is established, determining precisely when such anomalous statistics emerge.

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I. INTRODUCTION

Fluorescence methods based on induction or quenching via resonant energy or electron transfer have reached unprecedented levels of accuracy [1] and allow one to routinely analyze molecular distances and interactions [2–4]. Similarly, in the condensed phase relaxation phenomena can be measured at high accuracy, for instance, by NMR relaxometry [5] or dynamic light scattering [6]. Concurrently to this development scientists realized that the standard Debye relaxation, given by the exponential tail distribution function $\phi(t) \propto \exp(-t/\tau)$, where τ is some characteristic time scale, fails to describe the observed relaxation dynamics even on molecular scales [2,7,8]. Generalized relaxation models accommodating the experimental data include the stretched-exponential relaxation, also known as the Kohlrausch-Williams-Watts law, and mathematically given by the Weibull tail distribution function $\phi(t) \propto \exp(-[t/\tau]^{\alpha})$ with exponent $0 < \alpha < 1$ [9–11]. Another prevalent model is the power-law relaxation, also known as the Nutting law, which is given by the Pareto tail distribution function $\phi(t) \propto 1/(1 + [t/\tau]^{\alpha})$ with exponent $0 < \alpha < 1$ [12,13]. A third common approach to nonexponential dynamics is given by fractional relaxation models [13-16] leading to the Mittag-Leffler behavior $\phi(t) \propto E_{\alpha}(-[t/\tau]^{\alpha}) = \sum_{k=0}^{\infty} (-[t/\tau]^{\alpha})^k / \Gamma(1+\alpha k),$ which interpolates between an initial stretched-exponential behavior $\simeq \exp\{-[t/\tau]^{\alpha}/\Gamma(1+\alpha)\}$ as $t \to 0$ and a terminal power-law behavior $\simeq (\tau/t)^{\alpha}/\Gamma(1-\alpha)$ as $t \to \infty$ [13,14,16]. Generalized relaxation models can also be decomposed into a continuum of exponential relaxation modes in terms of the so-called relaxation time distribution [17].

There exist various generalized relaxation models to account for the observed deviations from the single exponential pattern. Among others, the concept of parallel relaxation channels goes back to Förster [18,19], and it was shown that hierarchically constrained dynamics give rise to complex serial relaxation [20]. From a more stochastic point of view, defect diffusion models have been discussed [21]. In particular, for the stretched-exponential law it was demonstrated that there are common universal principles behind different approaches [22–24]. There exist also extensions of stretched exponentials in models of dynamic relaxation channels [25]. Related to the above-mentioned Mittag-Leffler relaxation function, fractional-order viscoelastic mechanical bodies combine Mittag-Leffler modes to generate complex yet analytically treatable relaxation behaviors in mechanical [13,26–28] and dielectric [29,30] relaxation.

Both the stretched-exponential and the power-law relaxations exhibit a heavy-tail behavior. In the stretchedexponential relaxation the corresponding probability density function follows the diverging power-law behavior $t^{\alpha-1}$ at zero, $t \to 0$. In the power-law relaxation the corresponding probability density function follows the power-law behavior $t^{-\alpha-1}$ at infinity, $t \to \infty$. These power-law asymptotics manifest anomalous statistics: an exceptionally high concentration of probability at either very small outliers (in the stretchedexponential relaxation model) or very large outliers (in the power-law relaxation model).

The goal of this paper is to comprehensively explore the emergence of heavy-tail behaviors in the context of the recently introduced random relaxation (RARE) model [31]. Generalizing previous approaches by Thomas et al. [32] and Blumen [33], in the context of donor-acceptor recombination dynamics, the RARE model is a highly robust model for random relaxations in random environments. The RARE model considers general random reactions taking place in general random environments as follows. A countable collection of excitations is spatially distributed, according to a random Poisson scattering (which may or may not be homogeneous), across a metric space containing a reaction center. The excitations react randomly with the center, and the reaction rates depend on the excitations' distances from the center. A relaxation event occurs upon the first reaction between an excitation and the center.

The RARE model has two deterministic inputs: (i) a scattering function quantifying the distribution of the distances

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of the excitations from the reaction center, and (ii) a reactivity function quantifying the distance-dependent reaction rates of the excitations. A host of scenarios (of random reactions in random environments) can be modeled via this pair of input functions. The two stochastic outputs of the RARE model are (i) a reaction time representing the relaxation epoch, i.e., the first reaction between an excitation and the center, and (ii) a reaction range representing the relaxation distance, i.e., the distance between the first-reacting excitation and the center. In this paper we study in detail the anomalous statistics of the pair of outputs and establish closed-form analytic answers to the following question: When do the reaction time and the reaction range display heavy tails at either zero or infinity?

The paper is organized as follows. We begin with a concise description of the RARE model in Sec. II, followed by the precise probabilistic notion of heavy tails in Sec. III. The anomalous statistics of the reaction time and the reaction range are presented in Secs. IV and V, respectively. Power-law coupling between the scattering function and the reactivity function, leading to the emergence of stretched-exponential relaxation, is studied in Secs. VI and VII. Exponential coupling between the scattering function and the reactivity function, leading to the emergence of (asymptotic) power-law relaxation, is studied in Sec. VIII. We conclude in Sec. IX and compile the technical calculations and the detailed proofs in the Appendices to keep the exposition in the main part of the text more streamline and accessible to the reader.

This study provides researchers with a handy and easily applicable toolbox for the study of anomalous statistics in the context of random relaxations in complex environments. The application of the toolbox is straightforward: Identify the scattering function and the reactivity function in the system of interest and plug these functions in the set of closed-form formulas presented below. While the mathematics used to establish the results is somewhat involved, all technical details are deferred to the Appendices. The emergence of the anomalous-statistics results is immediately accessible from the scattering and reactivity functions.

II. THE RARE MODEL

The RARE model was introduced in Ref. [31] and is briefly described as follows. A reaction center is placed at an arbitrary point *P* of a general metric space \mathcal{M} and a countable collection of excitations is scattered randomly across the space. The excitations are labeled by the index *i* and the position of excitation *i* is the random point P_i . The distance in the metric space \mathcal{M} is measured by a general metric function $\mathbf{d}(.,.)$ and the distance between the reaction center and excitation *i* is $D_i = \mathbf{d}(P_i, P)$.

The random points $\{P_i\}$ are assumed to form a general Poisson process on the metric space \mathcal{M} [34]. Consequently, the displacement theorem of the theory of Poisson processes (see Sec. 5.5 in Ref. [34]) implies that the distances $\{D_i\}$ form a general Poisson process on the positive half line $(0, \infty)$. In what follows we denote by $\rho(x)$ the mean number of excitations that are within a distance x of the reaction center, i.e.,

$$\rho(x) = \mathbf{E}\left[\sum_{i} \mathbf{I}(D_i \leqslant x)\right],\tag{1}$$

with $x \ge 0$. The intensity of the Poisson process $\{D_i\}$ is the derivative $\rho'(x)$ of the function $\rho(x)$. In Eq. (1) the symbol **E** denotes the mathematical expectation. Namely, if ξ is a real-valued random variable governed by the probability density function $f_{\xi}(x)$ (x real) and $\phi(x)$ is a real-valued function defined on the real line, then $\mathbf{E}[\phi(\xi)] = \int_{-\infty}^{\infty} \phi(x) f_{\xi}(x) dx$.

Excitation *i* is equipped with a random timer T_i and the timers $\{T_i\}$ are assumed to be conditionally independent and exponentially distributed random variables—given the Poisson process D_i . The exponential distribution of the timer T_i is determined by the distance D_i and in what follows we denote by $\eta(x)$ the exponential rate of the timers as a function of the distance variable (x). Namely, given the distance D_i , the random timer T_i is exponentially distributed with mean $1/\eta(D_i)$ and hence

$$\Pr(T_i > t | D_i) = \exp\{-\eta(D_i)t\},\tag{2}$$

with $t \ge 0$.

