

# Mathematical functions for the analysis of luminescence decays with underlying distributions 1. Kohlrausch decay function (stretched exponential)

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## Abstract

The Kohlrausch (stretched exponential) decay law is analyzed in detail. Analytical and approximate forms of the distribution of rate constants and related functions are obtained for this law. A simple generalization of the Kohlrausch decay law that eliminates unphysical aspects of the original form is introduced and fully characterized. General results concerning the relation between decay law and distribution of rate constants are also obtained.

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## 1. Introduction

Time-resolved luminescence spectroscopy is widely used in the physical, chemical and biological sciences to get information on the structure and dynamics of molecular, macromolecular, supramolecular, and nano systems [1]. In the simplest cases, the luminescence decay curves can be satisfactorily described by a sum of discrete exponentials and the pre-exponential factors and decay times have clear physical meaning. But distributions of decay times or rate constants must be anticipated to best account for the observed phenomena in various cases: fluorophores incorporated in micelles [2,3], cyclodextrins [3–6], rigid solutions [7], sol–gel matrices [8], polymers [9], proteins [10–12], vesicles or membranes [13–15], biological tissues [16], fluorophores adsorbed on surfaces [17], or

linked to surfaces [18–20], quenching of fluorophores in micellar solutions [21], energy transfer in assemblies of like or unlike fluorophores [22–24], etc.

In such cases, the luminescence decay can be written in the following form:

$$I(t) = \int_0^{\infty} H(k)e^{-kt} dk, \quad (1)$$

with  $I(0) = 1$ . This relation is always valid because  $H(k)$  is the inverse Laplace transform of  $I(t)$ . The function  $H(k)$ , also called the eigenvalue spectrum (of a suitable kinetic matrix), is normalized, as  $I(0) = 1$  implies that  $\int_0^{\infty} H(k) dk = 1$ . In most situations (e.g., in the absence of a rise-time), the function  $H(k)$  is nonnegative for all  $k > 0$ , and  $H(k)$  can be understood as a distribution of rate constants (strictly, a probability density function). This is the situation that will be addressed in this work.

Recovery of the distribution  $H(k)$  from the experimental decay  $I(t)$  is very difficult because this is an ill-

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conditioned problem [25]. In other words, a small change in  $I(t)$  can cause an arbitrarily large change in  $H(k)$ . The quality of the experimental data is of course of major importance. Depending on the level of precision, a decay can be fitted with a sum of two or three exponentials with satisfactory chi-squared values and weighted residuals in spite of the existence of an underlying distribution.

$H(k)$  can be recovered from decay analysis by three approaches: (i) data analysis with a theoretical model for  $H(k)$  that may be supported by Monte-Carlo simulations; (ii) data analysis by methods that do not require an a priori assumption of the distribution shape; (iii) data analysis with a mathematical function describing the distribution. The present series of papers is devoted to the third approach, but it is worth to briefly recall the main features of the first two.

Examples of the first approach can be found in theoretical investigations of the luminescence of polymer chains, where the eigenvalue spectrum was obtained using Monte-Carlo simulations of chain configuration and dynamics [26–30]. The survival probability (in this case in direct relation to the luminescence anisotropy) and the eigenvalue spectrum of finite and closed one-dimensional chains of molecules with nearest-neighbour interaction were investigated [26–30]. A wide range of systems was also considered in [23]. All cited papers show that the eigenvalue spectrum gives important information on the dynamics of energy transfer in condensed matter.

In the absence of a physical model, the best way to recover the eigenvalue spectrum appears to be, at first sight, the second approach, i.e., the use of methods without assumption of the distribution shape such as the maximum entropy method or other numerical approaches [31,32]. However, in these calculations the obtained eigenvalue spectrum can be extremely sensitive to data quality and truncation effects [25]. Because of the ill-conditioned nature of the lifetime distribution analysis, instability of the recovered distribution can be observed from repeated experiments under exactly the same conditions, even when data are of excellent quality [17]. A set of physically plausible results can be obtained after a regularization technique is employed in the data reduction [17].

In the third approach, a mathematical function that is expected to best describe the distribution is used. In many studies, e.g., biophysics experiments, the eigenvalue spectrum is often approximated by specific empirical functions with a continuous distribution of rate constants, e.g., Lorentzian or Gaussian functions [33,34].

In the first paper of this series, we discuss the distribution of rate constants of the stretched exponential (or Kohlrausch) function, written as

$$I(t) = \exp \left[ -(t/\tau_0)^\beta \right], \quad (2)$$

where  $0 < \beta \leq 1$ , and  $\tau_0$  is a parameter with the dimensions of time. This simple and relatively flexible function has been indeed successfully used in various fields, as recalled in the next section, and it deserves thus special attention.

## 2. Stretched exponential function in decay data analysis

The first use of the stretched exponential function to describe the time evolution of a nonequilibrium quantity is usually credited (with references almost invariably incorrect) to Rudolph Kohlrausch (1809–1858), who in 1854 [35] applied it to the discharge of a capacitor, after concluding that a simple exponential of time was inadequate [36]. The rediscovery of the stretched exponential relaxation function by Williams and Watts in 1970, who introduced it in the field of dielectrics [37], while certainly important, is in our opinion insufficient to warrant the association of these names to the general law, as is sometimes found in the literature (KWW law), especially when luminescence is concerned. In fact, in this field the stretched exponential has long been in use, namely to describe decays in the presence of energy transfer [22].

In studies of the relaxation of complex systems, the Kohlrausch function is frequently used as a purely empirical decay law (see below), although there are theoretical arguments to justify its common occurrence. In the field of molecular luminescence, Eq. (2) has firm grounds on several models of luminescence quenching, namely diffusion-controlled contact quenching [38], where  $\beta = 1/2$ , and diffusionless resonance energy transfer by the dipole–dipole mechanism, with  $\beta = 1/6$ ,  $1/3$  and  $1/2$  for one-, two- and three-dimensional systems, respectively [22]. Other rational values of  $\beta$  are obtained for different multipole interactions, e.g.,  $\beta = 3/8$ ,  $3/10$ , for the dipole–quadrupole and quadrupole–quadrupole mechanisms in three-dimensions [39,40]. In Huber's approximation, energy transport as measured by fluorescence anisotropy shows the same time-dependence as direct energy transfer [23,41,42], and is characterized by the same values of  $\beta$ .

Luminescence decays in fractals in the presence of resonance energy transfer (RET) are also described by the Kohlrausch function [43–45] with  $\beta = d/s$ , where  $d$  is the fractal dimension and  $s$  depends on the RET mechanism, being equal to 6, 8, or 10 for dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively.

