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Luminescence decays with underlying distributions: General properties and analysis with mathematical functions

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Abstract

In this work, an analysis of the general properties of the luminescence decay law is carried out. The conditions that a luminescence decay law must satisfy in order to correspond to a probability density function of rate constants are established. From an analysis of the general form of the luminescence decay law, it is concluded that the decay must be either exponential or sub-exponential for all times, in order to be represented by a distribution of rate constants $H(k)$. Sub-exponentiality is nevertheless not a sufficient condition. Only decays that are completely monotonic have a probability density function of rate constants. The construction of the decay function from cumulant and moment expansions is studied, as well as the corresponding calculation of $H(k)$ from a cumulant expansion. The asymptotic behavior of the decay laws is considered in detail, and the relation between this behavior and the form of $H(k)$ for small k is explored. Several generalizations of the exponential decay function, namely the Kohlrausch, Becquerel, Mittag-Leffler and Heaviside decay functions, as well as the Weibull and truncated Gaussian rate constant distributions are discussed.

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1. Introduction

Time-resolved luminescence techniques are widely used in various fields for time scales ranging from picoseconds to hours, i.e., spanning 15 orders of magnitude. The data are usually analyzed with a sum of discrete exponentials, but there are many cases where a continuous distribution of decay times best describes the observed phenomena: luminophores incorporated in micelles, cyclodextrins, rigid solutions, inorganic solids, sol–gel matrices, proteins, vesicles or membranes, biological tissues, luminophores adsorbed on surfaces, or linked to surfaces, quenching of luminophores in micellar solutions, energy transfer in assemblies of like or unlike fluorophores, etc.

In the most general case, a luminescence decay can be written in the following form:

$$I(t) = \int_0^\infty H(k)\,\mathrm{e}^{-kt}\,\mathrm{d}k, \tag{1}$$

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 $\int_0^\infty H(k)\,\mathrm{d}k = 1$. In most situations (e.g. in the absence of a rise-time), the function $H(k)$ is non-negative for all $k>0$, and $H(k)$ can be regarded as a distribution of rate constants (strictly, a probability density function, PDF). The designation 'decay law' is usually taken as a synonym for 'luminescence time evolution', thus encompassing the cases where the intensity initially increases with time, as observed for intermolecular excimer emission, and the non-

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monotonic intensity decreases displaying quantum beats. In the present work, however, we will consider only stricto sensu (monotonic) decays.

Recovery of the distribution $H(k)$ from experimental data is very difficult because this is an ill-conditioned problem [1]. $H(k)$ can in principle be recovered from the experimental luminescence decay 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 form for the PDF of rate constants; and (iii) data analysis with a definite mathematical function corresponding to the PDF that contains adjustable parameters. The present work is devoted to the third approach. In such an approach, a mathematical function that is expected to best describe the distribution of rate constants is used. The choice is very wide, but some specific empirical functions with a continuous distribution of rate constants enjoy special popularity, such as the stretched exponential, or the decay functions resulting from the Lorentzian and the Gaussian PDFs. In the first two papers of this series, we specifically discussed the stretched exponential (or Kohlrausch) function [2],

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

and the less-known compressed hyperbola (or Becquerel) function [3],

$$I(t) = \frac{1}{\left[1+(1-\beta)\,t/\tau_0\right]^{(1/1-\beta)}}, \tag{3}$$

where $0<\beta\leqslant 1$, and τ_0 is a parameter with the dimensions of time. Both functions conveniently reduce to an exponential function for $\beta = 1$.

In this work, an analysis of the general properties of the luminescence decay law is carried out. In Section 2, the nature of the luminescence decay law and of the PDF of rate constants is discussed. The conditions that a luminescence decay law must satisfy in order to correspond to a PDF of rate constants are examined in Section 3. The construction of the decay function from cumulant and moment expansions is next studied in Section 4, and the corresponding calculation of the PDF from a cumulant expansion is discussed in Section 5. The asymptotic behavior of the decay law is considered in detail in Section 6, and the relation between this behavior and the form of $H(k)$ for small k explored. Several generalizations of the exponential function are examined in Section 7. The final discussion and main conclusions are presented in Section 8.

2. Nature and limitations of the luminescence decay law and of the distribution of rate constants

2.1. Luminescence decay law

What is named a decay law $I(t)$ can be, in some circumstances (single species initially excited), related to a probability of emission between t and $t+\mathrm{d}t$, $P(t)$, which is a more fundamental quantity,

$$P(t) = -\frac{\mathrm{d}I}{\mathrm{d}t}. \tag{4}$$

In this case it is assumed that $I(t)$ corresponds to an experiment where all photons emitted by the system under study (or a fixed fraction of these) are collected. $P(t)$ is the probability of emission of the photon between t and $t+\mathrm{d}t$, given that it was emitted (hence no quantum yield correction is necessary). With this generality, $P(t)$ implies an integration over emission wavelengths, and information concerning internal dynamics in the system may be lost.

The probability of emission $P(t)$ can be written as

$$P(t) = \int_0^{\infty} H(k) P_k(t)\,\mathrm{d}k, \tag{5}$$

i.e., as a weighted distribution of emission probabilities for exponential decays, given by

$$P_k(t) = k_{\mathrm{e}}^{-kt}. \tag{6}$$

More frequently, the emission is recorded for a narrow wavelength range, and results from a sum of weighted contributions of several emitting species. The decay law is then a technical quantity, whose normalization at $t = 0$ is performed for convenience. The decay law can in principle be related to a detailed model describing the luminescence mechanism and respective dynamics, but remains a valuable formal description of the time evolution of the luminescence even in the absence of such a model.

Another important aspect relates to the preparation of the emissive state. It is assumed here that this state is instantaneously generated, e.g. by light absorption (photoluminescence). In fact, a transition to an upper vibrational or electronic excited state is followed by electronic and/or vibrational relaxation, processes that may take up to a few picoseconds. For these short time scales, not considered here, the inclusion of a rise time in the decay law is clearly essential.

In the following, it will also be assumed that spontaneous emission is the dominant radiative decay path, i.e., that emission is incoherent.