The inputs of the RARE model are the aforementioned scattering function $\rho(x)$ and the reactivity function $\eta(x)$. The scattering function $\rho(x)$ quantifies the underlying spatial scattering of the excitations and the reactivity function $\eta(x)$ quantifies the underlying distance-dependent reaction rates. We henceforth assume that the scattering function $\rho(x)$ is monotonically increasing from zero $[\rho(0) = 0]$ to infinity $[\rho(\infty) = \infty]$ and that the reactivity function $\eta(x)$ is monotonically decreasing to zero $[\eta(\infty) = 0]$.

In the RARE model relaxation occurs upon the first timer-expiration event, i.e., upon the first reaction between the excitations and the reaction center. Consequently, the outputs of the RARE model are the reaction time T and the reaction range X, a pair of random variables that are defined as follows. The reaction time T is the time elapsing until the first timer expires,

$$T = \min_{i} \{T_i\}.$$
 (3)

The reaction range X is the distance between the reaction center and the excitation whose timer first expired,

$$X = \sum_{i} D_i \mathbf{I}(T = T_i).$$
(4)

We note that by considering the space \mathcal{M} to be a general metric space and setting the random points $\{P_i\}$ to be a general Poisson process on \mathcal{M} , the RARE model becomes a highly versatile model of random reactions in random environments. Indeed, \mathcal{M} can be a Euclidean space of arbitrary dimension, a non-Euclidean space such as a hyperbolic space, a general surface or landscape, a fractal object, a network, etc. Also, Poisson processes represent a highly effective statistical methodology to model the random scattering of points in general spaces, with a vast span of applications ranging from insurance and finance [35] to queuing systems [36] and from fractals [37] to power laws [38]. Consequently, in a statistical sense, no matter how elaborate the space and how intricate the scattering of the excitations across the space, the spatial facet of the RARE model is quantified by the monotonically increasing scattering function $\rho(x)$. Also, no matter how complex the mechanisms governing the reactions between the excitations and the reaction center, the chemical facet of the RARE model is quantified by the monotonically decreasing reactivity function $\eta(x)$. Thus, with only two intuitively comprehensible parameters, the scattering function $\rho(x)$ and the reactivity function $\eta(x)$, the RARE model is capable of encompassing a wide span of scenarios of random reactions in random environments.

III. HEAVY TAILS

The goal of this paper is to explore anomalous statistics of the reaction time T and the reaction range X of the RARE model. Both the reaction time T and the reaction range Xare positive-valued random variables. Anomalous statistics of a positive-valued random variable ξ are displayed when its distribution possesses heavy tails at either zero or infinity [39]. A heavy tail at zero implies a high-probability occurrence of very small outliers, whereas a heavy tail at infinity implies a high-probability occurrence of very large outliers. Informally, the heavy tails of the random variable ξ are characterized by power-law asymptotics of its probability density function. The precise definition of heavy tails involves the mathematical notion of regular variation, which we briefly review.

Consider a non-negative-valued function f(x) defined on the positive half line (x > 0). The function f(x) is said to be [40]: (i) slowly varying at zero if the limit $\lim_{l\to 0} f(lx)/f(l) = 1$ holds for all x > 0; and (ii) slowly varying at infinity if the limit $\lim_{l\to\infty} f(lx)/f(l) = 1$ holds for all x > 0. A function f(x) is slowly varying at zero if and only if the function f(1/x) is slowly varying at infinity; the class of functions that are slowly varying at infinity includes asymptotically constant functions, logarithmic functions, powers of slowly varying functions (at infinity). The class of slowly varying functions (at infinity). The class of slowly varying functions (at zero and at infinity).

The aforementioned function f(x) is said to be [40]: (i) regularly varying at zero if the limit $L_0(x) = \lim_{l\to 0} f(lx)/f(l)$ exists for all x > 0; and (ii) regularly varying at infinity if the limit $L_{\infty}(x) = \lim_{l\to\infty} f(lx)/f(l)$ exists for all x > 0. It is straightforward to observe that regular variation at zero implies that the condition $L_0(xy) = L_0(x)L_0(y)$ holds for all x, y > 0, and that regular variation at infinity implies that the condition $L_{\infty}(xy) = L_{\infty}(x)L_{\infty}(y)$ holds for all x, y > 0. These observations in turn imply that the aforementioned limits are power laws: $L_0(x) = x^{\epsilon_0}$ and $L_{\infty}(x) = x^{\epsilon_{\infty}}$, where ϵ_0 and ϵ_{∞} are real-valued exponents.

On the one hand, slowly varying functions are a special case of regularly varying functions. Indeed, slowly varying functions are regularly varying functions with zero exponents ($\epsilon_0 = 0$ and $\epsilon_{\infty} = 0$). On the other hand, regularly varying functions are based on slowly varying functions: (i) A function f(x) is regularly varying at zero with exponent ϵ_0 if and only if it admits the representation $f(x) = x^{\epsilon_0}\phi_0(x)$, where the function $\phi_0(x)$ is slowly varying at zero; and (ii) a function f(x) is regularly varying at infinity with exponent ϵ_{∞} if and only if it admits the representation $f(x) = x^{\epsilon_{\infty}}\phi_{\infty}(x)$, where the function $\phi_{\infty}(x)$ is slowly varying at infinity.

The class of regularly varying functions is a generalization of the class of asymptotic power-law functions (at zero and at infinity) and it plays a focal role in various fields of mathematical analysis and probability theory [40]. Equipped with the notion of regular variation, we are now in the position to rigorously define the heavy tails of a positive-valued random variable ξ . (i) The random variable ξ is heavy tailed at zero with exponent α (0 < α < 1) if its cumulative distribution function $Pr(\xi \leq x)$ is regularly varying at zero with exponent $\epsilon_0 = \alpha$, i.e.,

$$\lim_{l \to 0} \frac{\Pr(\xi \le lx)}{\Pr(\xi \le l)} = x^{\alpha},\tag{5}$$

with x > 0. (ii) The random variable ξ is heavy tailed at infinity with exponent β ($0 < \beta < 1$) if its tail distribution function $Pr(\xi > x)$ is regularly varying at infinity with exponent $\epsilon_{\infty} = -\beta$, i.e.,

$$\lim_{l \to \infty} \frac{\Pr(\xi > lx)}{\Pr(\xi > l)} = \frac{1}{x^{\beta}},\tag{6}$$

with x > 0.

We note that if the random variable ξ is heavy tailed at zero then its probability density function diverges at zero, a phenomenon manifesting the high-probability occurrence of very small outliers. Analogously, if the random variable ξ is heavy tailed at infinity then its mean diverges, a phenomena manifesting the high-probability occurrence of very large outliers. The connection between heavy tails at zero and at infinity is as follows: The random variable ξ is heavy tailed at zero with exponent α ($0 < \alpha < 1$) if and only if its reciprocal, the random variable $1/\xi$, is heavy tailed at infinity with the same exponent.

IV. ANOMALOUS STATISTICS OF THE REACTION TIME

In this section we study the anomalous statistics of the reaction time T of the RARE model. The probability distribution of the reaction time T is governed by the tail distribution function

$$\Pr(T > t) = \exp\left(-\int_0^\infty [1 - \exp\{-\eta(x)t\}]\rho(dx)\right), \quad (7)$$

with $t \ge 0$ [31]. Based on the tail distribution function of Eq. (7), a stochastic analysis detailed in Appendix A asserts that the heavy tails of the reaction time *T*, in terms of the scattering function $\rho(x)$ and the reactivity function $\eta(x)$, are characterized as follows.

(i) The reaction time *T* is heavy tailed at zero with exponent α (0 < α < 1) if and only if the scattering function $\rho(x)$ and the reactivity function $\eta(x)$ satisfy the connection

$$\rho(x) = \frac{\phi(\eta(x))}{\eta(x)^{\alpha}},\tag{8}$$

with x > 0, where the function $\phi(x)$ is slowly varying at infinity.

