Brill Academic Publishers
P.O. Box 9000, 2300 PA Leiden
The Netherlands

Lecture Series on Computer
and Computational Sciences
Volume 4, 2005, pp. 70-73

Inverse Laplace transforms of luminescence relaxation functions

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Received 14 June, 2005; accepted in revised form 12 July, 2005

Abstract: Laplace transforms find application in many fields, including time-resolved luminescence. In this work, relations that allow a direct (i.e., dispensing contour integration) analytical calculation of the original function from its transform are re-derived and used for the determination of the distributions of rate constants of several relaxation functions, including the stretched exponential (Kohlrausch) and the compressed hyperbola (Becquerel) luminescence decay laws, and the asymptotic power law and the Mittag-Leffler relaxation functions. General results concerning the relation between relaxation function and distribution of rate constants are also obtained.

Keywords: Laplace transform, luminescence decay kinetics, relaxation function, stretched exponential, asymptotic power law, Mittag-Leffler function.

Mathematics Subject Classification: 33E12, 44A10, 60E07

PACS: 02.30.Gp, 02.30.Uu, 32.50.+d

1. Introduction

The Laplace transform $F(s)$ of a function $f(t)$ is defined by [1-3]

$$F(s)=\int_0^\infty f(t)e^{-st}\,dt\,. \tag{1}$$

The Laplace transform is a powerful tool for solving linear differential equations, ordinary and partial; linear difference equations; and linear equations involving convolutions. For this reason, it finds application in many fields. Furthermore, in relaxation processes, including time-resolved luminescence spectroscopy, the relaxation function is either the transform or the original function of a Laplace transform pair, the other function of the pair being also of physical relevance.

Luminescence decays are widely used in the physical, chemical and biological sciences to get information on the structure and dynamics of molecular, macromolecular, supramolecular, and nano systems [4]. In the simplest cases, luminescence decay curves can be satisfactorily described by a sum of discrete exponentials, and the respective pre-exponential factors and decay times have a clear physical meaning. However, the luminescence decays of inorganic solids are usually complex. Continuous distributions of decay times or rate constants are also necessary to account for the observed fluorescence decays of molecules incorporated in micelles, cyclodextrins, rigid solutions, sol-gel matrices, proteins, vesicles and membranes, biological tissues, molecules adsorbed on surfaces or linked to surfaces, energy transfer in assemblies of like or unlike molecules, etc.

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

$$I(t)=\int_0^\infty H(k)e^{-kt}\,dk\,, \tag{2}$$

with $I(0)=1$. This relation is always valid because $H(k)$ is the inverse Laplace transform of $I(t)$, which is a well-behaved function. 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

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rise-time in the decay), 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, PDF). This PDF, or distribution of rate constants, gives important information on the dynamics of the luminescent systems [5,6], but is not always easy to infer from the decay law $I(t)$. In the remaining of this work, and in view of the specific application to be considered, the notation of Eq. (2) will be retained.

The more difficult step in the application of Laplace transforms is the inversion of the transform to obtain the desired solution. In many cases, the inversion is accomplished by consulting published tables of Laplace transform pairs [1-3]. More generally, and in the absence of such a pair, the inversion integral can be applied [2,3]. This integral is

$$H(k)=\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} I(t)e^{kt}\,dt\,, \tag{3}$$

where c is a real number larger than c_0, c_0 being such that $I(z)$ has some form of singularity on the line $Re(z) = c_0$ but is analytic in the complex plane to the right of that line, i.e., for $Re(z) > c_0$. Eq. (3) is usually evaluated by contour integration [2,3].

2. General inverse Laplace transform

A simple form of the inverse Laplace transform of a relaxation function can be obtained by the method outlined in [7]. Briefly, the three following equations can be used for the direct inversion of a function $I(t)$ to obtain its inverse $H(k)$,

$$H(k)=\frac{e^{ck}}{\pi}\int_0^{\infty}\big[\mathrm{Re}[I(c+i\omega)\,]\cos(k\omega)-\mathrm{Im}[I(c+i\omega)]\sin(k\omega)\big]\,d\omega\,, \tag{4}$$

$$H(k)=\frac{2e^{ck}}{\pi}\int_0^{\infty}\mathrm{Re}[I(c+i\omega)\,]\cos(k\omega)\,d\omega \qquad k>0\,, \tag{5}$$

$$H(k)=-\frac{2e^{ck}}{\pi}\int_0^{\infty}\mathrm{Im}[I(c+i\omega)\,]\sin(k\omega)\,d\omega \qquad k>0\,. \tag{6}$$

where c was defined in Eq. (3).