2.2. Distribution of rate constants

Turning now our attention to $H(k)$, the integration limits in Eq. (1) deserve consideration. It has been argued that a positive cut-off value $k_{\min}$ must be imposed, in order to avoid a finite number of molecules with a physically unacceptable decay rate equal to zero [4]. The argument is however incorrect, as this happens only if $H(k)$ contains $\delta(k)$; otherwise $H(k)$ can even tend to infinity when $k\rightarrow 0$, while still having $I(t)\rightarrow 0$ when $t\rightarrow\infty$, as will be discussed in Section 6. It may nevertheless be objected that in certain cases the decay rate cannot be lower than a certain radiative decay rate. For well-defined molecular species this is in principle correct, but even in this case the effect of such a cut-off can be statistically and/or experimentally negligible, given a certain time window. Furthermore, a distribution of rate constants $H(k)$ is in most cases introduced to take into account additional decay processes, and the intrinsic unimolecular decay (that includes the radiative decay) appears as a multiplicative exponential [2].

An upper integration limit $k_{\max}$ is in general physically justified (there are no infinitely fast relaxation processes), but again it can be statistically irrelevant and mathematically inconvenient: for instance, in a study of fluorescence anisotropy decays in heptachromophoric systems undergoing excitation energy hopping [5,6], a distribution of rate constants with a hyperbolic decay toward infinity was successfully used, while a maximum rate constant had been identified and computed [6]; nevertheless, this upper limit was located well into the tail of the distribution, whose contribution to the overall decay was negligible.

3. Conditions that a decay law must satisfy in order to have a distribution of rate constants

3.1. Sufficient condition for $I(t)$

If $H(k)$ is a PDF, then

$$(-1)^n I^{(n)}(t) > 0 \; (n = 0, 1, 2, \ldots), \tag{7}$$

where $I^{(n)}(t)$ is the nth derivative of $I(t)$. Eq. (7) defines $I(t)$ as a *completely monotonic* function [7]. This follows directly from Eq. (1), as

$$I^{(n)}(t) = (-1)^n \int_0^\infty k^n \, H(k) \, \mathrm{e}^{-kt} \, \mathrm{d}k, \tag{8}$$

since $H(k) \geqslant 0$, the integral is positive for all t. The condition that all moments $\langle k^n \rangle = (-1)^n I^{(n)}(0)$ must be positive is a special case of Eq. (7) for $t = 0$.

3.2. Necessary conditions for $w(t)$

If the decay is written as

$$I(t) = \exp\left(-\int_0^t w(u) \, \mathrm{d}u\right), \tag{9}$$

where $w(t)$ is a time-dependent rate coefficient, then

$$w(t) = -\frac{\mathrm{d} \ln I(t)}{\mathrm{d}t} = -\frac{1}{I(t)} \frac{\mathrm{d} I(t)}{\mathrm{d}t}, \tag{10}$$

or

$$w(t) = \frac{\int_0^\infty k \, H(k) \mathrm{e}^{-kt} \, \mathrm{d}k}{\int_0^\infty H(k) \, \mathrm{e}^{-kt} \, \mathrm{d}k} = \int_0^\infty k \, J(k, t) \, \mathrm{d}k, \tag{11}$$

where

$$J(k, t) = \frac{H(k) \, \mathrm{e}^{-kt}}{\int_0^\infty H(k) \, \mathrm{e}^{-kt} \, \mathrm{d}k} \tag{12}$$

is a "renormalized" distribution of rate constants (valid for all times). This time-dependent PDF will play a central role in the remaining development. Note that Eq. (11) allows the calculation of $w(t)$ from $H(k)$.

One has from Eq. (11) that

$$\frac{\mathrm{d}^n w}{\mathrm{d}t^n} = \int_0^\infty k \frac{\partial^n J(k, t)}{\partial t^n} \, \mathrm{d}k \tag{13}$$

We now proceed to obtain the form of $w^{(n)}(t)$ explicitly.

3.2.1. First derivative of $w(t)$

It follows from Eq. (12) that

$$\frac{\partial J(k, t)}{\partial t} = [w(t) - k] \, J(k, t), \tag{14}$$

hence, using Eqs. (13) and (14)

$$\frac{\mathrm{d}w}{\mathrm{d}t} = \left[\left(\int_0^\infty k \, J(k, t) \, \mathrm{d}k\right)^2 - \int_0^\infty k^2 \, J(k, t) \, \mathrm{d}k\right], \tag{15}$$

or

$$\frac{\mathrm{d}w}{\mathrm{d}t} = M_1(t)^2 - M_2(t) = -C_2(t), \tag{16}$$

where the $M_i(t)$ are the raw moments of $J(k, t)$,

$$M_i(t) = \int_0^\infty k^i \, J(k, t) \, \mathrm{d}k, \tag{17}$$

and $C_i(t)$ its cumulants. The first cumulants of a PDF are [8]

$$\begin{aligned} C_1 &= M_1, \\ C_2 &= M_2 - M_1^2, \\ C_3 &= 2M_1^3 - 3M_1 M_2 + M_3, \\ C_4 &= -6M_1^4 + 12M_1^2 M_2 - 3M_2^2 - 4M_1 M_3 + M_4. \end{aligned} \tag{18}$$

From Eq. (16) we see that $w'(t)$ is the symmetrical of the variance of $J(k, t)$, which is a non-negative quantity. It is thus concluded that the decay must be either exponential ($w'(t) = 0$) or sub-exponential ($w'(t) < 0$) for all times, if $H(k)$ is to be a PDF. This also follows from an examination of Eq. (12), and its effect on Eq. (11), since Eq. (12) implies that in general the function $J(k, t)$ is progressively "compressed" to the left, as t increases. If $H(k) = \delta(k - k_0)$, no shape change in $J(k, t)$ occurs, $w(t)$ is a non-zero constant, and the decay is exponential for all times. If $H(k)$ is a non-delta distribution, but is equal to zero below some positive value of k, k_0, the "compression" process is effective and ultimately yields a delta function, $J(k, \infty) = \delta(k - k_0)$, $w(t)$ attains a non-zero constant value, and the decay becomes essentially exponential for sufficiently long times. If $k_0 = 0$ (with both $H(0) = 0$ and with $H(0) > 0$), then $w(t)$ will approach zero for long times, and the decay goes to zero according to a slower-than-exponential function. A more detailed discussion will be presented in Section 6.