(ii) The reaction time *T* is heavy tailed at infinity with exponent β ($0 < \beta < 1$) if and only if the scattering function $\rho(x)$ and the reactivity function $\eta(x)$ satisfy the limit connection

$$\lim_{x \to \infty} \frac{\rho(x)}{\ln[\eta(x)]} = -\beta.$$
(9)

We note that, in principle, the result regarding the heavy tails of the reaction time *T* at infinity holds for all positive exponents $\beta > 0$ and it is not restricted to the exponent range $0 < \beta < 1$.

An alternative approach to characterize heavy tails of the reaction time *T* is based on the notion of the hazard rate, which is commonly used in applied probability and in reliability theory [41–43]. The hazard rate $h_T(t)$ of the random variable *T* at time *t* is defined by

$$h_T(t) = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \Pr(T \le t + \Delta t | T > t),$$
(10)

with t > 0. Namely, $h_T(t)$ is the realization rate of the random variable T at time t provided the random variable T did not realize up to time t. The tail distribution function of the reaction time T is attainable from its hazard rate $h_T(t)$ via the formula

$$\Pr(T > t) = \exp\left(-\int_0^t h_T(\tau)d\tau\right),\tag{11}$$

with $t \ge 0$. Consequently, it is straightforward to deduce from Eqs. (7) and (11) that the hazard rate of the reaction time *T* is given by

$$h_T(t) = \int_0^\infty \exp[-\eta(x)t]\eta(x)\rho(dx), \qquad (12)$$

with t > 0.

A stochastic analysis detailed in Appendix B asserts that the heavy tails of the reaction time *T*, in terms of its hazard rate $h_T(t)$, are characterized by the following statements. (i) The reaction time *T* is heavy tailed at zero with exponent α (0 < α < 1) if and only if its hazard rate $h_T(t)$ is regularly varying at zero with exponent $\epsilon_0 = \alpha - 1$, i.e.,

$$\lim_{l \to 0} \frac{h_T(lt)}{h_T(l)} = t^{\alpha - 1},$$
(13)

with t > 0. (ii) The reaction time T is heavy tailed at infinity with exponent β ($0 < \beta < 1$) if and only if the following limit holds:

$$\lim_{t \to \infty} th_T(t) = \beta. \tag{14}$$

We note that the results of Eqs. (13) and (14) hold true for all positive-valued random variables. Indeed, the aforementioned results characterize the heavy tails of any positive-valued random variable in terms of its hazard rate. A stochastic analysis detailed in Appendix C further shows that when applying the general hazard-rate results to the specific hazard rate of the reaction time *T*, given by Eq. (12), we re-obtain the results of Eqs. (8) and (9).

V. ANOMALOUS STATISTICS OF THE REACTION RANGE

In this section we study the anomalous statistics of the reaction range X of the RARE model. The probability distribution of the reaction range X is governed by the tail distribution function

$$\Pr(X > x) = \int_{x}^{\infty} (1 - \mathbf{E}[\exp\{-\eta(s)T\}])\rho(ds), \quad (15)$$

with $x \ge 0$ [31]. Note that the tail distribution function of the reaction range X involves the Laplace transform of the reaction time T. Based on the tail distribution function of Eq. (15), a stochastic analysis detailed in Appendix D asserts that the heavy tails of the reaction range X, in terms of the

scattering function $\rho(x)$ and the reactivity function $\eta(x)$, are characterized as follows.

(i) The reaction range X is heavy tailed at zero with exponent γ (0 < γ < 1) if and only if the scattering function $\rho(x)$ is regularly varying at zero with exponent $\epsilon_0 = \gamma$, i.e.,

$$\lim_{l \to 0} \frac{\rho(lx)}{\rho(l)} = x^{\gamma}, \tag{16}$$

with x > 0.

(ii) If the reaction time T has a finite mean then the asymptotic behavior of the tail distribution function of the reaction range X is given by

$$\Pr(X > x) \approx \mathbb{E}[T] \int_{x}^{\infty} \eta(s) \rho(ds), \qquad (17)$$

with $x \to \infty$. Consequently, in this finite-mean case we obtain that the reaction range X is heavy tailed at infinity with exponent δ ($0 < \delta < 1$) if and only if the function $\eta(x)\rho'(x)$ is regularly varying at infinity with exponent $\epsilon_{\infty} = -1 - \delta$, i.e.,

$$\lim_{l \to \infty} \frac{\eta(lx)\rho'(lx)}{\eta(l)\rho'(l)} = \frac{1}{x^{1+\delta}},$$
(18)

with x > 0.

(iii) If the reaction time T is heavy tailed at infinity with exponent β (0 < β < 1) then the asymptotic behavior of the tail distribution function of the reaction range X is given by

$$\Pr(X > x) \approx \Gamma(1 - \beta) \int_{x}^{\infty} \Pr\left(T > \frac{1}{\eta(s)}\right) \rho(ds), \quad (19)$$

with $x \to \infty$. Consequently, in this heavy-tailed case the reaction range X is heavy tailed at infinity with exponent δ $(0 < \delta < 1)$ if and only if the function $\Pr[T > 1/\eta(x)]\rho'(x)$ is regularly varying at infinity with exponent $\epsilon_{\infty} = -1 - \delta$, i.e.,

$$\lim_{l \to \infty} \frac{\Pr\left(T > \frac{1}{\eta(x)}\right)\rho'(lx)}{\Pr\left(T > \frac{1}{\eta(l)}\right)\rho'(l)} = \frac{1}{x^{1+\delta}},$$
(20)

with x > 0. We will elaborate on this case in Sec. VIII below.

We note that, in principle, the results regarding the heavy tails of the reaction range X, at both zero and infinity, hold, respectively, for all positive exponents $\gamma, \delta > 0$ (and are not restricted to exponent ranges $0 < \gamma < 1$ and $0 < \delta < 1$).

VI. POWER-LAW COUPLING

In Sec. IV we established that the reaction time *T* is heavy tailed at zero with exponent α ($0 < \alpha < 1$) if and only if the scattering function $\rho(x)$ and the reactivity function $\eta(x)$ satisfy the relation given by Eq. (8). The simplest and most straightforward way to satisfy Eq. (8) is via the power-law coupling

$$\rho(x) = \eta(x)^{-\alpha}, \quad \eta(x) = \rho(x)^{-1/\alpha}.$$
(21)

Note that this power-law coupling implies that the reactivity function $\eta(x)$ is unbounded, i.e., $\eta(0) = \infty$.

Substituting the power-law coupling of Eq. (21) into Eq. (7), we obtain a stretched-exponential tail distribution function of the reaction time *T*,

$$Pr(T > t) = \exp[-\Gamma(1 - \alpha)t^{\alpha}], \qquad (22)$$

with t > 0. Note that this stretched-exponential tail distribution function implies that the reaction time *T* has convergent moments of all orders: $\mathbf{E}[T^m] < \infty$ for all m > 0. Moreover, Eq. (22) implies that the hazard rate of the reaction time *T* admits the power-law form

$$h_T(t) = \Gamma(1 - \alpha)\alpha t^{\alpha - 1}, \qquad (23)$$

with t > 0. Note that the hazard rate appearing in Eq. (23) indeed satisfies the hazard-rate characterization of heavy tails at zero, given by Eq. (13).

Using the fact that the reaction time T has a finite mean and substituting the power-law coupling of Eq. (21) into Eq. (17), a calculation yields the asymptotic form of the tail distribution function of the reaction range X,

$$\Pr(X > x) \approx c_{\alpha} \eta(x)^{1-\alpha} = c_{\alpha} \rho(x)^{-(1-\alpha)/\alpha}, \qquad (24)$$

with $x \to \infty$, where c_{α} is a constant whose precise value is given by $c_{\alpha} = \Gamma(1/\alpha)/[(1-\alpha)\Gamma(1-\alpha)^{1/\alpha}]$.