RET between donor and acceptor chromophores attached to a polymer chain has been widely used as a tool for studying polymer structure and dynamics. Theory shows [26–30,46–49] that the kinetics of donor luminescence quenching and the kinetics of depolarization of luminescence in polymer chains exhibit a Kohlrausch

time-dependence, where the parameter  $\beta$  of Eq. (2) depends on the mechanism of RET, the type of chromophore attachment (to the ends of the polymer chain or randomly distributed along the chain), and on the model of polymer chain considered (Gaussian or self-avoiding chain).

The Kohlrausch function is also found to apply to some luminescence decays of disordered [50] and ordered [51] inorganic solids, and of semiconductor nanoclusters [52].

The Kohlrausch decay law is convenient as a fitting function, even in the absence of a model, given that it allows gauging in simple way deviations to the “canonical” single exponential behaviour through the parameter  $\beta$ . Stretched exponentials were used for instance to analyze the fluorescence decay of fluorophores incorporated in a sol–gel matrix [8] and of fluorophores covalently bound to silica surfaces [18] or alumina surfaces [20]. The Kohlrausch decay function was recently used in the analysis of single-molecule fluorescence [9] and in the fluorescence lifetime imaging of biological tissues [16].

It is striking that a variety of microscopic mechanisms can give rise to stretched exponential relaxation although the origin of this behaviour is not fully understood. In this regard, dynamical models for stretched exponential relaxation developed by several authors [51,53–55] are conceptually interesting.

### 3. General considerations regarding distributions of rate constants

#### 3.1. Characteristic parameters

Let us consider the following phenomenological equation restricted to the first order:

$$\frac{dN}{dt} = -k(t)N, \quad (3)$$

where  $N$  is the number of luminophores (in a given volume) after delta excitation, and  $k$  is the rate constant with possible time dependence. That being the case, it will be called a rate coefficient.

The luminescence intensity is assumed to be proportional to  $N$ , the proportionality constant including the radiative rate constant. The normalized decay law  $I(t)$  is then simply

$$I(t) = \frac{N(t)}{N_0}, \quad (4)$$

$k(t)$  is thus given by

$$k(t) = -\frac{d \ln I(t)}{dt}, \quad (5)$$

and the decay can be written as

$$I(t) = \exp\left(-\int_0^t k(u) du\right). \quad (6)$$

Using Eq. (1), that expresses a luminescence decay with an underlying distribution  $H(k)$ , the time-dependent rate coefficient becomes

$$k(t) = \frac{\int_0^\infty kH(k)e^{-kt} dk}{\int_0^\infty H(k)e^{-kt} dk}. \quad (7)$$

This time-dependent rate coefficient can in principle exhibit a complex time dependence, but for monotonic decays there are only three important cases: exponential decay, when  $k(t)$  is constant; super-exponential decay, when  $k(t)$  increases with time; and sub-exponential decay, when  $k(t)$  decreases with time.

Several average quantities that can be obtained from the decay law need to be carefully specified at the outset. The most direct one, the average decay time, is defined by

$$\bar{\tau} = \frac{\int_0^\infty tI(t) dt}{\int_0^\infty I(t) dt}. \quad (8)$$

Similarly, the time-averaged rate constant is

$$\bar{k} = \frac{\int_0^\infty k(t)I(t) dt}{\int_0^\infty I(t) dt} = \frac{1}{\int_0^\infty I(t) dt}. \quad (9)$$

The convention of a bar (e.g.,  $\bar{k}$ ) for the time average, and of brackets (e.g.,  $\langle k \rangle$ ) for the distribution (“ensemble”) average will be followed throughout.

Instead of a distribution of rate constants, a distribution of time constants is also sometimes defined, such that, instead of Eq. (1), the decay is written as

$$I(t) = \int_0^\infty f(\tau)e^{-t/\tau} d\tau, \quad (10)$$

the relation between  $f(\tau)$  and  $H(k)$  being

$$f(\tau) = \frac{1}{\tau^2}H\left(\frac{1}{\tau}\right). \quad (11)$$

An average time constant can now be defined,

$$\langle \tau \rangle = \int_0^\infty \tau f(\tau) d\tau = \int_0^\infty I(t) dt, \quad (12)$$

hence

$$\langle \tau \rangle = \frac{1}{\bar{k}} = \left\langle \frac{1}{k} \right\rangle. \quad (13)$$

The average time constant  $\langle \tau \rangle$  and the average decay time  $\bar{\tau}$  are not identical in general, and are related by

$$\bar{\tau} = \frac{\langle \tau^2 \rangle}{\langle \tau \rangle}. \quad (14)$$

On the other hand, the average rate constant is

$$\langle k \rangle = \int_0^\infty kH(k) dk = -I'(0) = k(0), \quad (15)$$

and therefore

$$\langle k \rangle = \left\langle \frac{1}{\tau} \right\rangle, \quad (16)$$

while

$$\bar{\tau} = \frac{\left\langle \frac{1}{k^2} \right\rangle}{\left\langle \frac{1}{k} \right\rangle}. \quad (17)$$

### 3.2. Influence of the intrinsic decay

In many cases (e.g., energy transfer), the full decay expression contains as a multiplicative factor the intrinsic exponential decay,

$$I(t) = \exp\left(-\frac{t}{\tau_0}\right) \left( \int_0^\infty \exp(-kt) H(k) dk \right). \quad (18)$$

In such a situation, the full rate constant distribution is simply the shifted  $H(k)$ ,

$$H_t(k) = H(k) \otimes \delta\left(k - \frac{1}{\tau_0}\right) = \begin{cases} 0 & \text{if } k < \frac{1}{\tau_0}, \\ H\left(k - \frac{1}{\tau_0}\right) & \text{otherwise,} \end{cases} \quad (19)$$

where  $\otimes$  stands for the convolution between two functions.

Also, in this case the condition that the integral of the decay  $\int_0^\infty I(t) dt$  must be finite applies to the decay as a whole, but not to the reduced decay where the “natural” decay has been removed. One thus encounters decay laws where the integral diverges ( $\langle \tau \rangle$  is infinite), because they must always be multiplied by the natural decay to give the total decay, and represent in fact only additional decay pathways. The same applies to anisotropy decays,  $r(t)$ , since there is no need for normalization (in the sense of  $\int_0^\infty r(t) dt = 1$ ) in this case.

### 3.3. The transform ladder

The distribution of rate constants  $H(k)$  is not the only relevant transform for the study of luminescence decays. One can in fact consider the following sequence of functions, connected by successive Laplace and inverse Laplace transforms:

$$G(s) \xrightleftharpoons[\varphi^{-1}]{\varphi} H(k) \xrightleftharpoons[\varphi^{-1}]{\varphi} I(t) \xrightleftharpoons[\varphi^{-1}]{\varphi} J(\omega).$$

The functions  $H(k)$  and  $I(t)$  have already been discussed. The function  $J(\omega)$ , which occurs in the response to a harmonic excitation, is central in the luminescence technique of phase-modulation [1,56], and also in dielectric relaxation theory [57], but will not be further developed here.