It is also to be noted that the conditions expressed by Eq. (7) can be rewritten as $M_n(t) > 0$, i.e., all moments of $J(k, t)$ must be positive.

3.2.2. Higher derivatives of $w(t)$

From Eqs. (14) and (17) it follows that

$$\frac{\mathrm{d}M_i}{\mathrm{d}t} = M_1 M_i - M_{i+1}\ (i = 2, 3, \ldots). \tag{19}$$

Using this identity, it is easy to compute the higher derivatives of $w(t)$, starting from Eq. (16),

$$\frac{d^2 w}{\mathrm{d}t^2} = \frac{d}{\mathrm{d}t}(M_1^2 - M_2) = 2M_1^3 - 3M_1 M_2 + M_3, \tag{20}$$

$$\frac{d^3 w}{\mathrm{d}t^3} = \frac{d}{\mathrm{d}t}(2M_1^3 - 3M_1 M_2 + M_3) = 6M_1^4 - 12M_1^2 M_2 + 4M_1 M_3 - M_4, \tag{21}$$

etc. Comparison with Eqs. (18) leads to the compact forms:

$$\frac{\mathrm{d}^n w}{\mathrm{d}t^n} = -\frac{\mathrm{d}^{n-1} C_1}{\mathrm{d}t^{n-1}} = (-1)^n C_{n+1}(t). \tag{22}$$

Constraints on $w(t)$ also follow from these equalities. For instance, $C_3(t)$ should be negative for a so-called negative asymmetric distribution (i.e. a left asymmetric distribution) $J(k,t)$, as must happen to any sub-exponential decay for sufficiently long times.

Incidentally, Eq. (22) provides an easy (but sequential) way of obtaining the explicit form of a cumulant of any order.

4. Construction of the decay from cumulant and moment expansions

Eq. (22) implies that a Maclaurin expansion of $w(t)$ is

$$w(t) = C_1(0) - C_2(0)t + C_3(0)\frac{t^2}{2!} - \ldots, \tag{23}$$

where the cumulants of $J(k,t)$ at time zero are also the cumulants of $H(k)$. Insertion of this equation into Eq. (9) gives

$$I(t) = \exp\left[-C_1(0)t + C_2(0)\frac{t^2}{2!} - C_3(0)\frac{t^3}{3!} + \ldots\right], \tag{24}$$

that allows to reconstruct the decay $I(t)$ from the cumulants of $H(k)$. An analogous equation is used for the analysis of dynamic light-scattering data, in order to recover the distribution of particle sizes from the auto-correlation function [9,10].

The interesting aspect is that with Eq. (22) we can generalize Eq. (24), by using a Taylor series expansion around any time t_0:

$$I(t) = \exp\left[-C_1(t_0)(t - t_0) + C_2(t_0)\frac{(t-t_0)^2}{2!} - C_3(t_0)\frac{(t-t_0)^3}{3!} + \ldots\right], \tag{25}$$

where the cumulants now refer to $J(k,t)$.

Similarly, the moment expansion:

$$I(t) = 1 - M_1(0)t + M_2(0)\frac{t^2}{2!} - M_3(0)\frac{t^3}{3!} + \ldots \tag{26}$$

can be generalized to give

$$I(t) = (t_0)\left[1 - M_1(t_0)(t - t_0) + M_2(t_0)\frac{(t-t_0)^2}{2!} - M_3(t_0)\frac{(t-t_0)^3}{3!} + \ldots\right]. \tag{27}$$

5. Calculation of $H(k)$ from the cumulants

The probability density function $H(k)$ can be formally written in terms of the respective cumulants, by means of the analytical inversion formula for Laplace transforms [11,12]:

$$H(k) = \frac{2}{\pi}\int_0^\infty \mathrm{Re}[I(\mathrm{i}\omega)]\cos(k\omega)\,\mathrm{d}\omega. \tag{28}$$

Using Eq. (24), Eq. (28) becomes

$$H(k) = \frac{2}{\pi}\int_0^\infty \mathrm{e}^{-\frac{\omega^2}{2!}C_2 + \frac{\omega^4}{4!}C_4 - \ldots\ldots} \times \cos\left(C_1\omega - C_3\frac{\omega^3}{3!} + \ldots\right)\cos(k\omega)\,\mathrm{d}\omega. \tag{29}$$

Eq. (29) allows—at least formally—the calculation of $H(k)$ from $w(t)$. There are in fact two problems with its practical use: (i) with the exception of the delta and Gaussian distributions, all PDFs have an infinite number of non-zero cumulants (Marcinkiewicz theorem [13]) and (ii) the cumulant series that appear in Eq. (29) usually have a finite radius of convergence [12].

We now compute the cumulants for the stretched exponential [2] and compressed hyperbola [3] decay laws. In the first case, we consider only a modified form [2]:

$$I(t) = \exp\left[1 - \left(1 + \frac{t}{\tau_0}\right)^\beta\right]. \tag{30}$$

The respective cumulants are obtained from a Maclaurin expansion of $\ln I(t)$,

$$\ln I(t) = 1 - \left(1 + \frac{t}{\tau_0}\right)^\beta = -\beta\left(\frac{t}{\tau_0}\right) - \frac{1}{2!}\beta(\beta-1)\left(\frac{t}{\tau_0}\right)^2 - \frac{1}{3!}\beta(\beta-1)(\beta-2)\left(\frac{t}{\tau_0}\right)^3 - \ldots, \tag{31}$$

hence,

$$C_n(0) = \frac{(-1)^{n+1}}{\tau_0^n}\beta(\beta-1)\ldots(\beta-n+1). \tag{32}$$

For the compressed hyperbola decay law,

$$\ln I(t) = \frac{1}{\beta-1}\ln\left[1+(1-\beta)\left(\frac{t}{\tau_0}\right)\right] = \frac{1}{\beta-1}\left\{(1-\beta)\left(\frac{t}{\tau_0}\right) - \frac{1}{2}\left[(1-\beta)\left(\frac{t}{\tau_0}\right)\right]^2 + \frac{1}{3}\left[(1-\beta)\left(\frac{t}{\tau_0}\right)\right]^3 - \ldots\right\}, \quad (33)$$

hence,

$$C_n(0) = \frac{(n-1)!}{\tau_0^n}(1-\beta)^{n-1}. \quad (34)$$

In both cases, the cumulants are always positive and increase indefinitely with n, after eventually passing through a minimum.