It can be further shown that the conditional distribution of the reaction range X, given the realization of the reaction time T, is governed by the conditional tail distribution function

$$\Pr(X > x | T = t) = \int_0^{t\eta(x)} \frac{\exp(-u)u^{-\alpha}}{\Gamma(1-\alpha)} du, \qquad (25)$$

with t, x > 0. Note that the integrand appearing on the righthand side of Eq. (25) is the probability density function of the Gamma distribution with exponent $1 - \alpha$. In turn, Eq. (25) implies that the asymptotic form of the conditional tail distribution function of the reaction range X is given by

$$\Pr(X > x | T = t)$$

$$\approx \frac{t^{1-\alpha}}{\Gamma(2-\alpha)} \eta(x)^{1-\alpha} = \frac{t^{1-\alpha}}{\Gamma(2-\alpha)} \rho(x)^{-(1-\alpha)/\alpha}, \quad (26)$$

with $x \to \infty$. Note that, up to a multiplicative factor, the asymptotics of the tail distribution functions of Eqs. (24) and (26) coincide; this coincidence stems from the fact that the reaction time *T* possesses a finite mean. The derivations of Eqs. (22)–(26) are detailed in Appendix E.

VII. STRETCHED-EXPONENTIAL REACTION TIMES

In the preceding section we saw that the power-law coupling of Eq. (21) gives rise to a stretched-exponential distribution of the reaction time T. Up to a time-scale factor, a stretchedexponential distribution of the reaction time T is characterized by the tail distribution function of Eq. (22).

The stretched-exponential distribution is the prototypical phenomenological model in the physical sciences of relaxation in disordered systems [44]. This distribution was first introduced in 1854 by R. Kohlrausch to describe capacitor discharge [9] and was applied by F. Kohlrausch to describe torsional relaxation [10]. It was further applied as a description of luminescence decays [45], luminescence quenching [46], and electronic energy transfer [18,47,48]. The use of the stretched-exponential distribution became widespread following the paper of Williams and Watts on dielectric relaxation [11]; the nowadays common term stretched exponential first appeared in Ref. [49]. Additional examples and applications of the stretched-exponential distribution include Ising spin glasses [50], relaxation in disordered systems [22], electric polarization [51] and electric birefringence [52], supercooled liquids [53], molecular and electronic glasses [54], Lennard-Jones systems [55], random walks on hypercubes [56], and universality in relaxation processes [38].

The importance and the significance of the stretchedexponential distribution gives rise to the following question: When does the RARE model result in a stretched-exponential distribution of its reaction time T? In this section we answer this reverse-engineering question: We identify RARE inputs, i.e., pairs of scattering functions $\rho(x)$ and reactivity functions $\eta(x)$, that yield the stretched-exponential output of Eq. (22).

In what follows we consider the reactivity function to be unbounded, $\eta(0) = \infty$. Applying the change of variables $s = \eta(x)t$ to the integral appearing on the right-hand side of Eq. (7) yields the following representation of the tail distribution function of the reaction time *T*:

$$\Pr(T > t) = \exp\left\{-\int_0^\infty \exp(-s)\left[\rho\left(\eta^{-1}\left(\frac{s}{t}\right)\right)\right]ds\right\},\tag{27}$$

with $t \ge 0$. From this relation it is evident that the stretchedexponential tail distribution function of Eq. (22) can be obtained if and only if the function $\rho(\eta^{-1}(y))$ is a power with exponent $-\alpha$, namely,

$$\rho(\eta^{-1}(y)) = y^{-\alpha},$$
(28)

with y > 0. Consequently, applying the change of variables $y = \eta(x)$, we obtain that

$$\rho(x) = \eta(x)^{-\alpha}, \tag{29}$$

with x > 0. Thus we conclude that the distribution of its reaction time *T* is a stretched exponential if and only if the power-law coupling of Eq. (21) is satisfied.

In the preceding section we established that the powerlaw coupling of Eq. (21) results in a stretched-exponential distribution of the reaction time T. In this section we further established that the power-law coupling of Eq. (21) uniquely characterizes stretched-exponential reaction times in the RARE model.

VIII. EXPONENTIAL COUPLING

In Sec. IV we established that the reaction time *T* is heavy tailed at infinity with exponent β ($0 < \beta < 1$) if and only if the scattering function $\rho(x)$ and the reactivity function $\eta(x)$ satisfy the limit connection given by Eq. (9). The simplest and most straightforward way to satisfy Eq. (9) is via the exponential coupling

$$\rho(x) = -\beta \ln[\eta(x)], \quad \eta(x) = \exp[-\rho(x)/\beta], \quad (30)$$

with x > 0. Note that the exponential coupling of Eq. (30) implies that the reactivity function $\eta(x)$ is bounded: $\eta(0) = 1$. In what follows we consider positive exponents $\beta > 0$ and do not restrict the exponent β to the heavy-tailed range $0 < \beta < 1$.

Substituting the exponential coupling of Eq. (30) into Eq. (7), a calculation yields the following asymptotically

Paretian [38,57–59] tail distribution function of the reaction time T,

$$\Pr(T > t) \approx \left(\frac{b}{t}\right)^{\beta},$$
 (31)

with $t \to \infty$, where *b* is a constant whose precise value of is given by $\ln(b) = \int_1^\infty [\exp(-u)/u] du - \int_0^1 \{[1 - \exp(-u)]/u\} du$. Note that the asymptotically Paretian tail distribution function of Eq. (31) implies that the reaction time *T* has convergent moments ($\mathbf{E}[T^m] < \infty$) in the range $0 < m < \beta$ and has divergent moments ($\mathbf{E}[T^m] = \infty$) in the range $m \ge \beta$. Moreover, substituting the exponential coupling of Eq. (30) into Eq. (12) yields the following asymptotically harmonic (as $t \to \infty$) hazard rate of the reaction time *T*,

$$h_T(t) = \beta \frac{1 - \exp(-t)}{t},$$
(32)

with t > 0. Note that the hazard rate appearing in Eq. (32) indeed satisfies the hazard-rate characterization of heavy tails at infinity given by Eq. (14).

We now turn to the reaction range X and distinguish between three different cases regarding the range of the exponent β : (i) $\beta > 1$, (ii) $\beta = 1$, and (iii) $\beta < 1$. These different cases yield the following different asymptotic forms of the tail distribution function of the reaction range X:

$$\Pr(X > x) \approx \begin{cases} \mathbf{E}[T]\beta\eta(x) = \mathbf{E}[T]\beta \exp[-\rho(x)/\beta] & \text{for } \beta > 1\\ -b\eta(x)\ln[\eta(x)] = b\exp[-\rho(x)]\rho(x) & \text{for } \beta = 1\\ \Gamma(1-\beta)b^{\beta}\eta(x)^{\beta} = \Gamma(1-\beta)b^{\beta}\exp[-\rho(x)] & \text{for } \beta < 1, \end{cases}$$
(33)

with $x \to \infty$, where *b* is the aforementioned constant. The first and third cases are obtained, respectively, via Eqs. (17) and (19); the second case is obtained following a specific asymptotic calculation of Eq. (15).

It can be further shown that the conditional distribution of the reaction range X, given the realization of the reaction time T, is governed by the conditional tail distribution function

$$\Pr(X > x | T = t) = \frac{1 - \exp[-t\eta(x)]}{1 - \exp(-t)},$$
(34)

with x > 0. In turn, Eq. (34) implies that the asymptotic form of the conditional tail distribution function of the reaction range X is given by

$$\Pr(X > x | T = t) \approx \frac{t}{1 - \exp(-t)} \eta(x) = \frac{t \exp[-\rho(x)/\beta]}{1 - \exp(-t)},$$
(35)

with $x \to \infty$. Note that, up to a multiplicative factor, the asymptotics of the tail distribution functions of Eqs. (33) and (35) coincide if and only if the reaction time *T* possesses a fine mean (i.e., if and only if $\beta > 1$). The derivations of Eqs. (31)–(34) are detailed in Appendix F.

IX. CONCLUSION

In this paper we presented a detailed analysis of anomalous statistics in the context of the RARE model of random relaxations in random environments. In the RARE model a countable collection of excitations are randomly scattered, according to a general Poisson process, across a general metric space containing a reaction center. The excitations randomly react with the center and the reaction rates depend on the distances between the excitations and the center. Relaxation occurs upon the first reaction between an excitation and the center.