The function  $G(s)$  was introduced in [24] for the analysis of anisotropy decays with long tails. It is not a den-

sity function, because it is not usually normalized ( $\int_0^\infty G(s) ds = H(0)$ ) and because it can take negative values, e.g., when  $H(0) = 0$ . In some cases, like that of an exponential decay, it cannot even be defined (it would be the inverse Laplace transform of the delta function). Since  $H(k)$  is normalized, one has, when  $G(s)$  exists,

$$\int_0^\infty \frac{G(s)}{s} ds = 1. \quad (20)$$

Also

$$\langle k \rangle = \int_0^\infty \frac{G(s)}{s^2} ds. \quad (21)$$

The maximum in the  $H(k)$  distribution (if it exists) is sometimes easier to obtain numerically from  $G(s)$ ,

$$\frac{dH}{dk} = 0 \Rightarrow \int_0^\infty e^{-ks} s G(s) ds = 0. \quad (22)$$

This also shows that in such a case  $G(s)$  takes necessarily both positive and negative values. The main interest of  $G(s)$  is nevertheless that  $I(t)$  can be written as a double Laplace transform [24], formerly called by some authors the Stieltjes transform [58,59],

$$I(t) = \int_0^\infty \frac{G(s)}{t+s} ds, \quad (23)$$

whenever  $G(s)$  exists. This representation of the decay, alternative to Eq. (1), suggests that in some cases the decay is well represented by a few terms of the discretization of Eq. (23), in an analogous way to what happens with Eq. (1) (sum of exponentials), i.e., when instead of Eq. (23) the decay is approximated by

$$I(t) = \sum_i \frac{a_i}{t + \tau_i}. \quad (24)$$

This representation is advantageous whenever the distribution of rate constants is broad and cannot be emulated by a few exponentials, while a few hyperbolae suffice to construct a broad distribution of rate constants [24], as each hyperbola corresponds by itself to an exponential distribution, and it is therefore the distribution  $H(k)$  that is reconstructed with a sum of exponentials,

$$H(k) = \sum_i a_i \exp(-k\tau_i), \quad (25)$$

while  $G(s)$  is approximated by

$$G(s) = \sum_i a_i \delta(s - \tau_i). \quad (26)$$

#### 4. Kohlrausch (stretched exponential) decay function

A time-dependent rate coefficient  $k(t)$  can be defined for the Kohlrausch decay law, Eq. (2), by using Eq. (5):

$$k_1(t) = \frac{\beta}{\tau_0} \left( \frac{t}{\tau_0} \right)^{\beta-1}, \quad (27)$$

where  $0 < \beta \leq 1$ . After Williams and Watts [37], the Kohlrausch decay law is often called the “slower-than-exponential” (with respect to an exponential of lifetime  $\tau_0$ ) function. Although sub-exponential, this is however somewhat of a misnomer, as a most characteristic aspect of the function is precisely the existence of two regimes: a faster-than-exponential (with respect to an exponential of lifetime  $\tau_0$  initial decay (indeed, the rate constant is infinite for  $t = 0$ ), and a slower-than-exponential decay (with respect to an exponential of lifetime  $\tau_0$ ) for times longer than  $\tau_0$ . These two regimes are very marked for small  $\beta$ , but become indistinct as  $\beta \rightarrow 1$ , see Fig. 1.

The initial part of the Kohlrausch law ( $\beta < 1$ ), resulting from a Lévy distribution of rate constants (see below), with its characteristic long tail, is sometimes “swept under the carpet” by using a  $\tau_0$  smaller than the shortest time of observation, and multiplying the decay law by a factor higher than 1, a procedure that obviously invalidates its correct normalization, but has no other apparent consequences (see however the discussion below).

The slowing down of the decay rate can be shown explicitly by the time-dependent rate coefficient, Eq. (27). As mentioned, this rate coefficient is initially infinite, which is an unphysical result. In the case of diffusion-controlled quenching of fluorescence, this only happens with the Smoluchowski model [60], for which an infinite quenching rate constant at contact is implicitly assumed. The problem no longer exists in the Collins–Kimball model, for instance [38,60]. In the field of energy transfer in homogeneous media, an initially infi-

nite rate coefficient arises when point particles are assumed [22]. If a distance of closest approach is postulated, then the initial part of the decay becomes exponential, and the decay obeys a stretched exponential only for longer times [61].

The average rate constant  $\langle k \rangle = k(0)$  is infinite for the Kohlrausch decay law. In general, the time-dependent rate coefficient cannot be infinite; hence this aspect results from the approximate nature of the physical model used, as mentioned for the collisional quenching and energy transfer phenomena.

The necessarily approximate nature of the stretched exponential decay function, owing to its unphysical short-time behaviour, was also noted in the field of dielectrics [57].

The average decay time is

$$\bar{\tau} = \tau_0 \frac{\Gamma(2/\beta)}{\Gamma(1/\beta)}, \quad (28)$$

whereas the average time constant is

$$\langle \tau \rangle = \frac{1}{\bar{k}} = \tau_0 \Gamma\left(1 + \frac{1}{\beta}\right). \quad (29)$$

The determination of  $H(k)$  for a given  $I(t)$  amounts to the computation of the respective inverse Laplace transform. In the case of the Kohlrausch function, Eq. (2), the calculation can be performed with the general inversion formula (Bromwich integral), as detailed in Appendix A. The result, first obtained by Pollard [62], is

$$H_\beta(k) = \frac{\tau_0}{\pi} \int_0^\infty \exp(-k\tau_0 u) \times \exp[-u^\beta \cos(\beta\pi)] \sin[u^\beta \sin(\beta\pi)] du, \quad (30)$$

an equivalent integral being (Appendix A)

$$H_\beta(k) = \frac{\tau_0}{\pi} \int_0^\infty \exp\left[-u^\beta \cos\left(\frac{\beta\pi}{2}\right)\right] \cos\left[u^\beta \sin\left(\frac{\beta\pi}{2}\right) - k\tau_0 u\right] du. \quad (31)$$

These integral forms are complementary: Eq. (30) is difficult to compute numerically for small values of  $k$ , owing to the rapid oscillations of the integrand when  $k$  is small, while Eq. (31) is difficult to compute for large values of  $k$ , again because of the rapid oscillations of the integrand when  $k$  is large. For  $\beta = 1$ , one has of course  $H_1(k) = \delta(k - 1/\tau_0)$ . For  $\beta \neq 1$ ,  $H_\beta(k)$  can be expressed in terms of elementary functions only for  $\beta = 1/2$  [62,63],

$$H_{1/2}(k) = \frac{\tau_0}{2\sqrt{\pi}(k\tau_0)^{3/2}} \exp\left(-\frac{1}{4k\tau_0}\right). \quad (32)$$

A form for  $\beta = 1/4$  displaying the asymptotic behavior for large  $k$  was recently obtained [64].