Consider the truncated Gaussian (i.e., for $k \geqslant 0$ only) PDF [12]:

$$H(k) = \sqrt{\frac{2}{\pi\sigma^2}}\frac{\exp\left[-1/2(k-\mu/\sigma)^2\right]}{1+\operatorname{erf}\left(\mu/\sqrt{2}\sigma\right)}. \quad (35)$$

It has the following associated decay law:

$$I(t) = \frac{\operatorname{erfc}\left(\sigma^2 t - \mu/\sqrt{2}\sigma\right)}{\operatorname{erfc}\left(-\mu\sqrt{2}\sigma\right)}\exp\left(-\mu t + \frac{1}{2}\sigma^2 t^2\right) \quad (36)$$

and has an infinite number of cumulants. Its first cumulant (the mean) is

$$\langle k\rangle = \mu + \sqrt{\frac{2}{\pi}}\sigma\frac{e^{-1/2(\mu/\sigma)^2}}{\operatorname{erfc}\left(-\mu/\sqrt{2}\sigma\right)}. \quad (37)$$

For $t \ll \mu/\sigma^2$, $I(t)$ coincides with that of a normal distribution, and the first two cumulants of this PDF suffice to describe its behavior,

$$I(t) \simeq \exp\left(-\mu t + \frac{1}{2}\sigma^2 t^2\right). \quad (38)$$

This equation has been used for the analysis of dynamic light-scattering data, in order to recover the distribution of particle sizes from the autocorrelation function [9,10], and applies to some luminescence decays for not too long times. The full Gaussian PDF (or a mixture of Gaussian PDFs) [14–16] and a Gaussian PDF truncated [4] at $k_0 > 0$ have been used to describe fluorescence decays. The truncated Gaussian reduces to the full Gaussian distribution for large μ/σ ratios.

Up to now, it was implicitly assumed that all moments and cumulants were finite. For some PDFs, however, not all moments and cumulants are finite. For the Lévy PDFs, for instance, only M_1 can be (but is not always) finite. This is precisely the case of the (unmodified) stretched exponential decay. The form of $J(k,t)$, Eq. (12), ensures that, even then, all moments will be finite for $t > 0$. The singularity is therefore limited to $t = 0$. This is one of the reasons why the expansions Eqs. (25) and (27) are of interest.

6. Decay law asymptotics

We will obtain relatively general equations relating the asymptotic behavior of the decay law $I(t)$ (i.e., for large t) to that of the PDF $H(k)$ for small k. From Eq. (1), it is indeed obvious that the behavior of $H(k)$ for small k will define the shape of the decay $I(t)$ for long times.

According to the discussion presented in Section 3, it is convenient to consider separately the cases where the PDF of rate constants is non-zero at $k = 0$, or rises from zero immediately afterwards, from the case where $H(k) > 0$ only for $k > k_0$, with k_0 positive. The special case of partial relaxation will also be treated in this section.

Consideration of the asymptotic behavior of a decay function is important, not only because it defines the long time form, that may or may not be experimentally accessible, but also because $\int_0^\infty I(t)\,dt$ is often computed from the decay law in order to obtain a quantity proportional to the steady-state intensity. This calculation may be meaningless if the major contribution to the above integral corresponds to a time window not experimentally observed, or if the integral diverges.

6.1. $H(0^+) > 0$

6.1.1. $H(k)$ admits a Maclaurin series expansion

In this case,

$$H(k) = H(0) + k\,H'(0) + \frac{k^2}{2!}H''(0) + \ldots, \quad (39)$$

and substitution in Eq. (1) gives immediately,

$$I(t) = \frac{H(0)}{t} + \frac{H'(0)}{t^2} + \frac{H''(0)}{t^3} + \ldots. \quad (40)$$

The effective power dependence with t for long times (asymptotic behavior) will be determined by the order of the first non-zero term of the Maclaurin series.

6.1.2. $H(k)$ is not analytic at the origin

A (so-called Tauberian) theorem in probability theory [7] that covers a broad range of cases (including the previous one), is the following, reformulated for our purposes.

If the cumulative distribution function:

$$U(k) = \int_0^k H(u)\,du \quad (41)$$

has the asymptotic form:

$$U(k) \sim k^p L(k) \quad (42)$$

in the limit $k \to 0$, with $p > 0$, where $L(k)$ is a *slowly varying* function, i.e., a function that obeys

$$\frac{L(\alpha k)}{L(k)} \to 1, \quad (43)$$

also when $k \to 0$, for any constant α, then the decay law will have the following asymptotic behavior:

$$I(t) \sim U(1/t) \quad (44)$$

in the limit $t \to \infty$.

In most situations of physical interest, the last equation can be replaced by

$$I(t) \sim \frac{1}{t} H\left(\frac{1}{t}\right). \tag{45}$$

Note that PDFs that near the origin vary according to negative power laws ($0<p<1$) and therefore rise to infinity, are included.

On the other hand, $\int_0^\infty I(t)\,dt$ diverges for $p \leqslant 1$.

6.2. $H(0^+) = 0$

In this case, $H(k)>0$ only for $k>k_0$, with k_0 positive, and the above results are not valid without modification. But they can be applied by shifting the distribution $H(k)$ to the left, placing it next to the origin, and then moving it back to the right by k_0, in order to restore the original position. The distribution next to the origin, to which the above results apply, is

$$H_0(k) = H(k + k_0) \tag{46}$$

and the decay law becomes, after restoring the initial position,

$$I(t) = I_0(t)\,\exp(-k_0 t), \tag{47}$$

where $I_0(t)$ corresponds to the shifted distribution $H_0(k)$. The asymptotic behavior will be that of $H_0(k)$ times an exponential, hence dominated by the exponential. Note that in this case $\int_0^\infty I(t)\,dt$ is not divergent even if $I_0(t)$ has an asymptotic dependence with $p \leqslant 1$, owing to the exponential damping factor.