The RARE model is fully described by two parameters: (i) a scattering function quantifying the distribution of the excitations' distances from the reaction center, and (ii) a reactivity function quantifying the distance-dependent reaction rates. On the one hand, the RARE model is highly versatile as its underlying structure—the general embedding metric space, the general Poisson scattering, and the general reaction rates—allows for the accommodation of a host of settings and scenarios. On the other hand, the RARE model compresses this host of settings and scenarios to the aforementioned compact two-parameter description and is highly tractable and amenable to quantitative analysis. These features of the RARE model render it readily accessible to researchers from a span of scientific disciplines.

The outputs of the RARE model are the reaction time and the reaction range, a pair of positive-valued random variables. Anomalous statistics of these outputs are quantified by heavy tails at either zero or infinity that manifest, respectively, exceptionally high occurrence probabilities of very small and very large outliers. In this paper we analytically established a set of closed-form results determining, in terms of the RARE inputs, precisely when the RARE outputs display anomalous statistics. In particular, we showed that stretched-exponential relaxations are intimately related to power-law coupling of the RARE inputs and (asymptotic) power-law relaxations are intimately related to exponential coupling of the RARE inputs.

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APPENDIX A: HEAVY TAILS OF THE REACTION TIME

1. Heavy tails at zero

Set the function $\Psi(t)$ to be implicitly given by $Pr(T > t) = \exp[-\Psi(t)]$ with t > 0, assume that $\eta(0) = \infty$, and further set $\psi(y) = \rho(\eta^{-1}(y))$ with y > 0. Applying the change of variables $s = \eta(x)t$ to the integral appearing on the right-hand side of Eq. (7) implies that

$$\Psi(t) = \int_0^\infty \exp(-s)\psi(s/t)ds.$$
 (A1)

Note that

$$\lim_{l \to 0} \frac{\Pr(T \le lt)}{\Pr(T \le l)} = \lim_{l \to 0} \frac{1 - \Pr(T > lt)}{1 - \Pr(T > l)} = \lim_{l \to 0} \frac{1 - \exp[-\Psi(lt)]}{1 - \exp[-\Psi(l)]} = \lim_{l \to 0} \frac{\Psi(lt)}{\Psi(l)}$$
$$= \lim_{l \to 0} \frac{\int_0^\infty \exp(-s)\psi(s/lt)ds}{\int_0^\infty \exp(-s)\psi(s/l)ds} = \lim_{l \to \infty} \frac{\int_0^\infty \exp(-s)\psi(ls/t)ds}{\int_0^\infty \exp(-s)\psi(ls)ds} = \frac{\int_0^\infty \exp(-s)[\lim_{l \to \infty} \psi(ls/t)/\psi(l)]ds}{\int_0^\infty \exp(-s)[\lim_{l \to \infty} \psi(ls/t)/\psi(l)]ds}, \quad (A2)$$

where we used Eqs. (7) and (A1). From Eq. (A2) we see that the cumulative distribution function $Pr(T \le t)$ is regularly varying at zero if and only if the function $\psi(y)$ is regularly varying at infinity. Moreover, note that if the function $\psi(y)$ is regularly varying at infinity with exponent $\epsilon_{\infty} = -\alpha$ (0 < α < 1), then

$$\lim_{l \to 0} \frac{\Pr(T \le lt)}{\Pr(T \le l)} = \frac{\int_0^\infty \exp(-s)(s/t)^{-\alpha} ds}{\int_0^\infty \exp(-s)s^{-\alpha} ds} = t^\alpha \frac{\Gamma(1-\alpha)}{\Gamma(1-\alpha)},$$
(A3)

with t > 0, where $\Gamma(\cdot)$ denotes the Gamma function. Hence we conclude that the cumulative distribution function $\Pr(T \le t)$ is regularly varying at zero with exponent $\epsilon_0 = \alpha$ ($0 < \alpha < 1$) if and only if the function $\psi(y)$ is regularly varying at infinity with exponent $\epsilon_{\infty} = -\alpha$ ($0 < \alpha < 1$). In turn, the function $\psi(y)$ is regularly varying at infinity with exponent $\epsilon_{\infty} = -\alpha$ if and only if it admits the form $\psi(y) = \phi(y)/y^{\alpha}$, where the function $\phi(y)$ is slowly varying at infinity. Since $\psi(y) = \rho(\eta^{-1}(y))$, applying the change of variables $y = \eta(x)$ yields Eq. (8).

2. Heavy tails at infinity

Regarding the heavy tails of the reaction time T at infinity, Eq. (7) implies that

$$\lim_{l \to \infty} \frac{\Pr(T > lt)}{\Pr(T > l)} = \exp\left(\lim_{l \to \infty} \int_0^\infty \{\exp[-\eta(x)lt] - \exp[-\eta(x)l]\} \rho'(x) dx\right).$$
(A4)

In turn, we have

1

$$\lim_{l \to \infty} \int_{0}^{\infty} \{ \exp[-\eta(x)lt] - \exp[-\eta(x)l] \} \rho'(x) dx = \lim_{l \to \infty} \int_{0}^{\eta(0)l} [\exp(-y) - \exp(-yt)] \frac{\rho'(\eta^{-1}(y/l))}{l\eta'(\eta^{-1}(y/l))} dy = \int_{0}^{\infty} \frac{\exp(-y) - \exp(-yt)}{y} \times \left[\lim_{l \to 0} \frac{\eta(\eta^{-1}(ly))\rho'(\eta^{-1}(ly))}{\eta'(\eta^{-1}(ly))} \right] dy,$$
(A5)

where we applied the change of variables $y = \eta(x)l$ and used the assumptions of the RARE model. Note that

$$\lim_{l \to 0} \frac{\eta(\eta^{-1}(ly))\rho'(\eta^{-1}(ly))}{\eta'(\eta^{-1}(ly))} = \lim_{x \to \infty} \frac{\eta(x)\rho'(x)}{\eta'(x)} = \lim_{x \to \infty} \frac{\rho'(x)}{[\ln \eta(x)]'} = \lim_{x \to \infty} \frac{\rho(x)}{\ln[\eta(x)]},$$
(A6)

where we used the change of variables $x = \eta^{-1}(ly)$, the assumptions of the RARE model, and l'Hôpital's rule. In contrast,

$$\int_0^\infty \frac{\exp(-y) - \exp(-yt)}{y} dy$$

= $\int_0^\infty \frac{1}{y} \left(\int_1^t y \exp(-yu) du \right) dy$
= $\int_1^t \left(\int_0^\infty \exp(-yu) dy \right) du = \int_1^t \frac{1}{u} du = \ln(t), \quad (A7)$

by changing the order of the integration. From the combination of Eqs. (A5)-(A7) we conclude that

$$\lim_{l \to \infty} \frac{\Pr(T > lt)}{\Pr(T > l)} = \exp\left(\left[\lim_{x \to \infty} \frac{\rho(x)}{\ln[\eta(x)]}\right] \ln(t)\right)$$
$$= t^{\lim_{x \to \infty} \rho(x) / \ln[\eta(x)]}.$$
(A8)

Equation (A8) proves Eq. (9).

APPENDIX B: HAZARD-RATE CHARACTERIZATION OF HEAVY TAILS

1. Heavy tails at zero

Note that with l'Hôpital's rule

$$\lim_{l \to 0} \frac{\Pr(T \le lt)}{\Pr(T \le l)} = \lim_{l \to 0} \frac{\partial \Pr(T \le lt)/\partial l}{\partial \Pr(T \le l)/\partial l}$$
$$= \lim_{l \to 0} \frac{\Pr(T > lt)h_T(lt)t}{\Pr(T > l)h_T(l)} = t \lim_{l \to 0} \frac{h_T(lt)}{h_T(l)},$$
(B1)

where in the last two steps we used Eq. (11) and applied the fact that Pr(T > 0) = 1. From Eq. (B1) it is evident that the cumulative distribution function $Pr(T \le t)$ is regularly varying at zero with exponent $\epsilon_0 = \alpha$ if and only if the hazard rate $h_T(t)$ is regularly varying at zero with exponent $\epsilon_0 = \alpha - 1$.