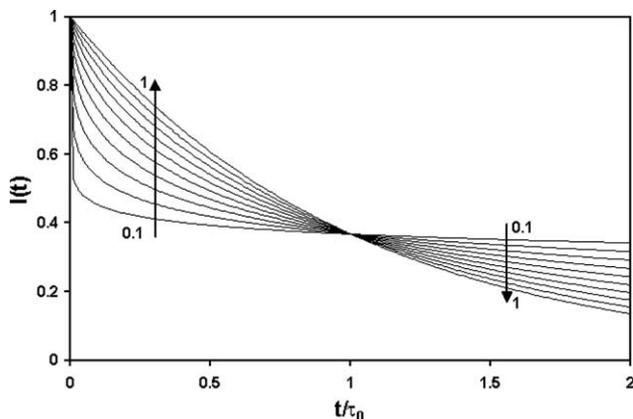


Fig. 1. The Kohlrausch (stretched exponential) decay law for several values of  $\beta$  (0.1, 0.2, ..., 0.9, 1). The decay is faster than that of an ordinary exponential ( $\beta = 1$ ) for  $t < \tau_0$ , and slower afterwards.

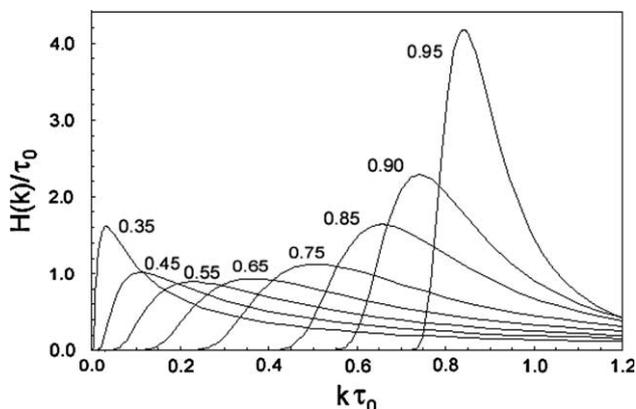


Fig. 2. Distribution of rate constants (probability density function) for the Kohlrausch decay law obtained by numerical integration of Eqs. (30) and (31). The number next to each curve is the respective  $\beta$ .

$$H_{1/4}(k) = \frac{\tau_0}{8\pi(k\tau_0)^{5/4}} \int_0^\infty u^{-3/4} e^{-\frac{1}{\sqrt{k\tau_0}u} + u} du. \quad (33)$$

It appears that for any rational value of  $\beta$ ,  $H_\beta(k)$  can be expressed in terms of confluent hypergeometric functions (results for  $\beta = 1/3$  and  $2/3$  are known; the authors have checked a number of other cases with the *Mathematica* package). A general solution can be given in terms of Fox functions [65].

The distribution  $H_\beta(k)$  is shown in Fig. 2 for several values of  $\beta$ .

In [66], a convergent power series was obtained for  $H_\beta(k)$

$$H_\beta(k) = \frac{\tau_0}{\pi} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{(k\tau_0)^{-(1+n\beta)}}{n!} \Gamma(1+n\beta) \sin(n\beta\pi). \quad (34)$$

It can be seen that the asymptotic form of  $H_\beta(k)$  is

$$H_\beta(k) = \frac{\tau_0}{\pi} \Gamma(1+\beta) \sin(\beta\pi) \frac{1}{(k\tau_0)^{(1+\beta)}}. \quad (35)$$

While the series is convergent for all  $k$ , in practice the terms can increase in magnitude to a tremendous extent and nearly completely cancel each other to yield a small number. Therefore, the asymptotic form is useful only for very large values of  $k$ . Lindsey and Patterson [67] used Eqs. (30) and (34) for the first time in the description of relaxation phenomena.

The function  $G_\beta(s)$  can be obtained either directly from the integrand of Eq. (30), or by term wise inversion of Eq. (34). The result is

$$G_\beta(s) = \frac{1}{2\pi} \text{Im} \left\{ \exp \left[ -e^{-i\beta\pi} \left( \frac{s}{\tau_0} \right)^\beta \right] - \exp \left[ -e^{i\beta\pi} \left( \frac{s}{\tau_0} \right)^\beta \right] \right\} + \frac{1}{\pi} \exp \left[ -\left( \frac{s}{\tau_0} \right)^\beta \cos(\beta\pi) \right] \sin \left[ \left( \frac{s}{\tau_0} \right)^\beta \sin(\beta\pi) \right]. \quad (36)$$

This function has an oscillatory behavior, controlled by the argument of the exponential, which is in turn defined by the value of  $\beta$ , see Fig. 3. For  $\beta = 1/2$ , the amplitude of the oscillations is constant; for  $\beta < 1/2$ , the amplitude of the oscillations decreases with  $s$ ; finally, for  $\beta > 1/2$ , the amplitude of the oscillations increases with  $s$ .

We present here a relatively simple and yet very accurate numerical equation for  $H_\beta(k)$  (see Appendix B for its derivation),