6.3. $H(k)$ contains $\delta(k)$

When there is a fraction α of luminophores not decaying by the mechanism under consideration (e.g. intermolecular resonance energy transfer to nearby acceptors), $H(k)$ is given by

$$H(k) = \alpha\,\delta(k) + (1-\alpha)H^+(k), \tag{48}$$

where $H^+(k)$ is the density function of positive rate constants. Insertion of this PDF in the decay law expression gives

$$I(t) = \alpha + (1-\alpha)I^+(t), \tag{49}$$

where $I^+(t)$ is the decay law corresponding to $H^+(k)$. In this case, the asymptotic form is a numerical constant, and $\int_0^\infty I(t)\,dt$ diverges, unless (as must happen in physically acceptable cases) the overall decay contains a multiplicative exponential.

6.4. Cases left out

There are some cases that are not covered by the results of the Tauberian theorem presented, namely PDFs $H(k)$ of rapid variation near the origin, like $\exp(-1/k)$. This is the case of the stretched exponential PDF. For $\beta = \frac{1}{2}$, for instance [2],

$$H_{1/2}(k) = \frac{1}{2\sqrt{\pi}\,k^{3/2}} \exp\left(-\frac{1}{4k}\right). \tag{50}$$

Only for very small β, when [2,17],

$$H(k) \simeq \frac{\beta}{k^{1+\beta}} \exp\left(-\frac{1}{k^\beta}\right) \simeq \frac{\beta}{e\,k} \exp\left[-\frac{1}{2}(\beta \ln k)^2\right], \tag{51}$$

Table 1
Relation between the type of luminescence decay function, the luminescence decay asymptotic behavior, and the PDF of rate constants

				$H(k)$	$w(t)$	$I(t)$
Exponential				$\delta(k-k_0)$	k_0	$e^{-k_0 t}$
Sub-exponential	Asymptotically exponential			$0 (k<k_0)$	$\sim k_0$	$\sim e^{-k_0 t}$
	Slower-than-exponential	Maclaurin or Puiseux valid	$H(0)=0$	$ak^p (p>0$, small $k)$	$\sim t^{-1}$	$\sim t^{-(1+p)}$
			$H(0)>0$	$H_0 + \ldots (H_0>0)$	$\sim t^{-1}$	$\sim t^{-1}$
		Maclaurin or Puiseux invalid	$H(0)=0$	One-sided Lévy	$\sim t^{-(1-\beta)}$	e^{-at^β}
			$H(0)=\infty$	$ak^{-p} (1>p>0$, small $k)$	$\sim t^{-1}$	$\sim t^{-(1-p)}$

Table 2
Examples of PDF of rate constants and respective luminescence decay functions

				$H(k)$	$I(t)$
Exponential				Delta	Exponential
Sub-exponential	Asymptotically exponential			Rectangular	$e^{-k_0 t}(1-e^{-\Delta k t})/(\Delta k t)$
	Slower-than-exponential	Maclaurin or Puiseux valid	$H(0)=0$	Gamma	Becquerel
			$H(0)>0$	Exponential	Hyperbolic
		Maclaurin or Puiseux invalid	$H(0)=0$	One-sided Lévy	Stretched exponential
			$H(0)=\infty$	Weibull ($\alpha<1$)	Weibull

does the application of the Tauberian theorem yield the correct result, $I(t) = \exp(-t^{\beta})$.

The several asymptotic cases discussed above are summarized in Table 1, and corresponding specific examples are given in Table 2.

7. Selected decay functions

As discussed above, PDFs that reduce to the delta function for some value(s) of the parameter(s), such as those of the stretched exponential and compressed hyperbola decay functions, and the Lorentzian and the Gaussian PDFs, are of special interest and/or of common use. All these functions may be considered as generalizations of the exponential function. There are other interesting generalizations of the exponential function that we will discuss below, see also Table 2.

There are at least two possible ways to generalize the exponential function. One is to select $H(k)$ PDFs that are known to reduce to the delta function $\delta(k-k_0)$ for some value(s) of the parameter(s). This is obviously the case for the Lorentzian and the Gaussian functions. Such a procedure automatically ensures that $H(k)$ will be a PDF. The other way is to work with the exponential decay law itself, changing it to a functional form that still reduces to the exponential for some value(s) of the parameter(s). This is the case in particular of the stretched exponential function. In these cases, one must compute $H(k)$, to check that it is still a PDF. A slightly different approach is to take the series expansion of the exponential decay function and to modify it. Distribution functions obtained in this way deserve attention. But it is of worth to first briefly recall the main characteristics of the stretched exponential (or Kohlrausch) function and of the compressed hyperbola (or Becquerel) function (for more details, the reader is referred to our recent papers [1,2]).

7.1. Stretched exponential (or Kohlrausch) function

The stretched exponential decay function is given by Eq. (2). This decay law was first used in luminescence by Werner [18]. In studies of the relaxation of complex systems, the Kohlrausch function is frequently used as a purely empirical decay law, 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, where $\beta = \frac{1}{2}$, and diffusionless resonance energy transfer by the dipole-dipole mechanism, with $\beta = \frac{1}{6}$, $\frac{1}{3}$ and $\frac{1}{2}$ for one-, two- and three-dimensional systems, respectively. Other rational values of β are obtained for different multipole interactions, e.g. $\beta = \frac{3}{8}$, $\frac{3}{10}$, for the dipole–quadrupole and quadrupole–quadrupole mechanisms in three-dimensions. In Huber's approximation, energy transport as measured by fluorescence anisotropy shows the same time-dependence as direct energy transfer, and is characterized by the same values of β. Resonance energy transfer 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 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 β of Eq. (2) depends on the mechanism of transfer, 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) [2]. The Kohlrausch function is also found to apply to some luminescence decays of disordered and ordered inorganic solids, and of semiconductor nanoclusters [2,19].

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 behavior through the parameter β. Stretched exponentials were used for instance to analyze the fluorescence decay of fluorophores incorporated in a sol–gel matrix and of fluorophores covalently bound to silica and alumina surfaces [2]. The Kohlrausch decay function was also recently used in the analysis of single-molecule fluorescence, quantum dot luminescence, and in the fluorescence lifetime imaging of biological tissues [2].