2. Heavy tails at infinity

Equation (11) implies that

$$\lim_{l \to \infty} \frac{\Pr(T > lt)}{\Pr(T > l)} = \lim_{l \to \infty} \exp\left(-\int_{l}^{lt} h_{T}(u)du\right)$$
$$= \lim_{l \to \infty} \exp\left(-\int_{1}^{t} h_{T}(lv)ldv\right), \quad (B2)$$

where we applied the change of variables u = lv. Further transformations lead us to

$$\lim_{l \to \infty} \frac{\Pr(T > lt)}{\Pr(T > l)}$$

$$= \exp\left(-\int_{1}^{t} \frac{1}{v} \left[\lim_{l \to \infty} lvh_{T}(lv)\right] dv\right)$$

$$= \exp\left(-\left[\lim_{\tau \to \infty} \tau h_{T}(\tau)\right] \int_{1}^{t} \frac{1}{v} dv\right)$$

$$= \exp\left\{-\left[\lim_{\tau \to \infty} \tau h_{T}(\tau)\right] \ln(t)\right\} = t^{-\lim_{\tau \to \infty} \tau h_{T}(\tau)}.$$
 (B3)

Equations (B2) and (B3) show that the tail distribution function Pr(T > t) is regularly varying at infinity with exponent $\epsilon_{\infty} = -\beta$ if and only if $\beta = \lim_{\tau \to \infty} \tau h_T(\tau)$.

APPENDIX C: HEAVY TAILS OF THE REACTION TIME VIA HAZARD-RATE CHARACTERIZATION

In this section we rederive the results regarding the heavy tails of the reaction time using the hazard-rate characterization of heavy tails, given by Eqs. (13) and (14). In what follows we assume that $\eta(0) = \infty$ and set $\psi(y) = \rho(\eta^{-1}(y))$ (y > 0). Note that Eqs. (11) and (A1) imply that

$$h_T(t) = \frac{-1}{t^2} \int_0^\infty \exp(-s) s \psi'\left(\frac{s}{t}\right) ds.$$
 (C1)

Also note that $\lim_{y\to\infty} \psi(y) = 0$ and hence l'Hôpital's rule leads to

$$\lim_{l \to \infty} \frac{\psi(ly)}{\psi(l)} = y \lim_{l \to \infty} \frac{\psi'(ly)}{\psi'(l)},$$
 (C2)

with y > 0.

1. Heavy tails at zero

By virtue of Eq. (C1) we have

$$\lim_{l \to 0} \frac{h_T(lt)}{h_T(l)} = \lim_{l \to 0} \frac{-(lt)^{-2} \int_0^\infty \exp(-s)s\psi'(s/lt)ds}{-l^{-2} \int_0^\infty \exp(-s)s\psi'(s/l)ds}$$
$$= \frac{1}{t^2} \lim_{l \to \infty} \frac{\int_0^\infty \exp(-s)s\psi'(ls/t)ds}{\int_0^\infty \exp(-s)s\psi'(ls)ds}.$$
 (C3)

With Eq. (C2), we perform the following steps:

$$\lim_{l \to 0} \frac{h_T(lt)}{h_T(l)} = \frac{1}{t^2} \frac{\int_0^\infty \exp(-s)s[\lim_{l \to \infty} \psi'(ls/t)/\psi'(l)]ds}{\int_0^\infty \exp(-s)s[\lim_{l \to \infty} \psi'(ls)/\psi'(l)]ds}$$
$$= \frac{1}{t^2} \frac{\int_0^\infty \exp(-s)s\left[\frac{t}{s}\lim_{l \to \infty} \psi(ls/t)/\psi(l)\right]ds}{\int_0^\infty \exp(-s)s\left[\frac{1}{s}\lim_{l \to \infty} \psi(ls/t)/\psi(l)\right]ds}$$
$$= \frac{1}{t} \frac{\int_0^\infty \exp(-s)[\lim_{l \to \infty} \psi(ls/t)/\psi(l)]ds}{\int_0^\infty \exp(-s)[\lim_{l \to \infty} \psi(ls/t)/\psi(l)]ds}.$$
(C4)

From Eqs. (C3) and (C4) it follows that the hazard rate $h_T(t)$ is regularly varying at zero if and only if the function $\psi(y)$ is regularly varying at infinity. Moreover, note that if the function $\psi(y)$ is regularly varying at infinity with exponent $\epsilon_{\infty} = -\alpha$

 $(0 < \alpha < 1)$ then

$$\lim_{l \to 0} \frac{h_T(lt)}{h_T(l)} = \frac{1}{t} \frac{\int_0^\infty \exp(-s)(t/s)^\alpha ds}{\int_0^\infty \exp(-s)(s)^{-\alpha} ds} = t^{\alpha - 1} \frac{\Gamma(1 - \alpha)}{\Gamma(1 - \alpha)},$$
(C5)

with t > 0. We conclude that the hazard rate $h_T(t)$ is regularly varying at zero with exponent $\epsilon_0 = \alpha - 1$ ($0 < \alpha < 1$) if and only if the function $\psi(y)$ is regularly varying at infinity with exponent $\epsilon_{\infty} = -\alpha$ ($0 < \alpha < 1$). In turn, the function $\psi(y)$ is regularly varying at infinity with exponent $\epsilon_{\infty} = -\alpha$ if and only if it admits the form $\psi(y) = \phi(y)/y^{\alpha}$, where the function $\phi(y)$ is slowly varying at infinity. Since $\psi(y) = \rho(\eta^{-1}(y))$, applying the change of variables $y = \eta(x)$ yields Eq. (8).

2. Heavy tails at infinity

Based on Eq. (C1) we see that

$$\lim_{t \to \infty} th_T(t) = -\lim_{t \to \infty} \frac{1}{t} \int_0^\infty e^{-s} s\psi'(s/t) ds$$
$$= -\int_0^\infty e^{-s} \left[\lim_{t \to \infty} (s/t)\psi'(s/t)\right] ds$$
$$= -\left[\lim_{y \to \infty} y\psi'(y)\right] \int_0^\infty e^{-s} ds.$$
(C6)

Differentiating the function $\psi(y) = \rho(\eta^{-1}(y))$, applying the change of variables $y = \eta(x)$, and using l'Hôpital's rule we find

$$\lim_{t \to \infty} th_T(t) = -\lim_{y \to \infty} y \frac{\rho'(\eta^{-1}(y))}{\eta'(\eta^{-1}(y))} = -\lim_{x \to \infty} \eta(x) \frac{\rho'(x)}{\eta'(x)}$$
$$= -\lim_{x \to \infty} \frac{\rho'(x)}{[\ln \eta(x)]'} = -\lim_{x \to \infty} \frac{\rho(x)}{\ln[\eta(x)]}.$$
 (C7)

Equations (C6) and (C7) imply that

$$\lim_{t \to \infty} th_T(t) = \beta \Leftrightarrow \lim_{x \to \infty} \frac{\rho(x)}{\ln[\eta(x)]} = -\beta.$$
(C8)

APPENDIX D: HEAVY TAILS OF THE REACTION RANGE

1. Heavy tails at zero

With Eq. (15) and l'Hôpital's rule we find that

$$\lim_{l \to 0} \frac{\Pr(X \le lx)}{\Pr(X \le l)} = \lim_{l \to 0} \frac{\int_0^{lx} (1 - \mathbb{E}\{\exp[-\eta(s)T]\})\rho(ds)}{\int_0^l (1 - \mathbb{E}\{\exp[-\eta(s)T]\})\rho(ds)}$$
$$= \lim_{l \to 0} \frac{(1 - \mathbb{E}\{\exp[-\eta(lx)T]\})\rho'(lx)x}{(1 - \mathbb{E}\{\exp[-\eta(l)T]\})\rho'(l)}$$
$$= \lim_{l \to 0} \frac{1 - \mathbb{E}\{\exp[-\eta(lx)T]\}}{1 - \mathbb{E}\{\exp[-\eta(lx)T]\}} \lim_{l \to 0} \frac{\rho'(lx)x}{\rho'(l)}$$
$$= \lim_{l \to 0} \frac{\rho(lx)}{\rho(l)}.$$
(D1)

From Eq. (D1) we see that the cumulative distribution function $Pr(X \le x)$ is regularly varying at zero with exponent $\epsilon_0 = \gamma$ if and only if the scattering function $\rho(x)$ is regularly varying at zero with the same exponent.