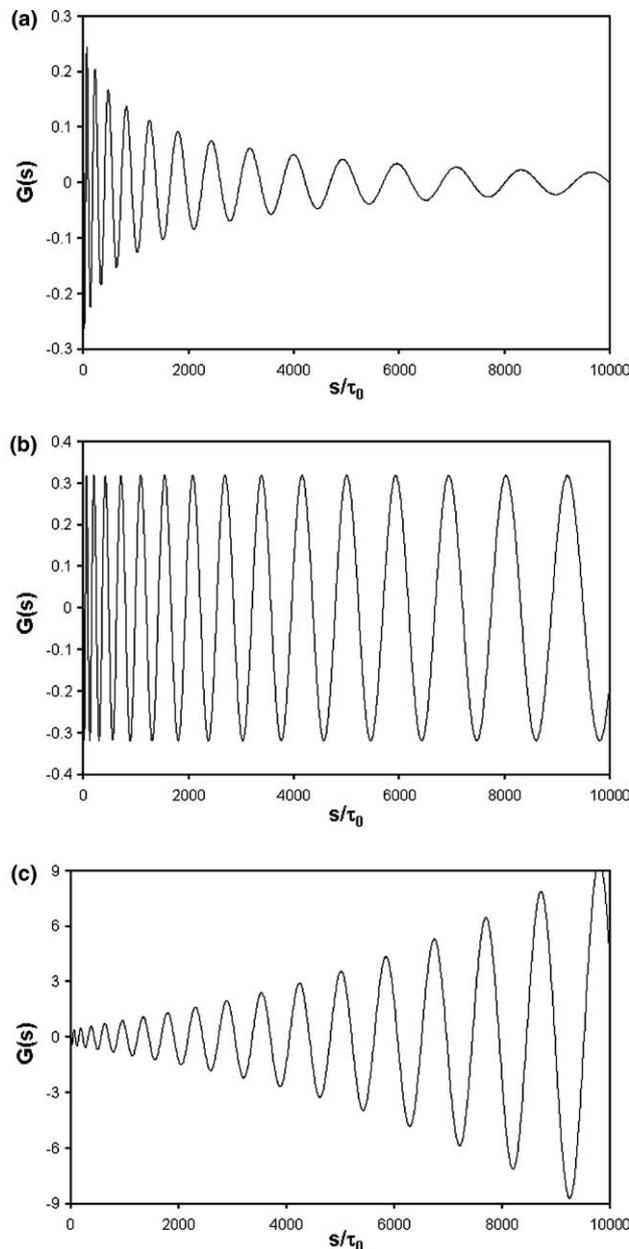


Fig. 3. Function  $G_\beta(s)$  for the Kohlrausch decay law, given by Eq. (36). Parameter  $\beta$  takes the values 0.49 (a), 0.50 (b), and 0.51 (c).

$$H_{\beta}(k) = \tau_0 \frac{B}{(k\tau_0)^{(1-\beta/2)/(1-\beta)}} \times \exp \left[ -\frac{(1-\beta)\beta^{\beta/(1-\beta)}}{(k\tau_0)^{\beta/(1-\beta)}} \right] f(k), \quad (37)$$

where the auxiliary function,  $f(k)$ , is

$$f(k) = \begin{cases} 1/[1 + C(k\tau_0)^{\delta}], & \delta = \beta(0.5 - \beta)/(1 - \beta), \\ \beta \leq 0.5, \\ 1 + C(k\tau_0)^{\delta}, & \delta = \beta(\beta - 0.5)/(1 - \beta), \\ \beta > 0.5. \end{cases} \quad (38)$$

and the parameters  $B$  and  $C$ , which are functions of  $\beta$ , are given in Table 1 for  $\beta = 0.1, 0.2, \dots, 0.9$ . For other values of  $\beta$  parameters  $B$  and  $C$  can be obtained by interpolation.

It is worth mentioning that the Kohlrausch decay law is the Laplace transform of the Lévy one-sided distribution  $L_{\beta,1}$ , i.e.,  $H_{\beta}(k)$  is a Lévy stable distribution [68].

Interestingly, if one takes  $\beta > 1$  in the Kohlrausch decay, which is the compressed exponential case, it is found that  $k(t)$  increases with time, starting from zero, and the decay is super-exponential, hence  $H_{\beta}(k)$  is no longer a distribution function. The compressed exponential function appears to apply to protein folding kinetics [69].

## 5. Modified Kohlrausch decay function

### 5.1. Origin of times at $\tau_0$

The problems associated with the undesirable short-time behavior of the Kohlrausch function (infinite initial rate, faster-than-exponential decay for short times) can be eliminated in a simple way. Given that the decay is faster than an exponential with lifetime  $\tau_0$  only up to  $t = \tau_0$ , we merely shift the origin of times to this point, and then renormalize the decay, which becomes,

$$I(t) = \exp \left[ 1 - \left( 1 + \frac{t}{\tau_0} \right)^{\beta} \right]. \quad (39)$$

The time-dependent rate coefficient of the generalized Kohlrausch function is

$$k(t) = \frac{\beta}{\tau_0} \left( 1 + \frac{t}{\tau_0} \right)^{\beta-1}, \quad (40)$$

and therefore it is now finite for all times. For short times, the decay is exponential (lifetime  $\tau_0/\beta$ ).

The parameters of the generalized Kohlrausch function are:

$$\langle k \rangle = k(0) = \frac{\beta}{\tau_0}, \quad (41)$$

$$\langle \tau \rangle = \frac{1}{\bar{k}} = \frac{e}{\beta} \Gamma \left( \frac{1}{\beta}, 1 \right) \tau_0, \quad (42)$$

$$\bar{\tau} = \left[ \frac{\Gamma \left( \frac{2}{\beta}, 1 \right)}{\Gamma \left( \frac{1}{\beta}, 1 \right)} - 1 \right] \tau_0, \quad (43)$$

where  $\Gamma(x,a)$  is the incomplete gamma function. The average decay time is not much affected by the modification, as it averages over all the decay, that usually differs only in a small, initial part, but the same does not happen to the other three parameters, that have in general values quite different from those of the original Kohlrausch decay (this is obvious for  $\langle k \rangle$ ). For instance if  $\beta = 0.1$ , Eq. (12) gives  $\langle \tau \rangle = 9.9 \times 10^6 \tau_0$ , while Eq. (42) gives  $\langle \tau \rangle = 3.6 \times 10^6 \tau_0$ , owing to a much larger concentration of the distribution in the short lifetimes, needed to account for the fast initial decay.

The decay law can be rewritten as

$$I(t) = \exp \left[ 1 - \left( 1 + \frac{\langle k \rangle t}{\beta} \right)^{\beta} \right]. \quad (44)$$

An interesting aspect of the generalized Kohlrausch function is that parameter  $\beta$  can also be higher than 1 to produce super-exponential decays with a simple limiting form,

$$\lim_{\beta \rightarrow \infty} I(t) = \exp[1 - e^{(k)t}], \quad (45)$$

see Fig. 4.

The function  $H_{\infty}(k)$  for this decay law is

$$H_{\infty}(k) = \frac{\tau_0 e}{\pi} \int_0^{\infty} e^{-\cos u} \cos(k\tau_0 u - \sin u) du, \quad (46)$$

and has the form of damped oscillations, taking both positive and negative values and therefore, as expected,  $H_{\infty}(k)$  is not a distribution function.

Table 1  
Exponent  $\delta$  and parameters  $B$  and  $C$  in Eqs. (37) and (38)

$\beta$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$\delta$	2/45	3/40	3/35	1/15	0	3/20	7/15	6/5	18/5
$B$	0.145	0.197	0.243	0.285	0.382	0.306	0.360	0.435	0.700
$C$	0.89	0.50	0.35	0.25	0	0.13	0.22	0.4015	0.33

For  $\beta = 0.5$ , the coefficients are exact:  $B = 1/(2\pi^{1/2})$  and  $C = 0$ . For  $\beta = 0.8$ , coefficient  $C$  is calculated as  $C = (1/\pi)\sin(\beta\pi)\Gamma(1 + \beta)/B$  to get the correct asymptote for  $H(k)$ .