The corresponding distribution of rate constants, shown in Fig. 1, is the one-sided Lévy PDF that can be written as [2]

$$H_{\beta}(k) = \frac{\tau_0}{\pi}\int_0^{\infty} \exp\left[-u^{\beta}\cos\left(\frac{\beta\pi}{2}\right)\right] \times \cos\left[u^{\beta}\sin\left(\frac{\beta\pi}{2}\right) - k\tau_0 u\right] \mathrm{d}u. \quad (52)$$

The stretched exponential luminescence decay function has an undesirable short-time behavior (infinite initial rate, faster-than-exponential decay for short times). For this

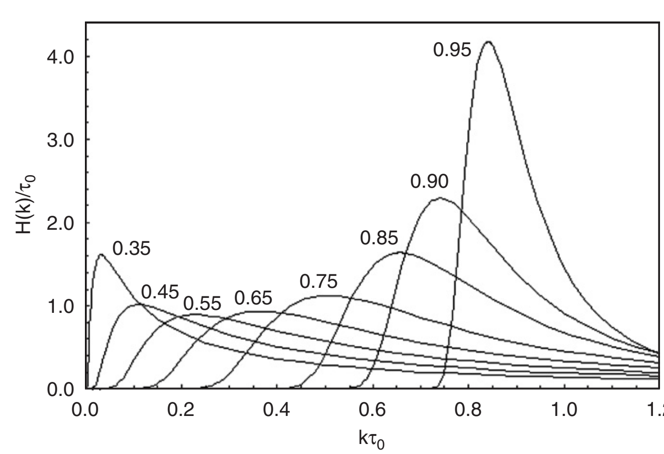

Fig. 1. Distribution of rate constants (probability density function) for the stretched exponential (Kohlrausch) decay law. The number next to each curve is the respective β.

reason, a modified form was proposed [2],

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

where α is a non-negative dimensionless parameter.

7.2. Compressed hyperbola (or Becquerel) function

The compressed hyperbola or Becquerel decay function is given by Eq. (3). The Becquerel function, as defined here, is a quite flexible decay function, although its less direct relation to the exponential decay has limited its use up to now mainly to the luminescence of phosphors [3]. Nevertheless, there are some recent applications in fluorescence [3]. For instance, Wlodarczyk and Kierdaszuk [20] showed that it provides good fits for fluorescence decays that slightly depart from the exponential behavior, implying a relatively narrow distribution of decay times around a mean value. The corresponding distribution of rate constants, shown in Fig. 2, is the gamma PDF [3],

$$H_{\beta}(k) = \frac{\tau_0}{(1-\beta)\ \Gamma(1/1-\beta)}\left(\frac{\tau_0\, k}{1-\beta}\right)^{(\beta/1-\beta)} \times \exp\left(-\frac{\tau_0 k}{1-\beta}\right). \quad (54)$$

As discussed previously [2], two possible approaches to fit luminescence decay laws with a discrete sum of terms are the use of exponentials and hyperbolae as base functions. Since the Becquerel decay law interpolates between these two extreme cases, it seems reasonable to assume that a sum of a few Becquerel functions, appropriately weighted, will be a powerful fitting function for complex decays [3].

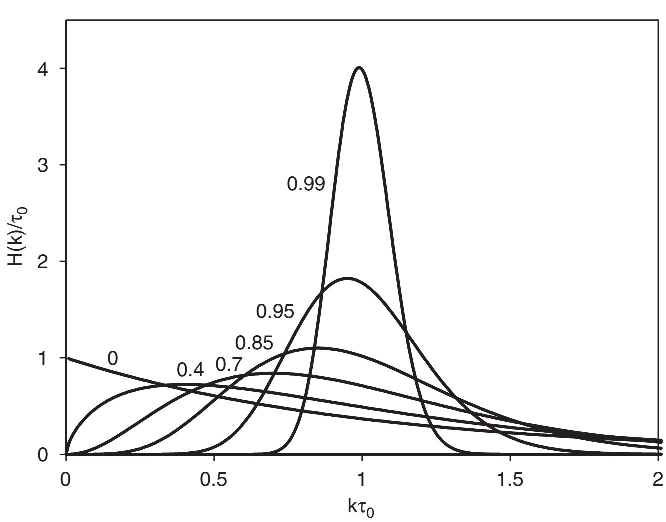

Fig. 2. Distribution of rate constants (probability density function) for the Becquerel decay law. The number next to each curve is the respective β.

7.3. Mittag-Leffler and Heaviside functions

We now turn our attention to the series expansion of the exponential decay function,

$$e^{-at} = \sum_{n=0}^{\infty}\frac{(-at)^n}{n!} = \sum_{n=0}^{\infty}\frac{(-at)^n}{\Gamma(n+1)}, \quad (55)$$

with the aim of generalizing it. Two simple generalizations are Mittag-Leffler's exponential function, or Mittag-Leffler function $E_{\alpha}(x)$ [21,23],

$$E_{\alpha}(-at) = \sum_{n=0}^{\infty}\frac{(-at)^n}{\Gamma(\alpha n+1)}, \quad (56)$$

and Heaviside's exponential function, $e_{\alpha}(x)$ [23],

$$e_{\alpha}(-at) = \sum_{n=0}^{\infty}\frac{(-at)^n}{\Gamma(n+1+\alpha)}, \quad (57)$$

where $0<\alpha\leqslant 1$ in the first case, and $\alpha\geqslant 0$ in the second case. For our purposes, it is convenient to define a *normalized* Heaviside's exponential function $\varepsilon_{\alpha}(x)$, so that $\varepsilon_{\alpha}(0)=1$,

$$\varepsilon_{\alpha}(x) = \Gamma(1+\alpha)\, e_{\alpha}(x) = \alpha\, \Gamma(\alpha)\, e_{\alpha}(x). \quad (58)$$

The $H(k)$ for these two decay laws are known, and are indeed PDFs. They are displayed in Figs. 3 and 4, respectively. The Mittag-Leffler PDF is (with $a=1$) [22,24,25],

$$H_{\alpha}(k) = \alpha^{-1}\, k^{-(1+\alpha^{-1})}\, L_{\alpha}\left(k^{-\alpha^{-1}}\right), \quad (59)$$

where $L_{\alpha}(x)$ is the one-sided Lévy PDF given by Eq. (52).