2. Heavy tails at infinity: The case of finite-mean reaction times

For finite-mean reaction times ($\mathbf{E}[T] < \infty$), we note that

$$\lim_{x \to \infty} \frac{\Pr(X > x)}{\mathbf{E}[T] \int_x^\infty \eta(s)\rho(ds)}$$

=
$$\lim_{x \to \infty} \frac{\int_x^\infty (1 - \mathbf{E}\{\exp[-\eta(s)T]\})\rho(ds)}{\mathbf{E}[T] \int_x^\infty \eta(s)\rho(ds)}$$

=
$$\lim_{x \to \infty} \frac{(1 - \mathbf{E}\{\exp[-\eta(x)T]\})\rho'(x)}{\mathbf{E}[T]\eta(x)\rho'(x)},$$

=
$$\lim_{y \to 0} \frac{1 - \mathbf{E}[\exp(-yT)]}{\mathbf{E}[T]y} = 1,$$
 (D2)

where we used Eq. (15), l'Hôpital's rule, and the change of variables $y = \eta(x)$. Equation (D2) proves Eq. (17). Now with Eq. (17) and l'Hôpital's rule,

$$\lim_{l \to \infty} \frac{\Pr(X > lx)}{\Pr(X > l)} = \lim_{l \to \infty} \frac{\mathbf{E}[T] \int_{lx}^{\infty} \eta(s)\rho(ds)}{\mathbf{E}[T] \int_{l}^{\infty} \eta(s)\rho(ds)}$$
$$= x \lim_{l \to \infty} \frac{\eta(lx)\rho'(lx)}{\eta(l)\rho'(l)}.$$
(D3)

Equation (D3) shows that the tail distribution function Pr(X > x) is regularly varying at infinity with exponent $\epsilon_{\infty} = -\delta$ if and only if the function $\eta(x)\rho'(x)$ is regularly varying at infinity with exponent $\epsilon_{\infty} = -1 - \delta$.

3. Heavy tails at infinity: The case of heavy-tailed reaction times

Consider the case of reaction times that are heavy tailed at infinity with exponent β (0 < β < 1). We have

$$\lim_{x \to \infty} \frac{\Pr(X > x)}{\int_x^{\infty} \Pr[T > 1/\eta(s)]\rho(ds)}$$

$$= \lim_{x \to \infty} \frac{\int_x^{\infty} (1 - \mathbb{E}\{\exp[-\eta(s)T]\})\rho(ds)}{\int_x^{\infty} \Pr[T > 1/\eta(s)]\rho(ds)}$$

$$= \lim_{x \to \infty} \frac{(1 - \mathbb{E}\{\exp[-\eta(x)T]\})\rho'(x)}{\Pr[T > 1/\eta(x)]\rho'(x)},$$

$$= \lim_{y \to 0} \frac{1 - \mathbb{E}[\exp(-yT)]}{\Pr(T > 1/y)} = \Gamma(1 - \beta), \quad (D4)$$

where we used Eq. (15), l'Hôpital's rule, the change of variables $y = \eta(x)$, and the Tauberian theorem (with respect to the reaction time *T*). Equation (D4) proves Eq. (19). Now, with Eq. (19) and l'Hôpital's rule, we obtain

$$\lim_{l \to \infty} \frac{\Pr(X > lx)}{\Pr(X > l)} = \lim_{l \to \infty} \frac{\Gamma(1 - \beta) \int_{lx}^{\infty} \Pr[T > 1/\eta(s)]\rho(ds)}{\Gamma(1 - \beta) \int_{l}^{\infty} \Pr[T > 1/\eta(s)]\rho(ds)}$$
$$= x \lim_{l \to \infty} \frac{\Pr[T > 1/\eta(lx)]\rho'(lx)}{\Pr[T > 1/\eta(l)]\rho'(l)}.$$
(D5)

From Eq. (D5) we conclude that the tail distribution function Pr(X > x) is regularly varying at infinity with exponent $\epsilon_{\infty} = -\delta$ if and only if the function $Pr[T > 1/\eta(x)]\rho'(x)$ is regularly varying at infinity with exponent $\epsilon_{\infty} = -1 - \delta$.

APPENDIX E: POWER-LAW COUPLING

1. Derivation of Eqs. (22) and (23)

The power-law coupling of Eq. (21) implies that

$$\rho'(x) = -\alpha \eta(x)^{-\alpha - 1} \eta'(x).$$
(E1)

Substituting Eq. (E1) into Eq. (12) yields

$$h_T(t) = \int_0^\infty \exp[-\eta(x)t]\eta(x)[-\alpha\eta(x)^{-\alpha-1}\eta'(x)]dx$$

= $-\alpha \int_0^\infty \exp[-\eta(x)t]\eta(x)^{-\alpha}\eta'(x)dx$
= $\alpha \int_0^\infty \exp(-yt)y^{-\alpha}dy = \Gamma(1-\alpha)\alpha t^{\alpha-1}$, (E2)

with the change of variables $y = \eta(x)$. Equations (E1) and (E2) yield Eq. (23). Moreover, Eq. (E2) implies that

$$\int_0^t h_T(\tau) d\tau = \int_0^t \Gamma(1-\alpha)\alpha \tau^{\alpha-1} d\tau = \Gamma(1-\alpha)t^{\alpha}.$$
 (E3)

Substituting Eq. (E3) into Eq. (11) yields Eq. (22).

2. Derivation of Eq. (24)

Equation (E1) implies that

$$\int_{x}^{\infty} \eta(s)\rho(ds)$$

$$= \int_{x}^{\infty} \eta(s)[-\alpha\eta(s)^{-\alpha-1}\eta'(s)]ds = -\alpha \int_{x}^{\infty} \eta(s)^{-\alpha}\eta'(s)ds$$

$$= \alpha \int_{0}^{\eta(x)} u^{-\alpha}du = \frac{\alpha}{1-\alpha}\eta(x)^{1-\alpha},$$
(E4)

with the change of variables $u = \eta(s)$. Also,

$$\mathbf{E}[T] = \int_0^\infty \Pr(T > t) dt = \int_0^\infty \exp[-\Gamma(1 - \alpha)t^\alpha] dt$$
$$= \int_0^\infty \exp[-\Gamma(1 - \alpha)u] \left(\frac{u^{1/\alpha - 1}}{\alpha}\right) du$$
$$= \frac{\Gamma(1/\alpha)}{\alpha\Gamma(1 - \alpha)^{1/\alpha}},$$
(E5)

using Eq. (22) and change of variables $u = t^{\alpha}$. Substituting Eqs. (E4) and (E5) into Eq. (17) yields Eq. (24).