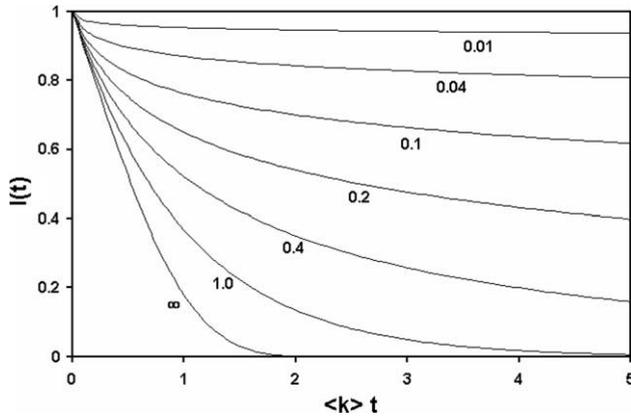


Fig. 4. The modified Kohlrausch decay law, Eq. (44), for several values of  $\beta$ . The number next to each curve is the respective  $\beta$ .

The parameters of this limit decay law are:

$$\langle \tau \rangle = \frac{1}{k} = \frac{e}{\langle k \rangle} \Gamma(0, 1) = \frac{0.596}{\langle k \rangle}, \quad (47)$$

$$\bar{\tau} = \lim_{\beta \rightarrow \infty} \left[ \frac{\Gamma\left(\frac{2}{\beta}, 1\right)}{\Gamma\left(\frac{1}{\beta}, 1\right)} - 1 \right] \frac{\beta}{\langle k \rangle} = \frac{0.446}{\langle k \rangle}. \quad (48)$$

For  $\beta > 1$ ,  $k(t)$  increases with time, starting from  $\beta/\tau_0$ , and the decay is super-exponential.

The distribution of rate constants for the modified Kohlrausch decay law  $H_\beta^m(k)$  ( $\beta < 1$ ), see Fig. 5, is easily obtained as

$$H_\beta^m(k) = \exp(1 - k\tau_0) H_\beta(k), \quad (49)$$

where  $H_\beta(k)$  is the distribution for the original Kohlrausch decay law. This seemingly small modification has a major consequence: The distribution ceased to be of the Lévy type, as the long tail (responsible for the fast initial decay) disappeared, owing to exponential damping. Indeed, the asymptotic form is now

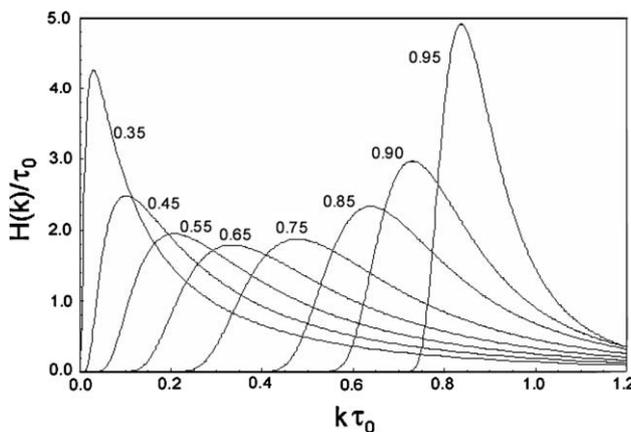


Fig. 5. Distribution of rate constants (probability density function) for the modified Kohlrausch decay law, obtained by numerical integration of Eq. (49). The number next to each curve is the respective  $\beta$ .

$$H_\beta^m(k) = \frac{\tau_0 e}{\pi} \Gamma(1 + \beta) \sin(\beta\pi) \frac{e^{-k\tau_0}}{(k\tau_0)^{1+\beta}}, \quad (50)$$

compare Eq. (34). The corresponding  $G_\beta^m(s)$  function is given by

$$G_\beta^m(s) = \begin{cases} 0 & \text{if } s < \tau_0, \\ \frac{1}{\pi} \exp \left[ 1 - \left( \frac{s}{\tau_0} - 1 \right)^\beta \cos(\beta\pi) \right] & \\ \times \sin \left[ \left( \frac{s}{\tau_0} - 1 \right)^\beta \sin(\beta\pi) \right] & \text{otherwise.} \end{cases} \quad (51)$$

In conclusion, the “slowest-than-exponential” character is preserved (for  $\beta < 1$ ) in the modified Kohlrausch function, and only the unwanted “faster-than-exponential” initial part of the original Kohlrausch function is suppressed. Additionally, the decay can be converted into a super-exponential one by taking  $\beta > 1$ . For large  $\beta$ , it becomes of the exponential of an exponential type.

### 5.2. Origin of times at $t_0 > \tau_0$

The choice of  $t = \tau_0$  as the origin of times for the modified stretched exponential is a natural one. However, any time larger than  $\tau_0$  can also be selected, and may prove to be a better choice in case of experimental fits. If this time is denoted by  $t_0$ , and if a dimensionless parameter  $\alpha$  is defined,

$$\alpha = \frac{t_0}{\tau_0}, \quad (52)$$

then

$$I(t) = \exp \left[ \alpha^\beta - \left( \alpha + \frac{t}{\tau_0} \right)^\beta \right], \quad (53)$$

and the time-dependent rate coefficient and distribution of rate constants are

$$k(t) = \frac{\beta}{\tau_0} \left( \alpha + \frac{t}{\tau_0} \right)^{\beta-1}, \quad (54)$$

$$H_\beta^m(k) = \exp(\alpha^\beta - \alpha k \tau_0) H_\beta(k). \quad (55)$$

The decay is thus initially single exponential with a lifetime

$$\tau = \tau_0 \frac{\alpha^{1-\beta}}{\beta}, \quad (56)$$

and the decay can be rewritten

$$I(t) = \exp \left\{ \alpha^\beta \left[ 1 - \left( 1 + \frac{1}{\beta \alpha^\beta \tau} \right)^\beta \right] \right\}. \quad (57)$$

For large  $\alpha$ , the decay is single exponential for most of the time window, and becomes of the stretched exponential type only for very long times. As can be seen from Eq. (55), an increase in parameter  $\alpha$  narrows and shifts

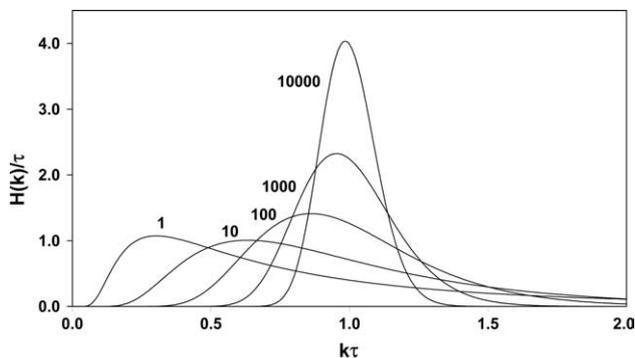


Fig. 6. Distribution of rate constants (probability density function) for the modified Kohlrausch decay law, Eq. (55), with  $\beta = 0.5$  and fixed  $\tau$  (Eq. (56)). The number next to each curve is the respective  $\alpha$ .

the distribution of rate constants to the left. For very large  $\alpha$ , an almost pure exponential decay is recovered,

$$H_{\beta}^m(k) \simeq \delta\left(k - \frac{\beta}{\alpha^{1-\beta}\tau_0}\right). \quad (58)$$

This behaviour is shown in Fig. 6 for  $\beta = 1/2$ .