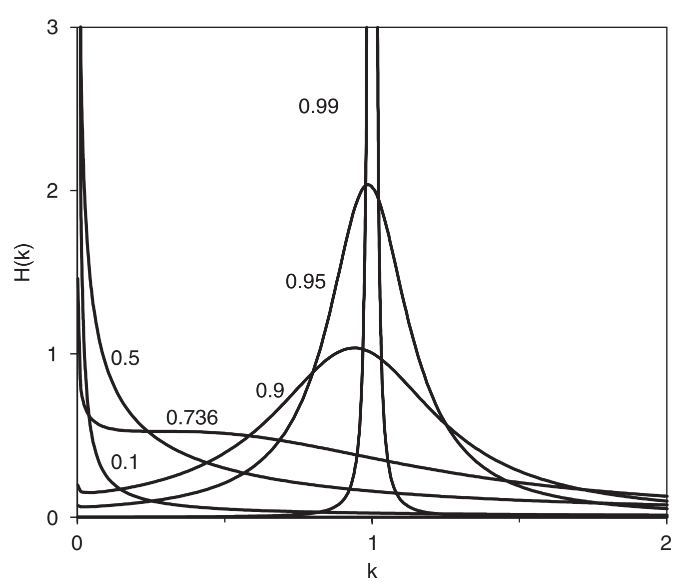

Fig. 3. Distribution of rate constants (probability density function) for the Mittag-Leffler decay law. The number next to each curve is the respective α.

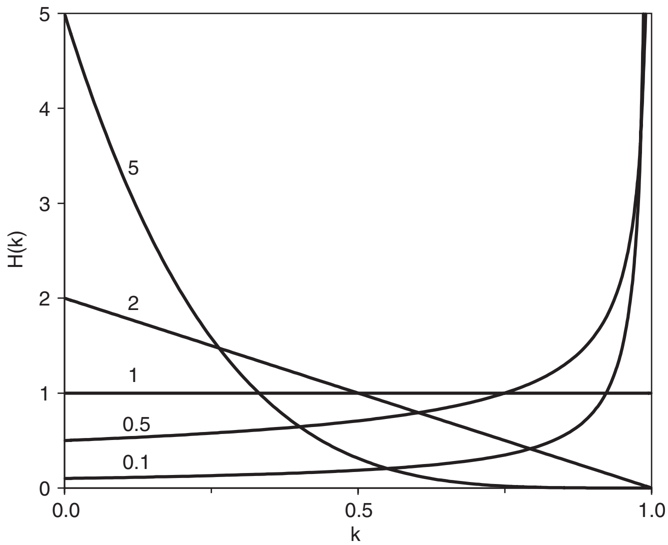

Fig. 4. Distribution of rate constants (probability density function) for the Heaviside decay law. The number next to each curve is the respective α.

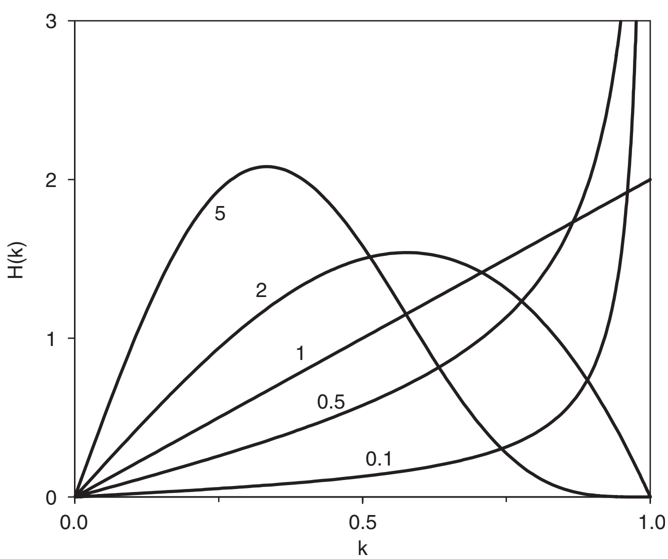

Fig. 5. Distribution of rate constants (probability density function) for the modified Heaviside decay law, with $\beta = 1$. The number next to each curve is the respective α.

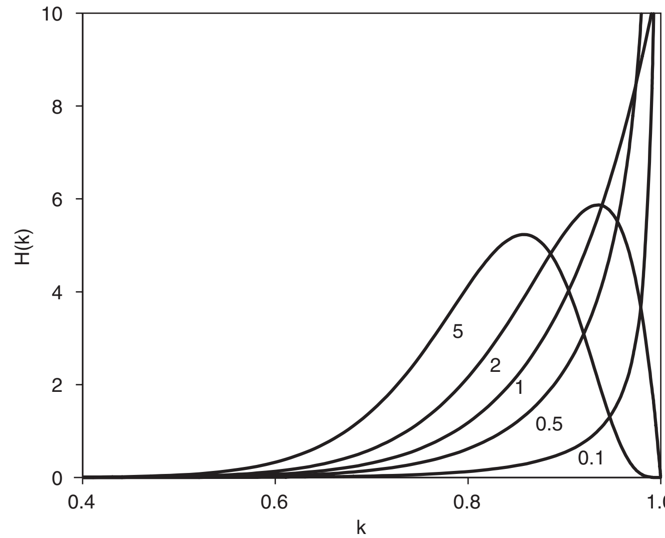

Fig. 6. Distribution of rate constants (probability density function) for the modified Heaviside decay law, with $\beta = 10$. The number next to each curve is the respective α.