3. Derivation of Eqs. (25) and (26)

The conditional distribution of the reaction range X, conditioned on the realization of the reaction time T, is given by the tail distribution function

$$\Pr(X > x | T = t) = \frac{\int_x^\infty \exp[-\eta(y)t]\eta(y)\rho(dy)}{\int_0^\infty \exp[-\eta(y)t]\eta(y)\rho(dy)},$$
(E6)

with x > 0 [31]. By virtue of Eq. (E1) and the change of variables $u = \eta(y)t$ we have

$$I(x;t) := \int_{x}^{\infty} \exp[-\eta(y)t]\eta(y)\rho(dy)$$

=
$$\int_{x}^{\infty} \exp[-\eta(y)t]\eta(y)[-\alpha\eta(y)^{-\alpha-1}\eta'(y)]dy \quad (E7)$$

In particular, Eq. (E8) implies that

$$I(0;t) = \alpha t^{\alpha-1} \int_0^\infty \exp(-u)u^{-\alpha} du = \Gamma(1-\alpha)\alpha t^{\alpha-1}.$$
 (E9)

Substituting Eqs. (E8) and (E9) into Eq. (E6) yields Eq. (25). Also,

$$\lim_{x \to \infty} \frac{\int_0^{t\eta(x)} \exp(-u)u^{-\alpha} / \Gamma(1-\alpha)du}{t^{1-\alpha}\eta(x)^{1-\alpha} / \Gamma(2-\alpha)}$$
$$= \frac{\Gamma(2-\alpha)}{\Gamma(1-\alpha)} \lim_{y \to 0} \frac{\int_0^y \exp(-u)u^{-\alpha}du}{y^{1-\alpha}}$$
$$= (1-\alpha) \lim_{y \to 0} \frac{\exp(-y)y^{-\alpha}}{(1-\alpha)y^{-\alpha}} = 1,$$
(E10)

using the change of variables $y = t\eta(x)$ and l'Hôpital's rule. Equation (E10) yields Eq. (26).

APPENDIX F: EXPONENTIAL COUPLING

1. Derivation of Eqs. (31) and (32)

Note that the exponential coupling of Eq. (30) implies that $\rho'(x) = -\beta \eta'(x)\eta(x)$. Substituting this relation into Eq. (12) yields

$$h_T(t) = \int_0^\infty \exp[-\eta(x)t]\eta(x)[-\beta\eta'(x)/\eta(x)]dx$$
$$= -\beta \int_0^\infty \exp[-\eta(x)t]\eta'(x)dx = \beta \int_0^1 e^{-yt}dy$$
$$= \beta \frac{1 - \exp(-t)}{t},$$
(F1)

with the change of variables $y = \eta(x)$. Equation (F1) yields Eq. (32). Moreover, Eq. (F1) implies that

$$\int_{0}^{t} h_{T}(u) du = \beta \int_{0}^{t} \frac{1 - \exp(-u)}{u} du.$$
 (F2)

Consequently, Eqs. (11) and (F2) imply that

$$\lim_{t \to \infty} \frac{\Pr(T > t)}{t^{-\beta}} = \lim_{t \to \infty} \frac{\Pr(T > t)}{\exp[-\beta \ln(t)]} = \lim_{t \to \infty} \frac{\exp\left(-\beta \int_0^t \frac{1 - \exp(-u)}{u} du\right)}{\exp[-\beta \ln(t)]} = \lim_{t \to \infty} \exp\left[\beta \left(\int_1^t \frac{1}{u} du - \int_0^t \frac{1 - e^{-u}}{u} du\right)\right]$$
$$= \lim_{t \to \infty} \exp\left[\beta \left(\int_1^t \frac{e^{-u}}{u} du - \int_0^1 \frac{1 - e^{-u}}{u} du\right)\right] = \exp\left[\beta \left(\int_1^\infty \frac{e^{-u}}{u} du - \int_0^1 \frac{1 - e^{-u}}{u} du\right)\right].$$
(F3)

Equation (F3) yields Eq. (31).

2. Derivation of Eq. (33) for $\beta > 1$

Consider the case $\beta > 1$. Equation (F1) implies that

$$\int_{x}^{\infty} \eta(s)\rho(ds) = \int_{x}^{\infty} \eta(s)[-\beta\eta'(s)/\eta(s)]ds$$
$$= -\beta \int_{x}^{\infty} \eta'(s)ds = \beta\eta(x).$$
(F4)

In the range $\beta > 1$ the mean is finite, $\mathbf{E}[T] < \infty$, and hence substituting Eq. (F4) into Eq. (17) yields Eq. (33).

3. Derivation of Eq. (33) for $\beta < 1$

Consider the case $\beta < 1$. Equations (31) and (F1) imply that

$$\int_{x}^{\infty} \Pr[T > 1/\eta(s)]\rho(ds)$$

$$\approx \int_{x}^{\infty} [b\eta(s)]^{\beta} \left(-\beta \frac{\eta'(s)}{\eta(s)}\right) ds = -b^{\beta} \int_{x}^{\infty} \beta \eta(s)^{\beta-1} \eta'(s) ds$$

$$= b^{\beta} \int_{0}^{\eta(x)} \beta u^{\beta-1} du = b^{\beta} \eta(x)^{\beta}, \quad (F5)$$

with the change of variables $u = \eta(s)$. In the range $\beta < 1$ the reaction time is heavy tailed at infinity and hence substituting Eq. (F5) into Eq. (19) yields Eq. (33).

4. Derivation of Eq. (33) for $\beta = 1$

Consider the case $\beta = 1$. Let $f_T(t)$ denote the probability density function of the reaction time *T*. Equations (11), (31), and (32) imply that

$$f_T(t) = \Pr(T > t)h_T(t) \approx \frac{b}{t} \frac{1}{t} = \frac{b}{t^2}$$
(F6)

at $t \to \infty$. Equation (F1) implies that

$$\int_{x}^{\infty} (1 - \mathbf{E}\{\exp[-\eta(s)T]\})\rho(ds)$$
$$= \int_{x}^{\infty} (1 - \mathbf{E}\{\exp[-\eta(s)T]\}) \left(-\frac{\eta'(s)}{\eta(s)}\right) ds$$
$$= \int_{0}^{\eta(x)} \frac{1 - \mathbf{E}[\exp(-uT)]}{u} du,$$
(F7)

with the change of variables $u = \eta(s)$. Note that

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$$\lim_{x \to \infty} \frac{\int_{0}^{\eta(x)} \{1 - \mathbf{E}[\exp(-uT)]\}/udu}{-\eta(x)\ln[\eta(x)]} = \lim_{y \to 0} \frac{\int_{0}^{y} \{1 - \mathbf{E}[\exp(-uT)]\}/udu}{-y\ln(y)} = \lim_{y \to 0} \frac{\{1 - \mathbf{E}[\exp(-yT)]\}/y}{-\ln(y) - 1} = \lim_{y \to 0} \frac{1 - \mathbf{E}[\exp(-yT)]}{-y\ln(y)} = \lim_{y \to 0} \frac{\mathbf{E}[\exp(-yT)T]}{-\ln(y) - 1} = \lim_{y \to 0} \frac{\mathbf{E}[\exp(-yT)T^{2}]}{1/y} = \lim_{y \to 0} \frac{y}{0} \int_{0}^{\infty} \exp(-yt)t^{2}f_{T}(t)dt = \int_{0}^{\infty} \exp(-u)\left\{\lim_{y \to 0} \left[\left(\frac{u}{y}\right)^{2}f_{T}\left(\frac{u}{y}\right)\right]\right\}du = \int_{0}^{\infty} \exp(-u)bdu = b, \quad (F8)$$

where we used the change of variables $y = \eta(x)$, l'Hôpital's rule, and Eq. (F6). Collecting our results, we conclude that

$$\lim_{x \to \infty} \frac{\int_x^\infty (1 - \mathbf{E}\{\exp[-\eta(s)T]\})\rho(ds)}{-\eta(x)\ln[\eta(x)]} = b.$$
(F9)

Substituting Eq. (F9) into Eq. (15) yields Eq. (33).

5. Derivation of Eq. (34)

With Eq. (F1) and the change of variables $u = \eta(y)$, we have

$$I(x;t) := \int_{x}^{\infty} \exp[-\eta(y)t]\eta(y)\rho(dy) = \int_{x}^{\infty} \exp[-\eta(y)t]\eta(y)\left(-\beta\frac{\eta'(y)}{\eta(y)}\right)dy$$

= $-\beta \int_{x}^{\infty} \exp[-\eta(y)t]\eta'(y)dy = \beta \int_{0}^{t\eta(x)} \exp(-u)du = \beta\{1 - \exp[-t\eta(x)]\}.$ (F10)

Equation (F10) implies that

$$I(0;t) = \beta[1 - \exp(-t)].$$
(F11)

Substituting Eqs. (F10) and (F11) into Eq. (E6) yields Eq. (34).

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