## 6. Conclusions

In this paper, the Kohlrausch (stretched exponential) decay law was analyzed in detail. This decay law is known to describe well the luminescence decay of several classes of systems, and has in some cases a strong theoretical basis. Analytical and approximate forms of the distribution of rate constants of the Kohlrausch law were given, including several new results. Computation of the distribution of rate constants  $H(k)$  by means of Eqs. (30), (31) or (37) is a simple and reliable procedure, dispensing the use of numerical inversion methods subject to considerable error. A simple and flexible generalization of the Kohlrausch decay law that eliminates shortcomings of the original form was introduced. General results concerning the relation between decay law and distribution of rate constants were also obtained.

## Appendix A. Calculation of Eq. (31)

For simplicity, we make the change of variable  $T = t/\tau_0$  in Eq. (2), which becomes

$$I(T) = \exp(-T^{\beta}). \quad (A.1)$$

The inverse Laplace transform of the stretched exponential is obtained by direct application of the Bromwich integral,

$$\begin{aligned} H(K) &= \lim_{\varepsilon \rightarrow 0} \frac{1}{2\pi i} \int_{\varepsilon - i\infty}^{\varepsilon + i\infty} I(T) e^{KT} dT \\ &= \lim_{\varepsilon \rightarrow 0} \frac{1}{2\pi i} \int_{\varepsilon - i\infty}^{\varepsilon + i\infty} \exp(-T^{\beta} + KT) dT. \end{aligned} \quad (A.2)$$

This integral implies integration along an axis parallel to the imaginary axis. For this purpose,  $T$  is rewritten as  $T = x + iy$ , where  $x$  and  $y$  are the real and imaginary parts of the complex number  $T$ . In Eq. (A.2),  $x = \varepsilon$  and therefore  $dT = i dy$ .

The complex number  $T$  can be written in polar coordinates as  $T = re^{i\varphi}$ , where  $\varphi$  is the polar angle (in Eq. (A.2),  $-\pi/2 < \varphi < \pi/2$ ) and  $r$  is the absolute value of  $T$  ( $r = |T| = \varepsilon/\cos\varphi$ ). In polar coordinates,  $y = \varepsilon \tan\varphi$  and  $dy = (\varepsilon/\cos^2\varphi) d\varphi$ . The integral (A.2) becomes

$$\begin{aligned} H(K) &= \lim_{\varepsilon \rightarrow 0} \frac{1}{2\pi} \int_{-\pi/2}^{\pi/2} \\ &\times \exp\left[-\left(\frac{\varepsilon}{\cos\varphi}\right)^{\beta} e^{i\beta\varphi} + K \frac{\varepsilon}{\cos\varphi} e^{i\varphi}\right] \frac{\varepsilon}{\cos^2\varphi} d\varphi. \end{aligned} \quad (A.3)$$

Using twice the equation  $e^{i\psi} = \cos\psi + i\sin\psi$ , Eq. (A.3) is changed into

$$\begin{aligned} H(K) &= \lim_{\varepsilon \rightarrow 0} \frac{1}{2\pi} \int_{-\pi/2}^{\pi/2} \exp\left[K\varepsilon - \left(\frac{\varepsilon}{\cos\varphi}\right)^{\beta} \cos\beta\varphi\right] \\ &\times (\cos\gamma - i\sin\gamma)(\cos\alpha + i\sin\alpha) \frac{\varepsilon}{\cos^2\varphi} d\varphi, \end{aligned} \quad (A.4)$$

where  $\gamma = (\varepsilon/\cos\varphi)^{\beta} \sin\beta\varphi$  and  $\alpha = K\varepsilon \tan\varphi$ . Note that  $\gamma$  and  $\alpha$  are odd functions of  $\varphi$ . Taking into account the identities  $\cos(\gamma - \alpha) = \cos\gamma \cos\alpha + \sin\gamma \sin\alpha$  and  $\sin(\alpha - \gamma) = \sin\alpha \cos\gamma - \cos\alpha \sin\gamma$ , Eq. (A.4) can be rewritten as

$$\begin{aligned} H(K) &= \lim_{\varepsilon \rightarrow 0} \frac{1}{2\pi} \int_{-\pi/2}^{\pi/2} \exp\left[K\varepsilon - \left(\frac{\varepsilon}{\cos\varphi}\right)^{\beta} \cos\beta\varphi\right] \\ &\times [\cos(\gamma - \alpha) + i\sin(\alpha - \gamma)] \frac{\varepsilon}{\cos^2\varphi} d\varphi. \end{aligned} \quad (A.5)$$

In Eq. (A.5), both the exponential term and  $\cos(\gamma - \alpha)$  are even functions of the angle  $\varphi$ , while  $\sin(\alpha - \gamma)$  is an odd function. Integration of the odd function in the interval  $[-\pi/2, \pi/2]$  gives zero, and the integrals of the even function in the intervals  $[-\pi/2, 0]$  and  $[0, \pi/2]$  are equal, hence

$$\begin{aligned} H(K) &= \lim_{\varepsilon \rightarrow 0} \frac{1}{\pi} \int_0^{\pi/2} \exp\left[K\varepsilon - \left(\frac{\varepsilon}{\cos\varphi}\right)^{\beta} \cos\beta\varphi\right] \\ &\times \cos\left[\left(\frac{\varepsilon}{\cos\varphi}\right)^{\beta} \sin\beta\varphi - K\varepsilon \tan\varphi\right] \frac{\varepsilon}{\cos^2\varphi} d\varphi. \end{aligned} \quad (A.6)$$

To take the limit in Eq. (A.6), let us change the variable of integration according to  $u = \varepsilon \tan\varphi$ . Using

$1/\cos^2\varphi = 1 + \tan^2\varphi$  and  $du = (\varepsilon/\cos^2\varphi) d\varphi$ , Eq. (A.6) becomes

$$H(K) = \lim_{\varepsilon \rightarrow 0} \frac{1}{\pi} \int_0^\infty \exp \left[ K\varepsilon - (\varepsilon^2 + u^2)^{\beta/2} \cos \beta\varphi \right] \times \cos \left[ (\varepsilon^2 + u^2)^{\beta/2} \sin \beta\varphi - Ku \right] du. \quad (\text{A.7})$$

In this equation, the angle  $\varphi$  is a function of  $u$ . As it can be seen from the definition of variable  $u$  ( $u = \varepsilon \tan\varphi$ ), for any finite value of  $u$ ,  $\varphi \rightarrow \pi/2$  when  $\varepsilon \rightarrow 0$ . Therefore, we obtain finally

$$H(K) = \frac{1}{\pi} \int_0^\infty \exp \left[ -u^\beta \cos \left( \frac{\beta\pi}{2} \right) \right] \cos \left[ u^\beta \sin \left( \frac{\beta\pi}{2} \right) - Ku \right] du. \quad (\text{A.8})$$

For a derivation of Eq. (A.8) without contour integration see [70].