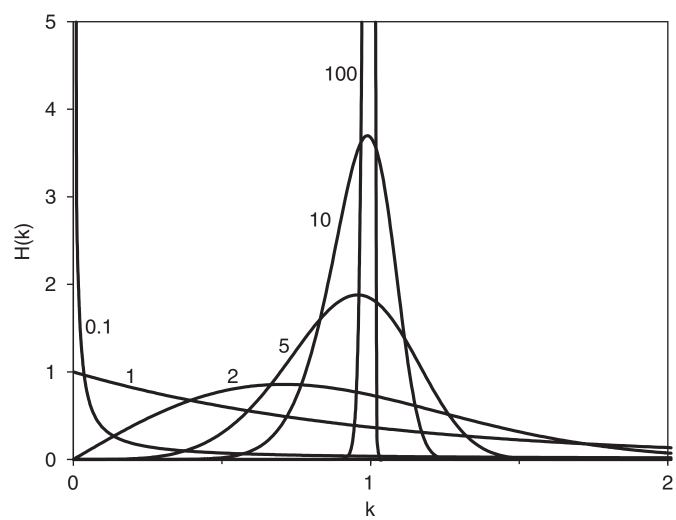

Fig. 7. Distribution of rate constants (probability density function) for the Weibull decay law. The number next to each curve is the respective α.

For Heaviside's normalized exponential, one has [23] (for $a = 1$) the following PDF,

$$H_\alpha(k) = \begin{cases} \alpha(1-k)^{\alpha-1} & \text{if} \quad k \leqslant 1, \\ 0 & \text{if} \quad k > 1. \end{cases} \tag{60}$$

It can be shown that both generalized exponentials asymptotically decay with t^{-1}. A simple modification of Heaviside's normalized exponential PDF is

$$H_\alpha(k) = \begin{cases} (\beta+1)\alpha k^{\beta}(1-k^{\beta+1})^{\alpha-1} & \text{if} \quad k \leqslant 1 \\ 0 & \text{if} \quad k > 1 \end{cases} \quad (\beta \geqslant 0). \tag{61}$$

This function, displayed in Figs. 5 and 6 for two positive values of parameter β, has $H_\alpha(0) = 0$ for $\beta > 0$, and asymptotically decays with $t^{-(1+\beta)}$.

To the best of our knowledge, the Mittag-Leffler and Heaviside functions have not been used yet in practical situations, but they are of potential interest.

7.4. Weibull probability density function

Another interesting generalization of the exponential decay, that also appears not to have been used thus far in the analysis of fluorescence decays results from the Weibull

PDF [7,26],

$$H_{\alpha,\beta}(k) = \frac{\alpha}{\beta}\left(\frac{k}{\beta}\right)^{\alpha-1}\exp\left[-\left(\frac{k}{\beta}\right)^{\alpha}\right], \quad (62)$$

where $\alpha > 0$. This PDF is displayed in Fig. 7 for a reduced variable k/β. The mean of $H_\alpha(k)$ is $\beta\Gamma(1+\alpha^{-1})$. For $\alpha = 1$ the distribution is exponential, for $\alpha = 2$ it reduces to the Rayleigh distribution, and in the limit $\alpha \to \infty$ the delta distribution $\delta(k-1)$ is recovered. The asymptotic behavior of the Weibull decay law illustrates several of the cases discussed in Section 6 (see Tables 1 and 2). The asymptotic decay is $I(t) \sim t^{-\alpha}$, and $H_\alpha(k) \sim k^{\alpha-1}$. For $\alpha < 1$, $H_\alpha(0)$ is infinite. For $\alpha = 1$, $H_\alpha(0) > 0$. In both cases $\int_0^\infty I(t)\,dt$ diverges. Finally, for $\alpha > 1$, $H_\alpha(0) = 0$, and $\int_0^\infty I(t)\,dt$ is finite.

7.5. Truncated Gaussian probability density function

This PDF was already introduced in Section 5. Writing $\tau_0 = 1/\mu$ and the coefficient of variation $\alpha = \sigma/\mu = \sigma\tau_0$, Eq. (38) becomes

$$I(t) = \exp\left[-\frac{t}{\tau_0} + \frac{1}{2}\alpha^2\left(\frac{t}{\tau_0}\right)^2\right]. \quad (63)$$

This simple decay function, not widely known, is adequate for $t/\tau_0 < 10$ (i.e., the full time range of interest) if $\alpha < 0.25$. The asymptotic form of the truncated Gaussian is, on the other hand,

$$I(t) = \sqrt{\frac{2}{\pi}}\frac{\exp(-1/2\alpha^2)}{\alpha\,\mathrm{erfc}(-1/\sqrt{2}\alpha)}\frac{\tau_0}{t}, \quad (64)$$

and goes as t^{-1}, as could be expected from the results of Section 6. Note that this asymptotic behavior switches to an exponential one if the Gaussian PDF is truncated above zero, however slightly.

8. Discussion and conclusions

In this work, an analysis of the general properties of the luminescence decay law was carried out. The conditions that a luminescence decay law must satisfy in order to correspond to a probability density function of rate constants were established. From an analysis of the general form of the decay law, it was concluded that the decay must be either exponential or sub-exponential for all times, if $H(k)$ is to be a probability density function. Take for instance the hypothetical "compressed exponential" decay law $I(t) = \exp[-((t/\tau_0))^2]$. This decay law is super-exponential, as $w(t)$ increases monotonically with time. Its $H(k)$ takes both positive and negative values, and is thus not a PDF. Sub-exponentiality is nevertheless not a sufficient condition. For the hypothetical sub-exponential decay law $1/[1 + (t/\tau_0) + (t/\tau_0)^2/2]$, the function $H(k)$ can be obtained in closed form and is $2\tau_0 \exp(-k\tau_0)\sin(k\tau_0)$, taking both positive and negative values. Only decays that are completely monotonic have a PDF of rate constants. A new PDF of rate constants, $J(k,t)$, emerged as the central PDF of the problem. Cumulant and moment expansions of the decay can be obtained from this PDF, that is shown to be well-behaved and with all moments finite for $t > 0$, even when $H(k)$ is of the Lévy type. The asymptotic behavior of the decay laws was considered in detail, and the relation between this behavior and the form of $H(k)$ for small k was explored. Finally, several generalizations of the exponential decay function, namely the Kohlrausch, Becquerel, Mittag-Leffler and Heaviside decay functions, as well as the Weibull and truncated Gaussian rate constant distributions were analyzed in detail.

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