## Appendix B. Calculation of Eq. (37)

The integral (A.2) can be approximately calculated by the method of steepest descent. Let us introduce the function  $g(T) = -T^\beta + KT$ . The method consists in finding the extremum  $g(T_0)$  of  $g(T)$  and then in expanding  $g(T)$  in a Taylor series around  $T_0$  up to the second order. This gives

$$H(k) \approx \frac{1}{2\pi i} \exp(g(T_0)) \int_{\varepsilon-i\infty}^{\varepsilon+i\infty} \exp \left[ \frac{1}{2} g''(T_0) (T - T_0)^2 \right] dT, \quad (\text{B.1})$$

i.e.,

$$H(k) \approx [2\pi g''(T_0)]^{-1/2} \exp(g(T_0)). \quad (\text{B.2})$$

The parameter  $T_0$  is obtained from  $g'(T) = 0$  and is equal to  $(\beta/k)^{1/(1-\beta)}$ , therefore  $g(T_0) = -(1-\beta)\beta^{\beta/(1-\beta)}/K^{\beta/(1-\beta)}$  and  $g''(T_0) = \beta(1-\beta)(K/\beta)^{(2-\beta)/(1-\beta)}$ .

Thus, we get finally

$$H(K) \approx \frac{\beta^{1/[2(1-\beta)]}}{\sqrt{2\pi(1-\beta)}} \frac{1}{K^{(1-\beta/2)/(1-\beta)}} \times \exp \left[ -\frac{(1-\beta)\beta^{\beta/(1-\beta)}}{K^{\beta/(1-\beta)}} \right]. \quad (\text{B.3})$$

This approximate distribution was first obtained in [71] together with two additional terms which were intended to increase the precision of Eq. (B.3).

Note that for  $\beta = 1/2$  Eq. (B.3) reproduces the exact result, Eq. (32). For other values of  $\beta$ , Eq. (B.3) is not exact. This can be seen for example from a comparison of the exact asymptote Eq. (34) with the approximate one derived from Eq. (B.3). For large  $K$ , the exact asymptote decreases as  $1/K^{1+\beta}$  while the approximate one decreases as  $1/K^{(1-\beta/2)/(1-\beta)}$ . For  $\beta = 1/2$ , the exponents in these two equations are equal. If  $\beta < 1/2$ ,  $1+\beta > (1-\beta/2)/(1-\beta)$  and the exact asymptote decreases faster with  $K$ . If  $\beta > 1/2$ , the exact asymptote decreases slower with  $K$ . The discrepancy between exact and approximate functions increases with  $|1/2 - \beta|$ . The situation becomes even worse if one takes into account the additional terms given in [71]. For large  $K$  and for  $\beta = 0.8$ , for example, the approximate function begins to increase with the increase of  $K$  if one takes into account one additional term and even takes negative values if two terms are used.

Owing to these facts, the empirical formula

$$H_0(K) = \frac{A}{K^{(1-\beta/2)/(1-\beta)}} \exp \left[ -\frac{(-\beta)\beta^{\beta/(1-\beta)}}{K^{\beta/(1-\beta)}} \right], \quad (\text{B.4})$$

that differs from Eq. (B.3) only by numerical coefficients, will be used. In Eq. (B.4), the numerical coefficient  $A$  is obtained from the best fit of Eq. (B.4) to the exact function, Eq. (31), for small and intermediate values of  $K$ . Values of  $A$  are given in Table 2.

The function  $H_0(K)$  can be used to obtain the decay law using Eq. (1). The difference between approximate and exact decays is observed only for short times owing to the incorrect value of  $H_0(K)$  for large values of  $K$ .

The approximate function given by Eq. (B.4) can be significantly improved by imposing the correct asymptotic behaviour, Eq. (34). For this, we multiply Eq. (B.4) by a correction function,  $f(K)$  that corrects the asymptotic behaviour but does not change  $H(K)$  for small  $K$ . In this way, a new approximate distribution,  $H(K)$ , must be proportional to  $H_0(K)f(K)$  and has as asymptote  $\sim 1/K^{1+\beta}$ , with  $f(K) \approx 1$  for small  $K$ . Thus, the corrected approximate distribution,  $H(K)$ , is

$$H(K) = \frac{B}{K^{(1-\beta/2)/(1-\beta)}} \exp \left[ -\frac{(1-\beta)\beta^{\beta/(1-\beta)}}{K^{\beta/(1-\beta)}} \right] f(K), \quad (\text{B.5})$$

where the empirical correction function,  $f(K)$ , has a simple form

Table 2  
Fitting parameter  $A$  in Eq. (2.4)

$\beta$	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$A$	0.1547	0.195	0.234	0.282	0.340	0.413	0.529	0.779

The precision of  $A$  is estimated as  $\pm 0.0005$  for  $\beta < 0.5$  and up to  $\pm 0.003$  for  $\beta > 0.8$ .

$$f(K) = \begin{cases} 1/(1 + CK^\delta), & \delta = \beta(0.5 - \beta)/(1 - \beta), \beta \leq 0.5, \\ 1 + CK^\delta, & \delta = \beta(\beta - 0.5)/(1 - \beta), \beta \geq 0.5. \end{cases} \quad (\text{B.6})$$

Exponent  $\delta$  in this equation was obtained from the condition that  $H(K)$  must have the asymptotic form  $1/K^{1+\beta}$ :  $(1 - \beta/2)/(1 - \beta) \pm \delta = 1 + \beta$ , where the signs  $+$  and  $-$  stand for  $\beta < 0.5$  and for  $\beta > 0.5$ , respectively. Parameters  $B$  and  $C$  are fitting parameters. They are obtained in order to provide the best fit to the exact distribution of rate constants (in a wide range of  $K$  values around the maximum of the distribution) and to the decay law. Values of the exponent  $\delta$  and of parameters  $B$  and  $C$  are given in Table 1. For this kind of fit, the numerical coefficient in the asymptotic form of  $H(K)$  does not coincide with the exact one,  $(1/\pi) \sin(\beta\pi)\Gamma(1 + \beta)$ , see Eq. (34). One can check that  $H(K)$  reproduces the distribution and the decay law with high accuracy, although the normalization condition for  $H(K)$  is fulfilled with a precision higher than 10% for  $\beta = 0.1$  and 0.2 and higher than 5% for other values of  $\beta$ . A second method for the computation of  $H(K)$ , based on the numerical evaluation of its series expansion, Eq. (34), is described in detail in [72].

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