3. An example of a continuous distribution: Stretched exponential (Kohlrausch) kinetics

For the stretched exponential (or Kohlrausch) decay law

$$I(t)=\exp\left[-\left(\frac{t}{\tau_0}\right)^{\beta}\right], \tag{7}$$

where τ_0 is a parameter with dimensions of time, one obtains, from Eqs. (4) and (7) [7,8]

$$H_\beta(k)=\frac{\tau_0}{\pi}\int_0^{\infty}\exp\left[-u^{\beta}\cos\left(\frac{\beta\pi}{2}\right)\right]\cos\left[k\tau_0 u-u^{\beta}\sin\left(\frac{\beta\pi}{2}\right)\right]du\,. \tag{8}$$

From Eqs. (5) and (6) alternative forms are ($k > 0$)

$$H_\beta(k)=\frac{2\tau_0}{\pi}\int_0^{\infty}\exp\left[-u^{\beta}\cos\left(\frac{\beta\pi}{2}\right)\right]\cos\left[u^{\beta}\sin\left(\frac{\beta\pi}{2}\right)\right]\cos\left(k\tau_0 u\right)du\,, \tag{9}$$

and

$$H_\beta(k)=\frac{2\tau_0}{\pi}\int_0^{\infty}\exp\left[-u^{\beta}\cos\left(\frac{\beta\pi}{2}\right)\right]\sin\left[u^{\beta}\sin\left(\frac{\beta\pi}{2}\right)\right]\sin\left(k\tau_0 u\right)du. \tag{10}$$

The function *$H_\beta(k)$* is plotted in Fig. 1 for several values of the parameter *β*.

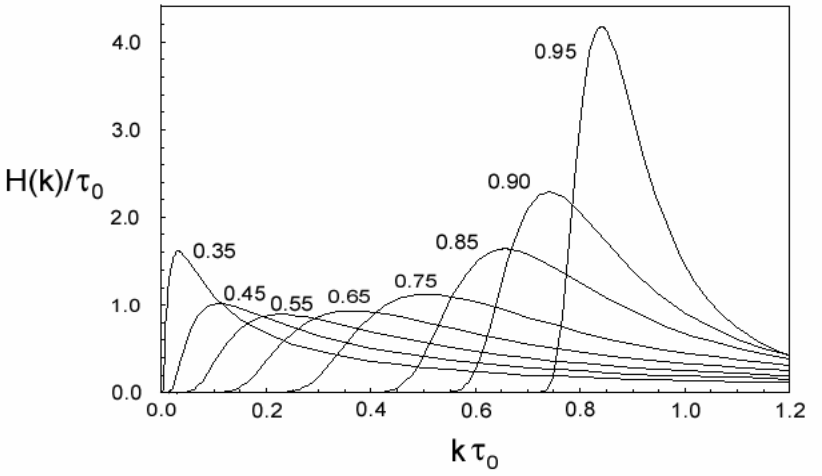

Figure 1: Distribution of rate constants (probability density function) for the Kohlrausch decay law obtained by numerical integration of Eqs. (8) and (13). The number next to each curve is the respective *β*.

$H_\beta(k)$ can be expressed by elementary functions only for *$\beta=1/2$*,

$$H_{1/2}(k)=\frac{e^{-\frac{1}{4k\tau_0}}}{\sqrt{4\pi k^3\tau_0}} \quad , \tag{11}$$

and is variously called Smirnov and Lévy PDF. A form explicitly displaying the asymptotic behavior for large *k* was recently obtained for *$\beta=1/4$* [9],

$$H_{1/4}(k)=\frac{\tau_0}{8\pi\,(k\tau_0)^{5/4}}\int_0^\infty u^{-3/4}\exp\left[-\frac{1}{4}\left(\frac{1}{\sqrt{k\tau_0 u}}+u\right)\right]du\ . \tag{12}$$

Pollard's relation [10] which is the only previously known integral representation of *$H_\beta(k)$*,

$$H_\beta(k)=\frac{\tau_0}{\pi}\int_0^\infty \exp\left(-k\tau_0 u\right)\exp\left[-u^\beta\cos\left(\beta\pi\right)\right]\sin\left[u^\beta\sin\left(\beta\pi\right)\right]du. \tag{13}$$

was obtained from Eq. (3) by defining a special contour. Eqs. (8)-(10) can also be obtained by contour integration [8], but not so directly as by the procedure described above.

4. An example of a discrete distribution: mixed first- and second-order kinetics

For mixed first- and second-order kinetics the decay of delayed fluorescence is [11]

$$I(t)=\left(\frac{\beta}{e^{k_1 t}-1+\beta}\right)^2, \tag{14}$$

where

$$\beta=\frac{k_1}{k_1+k_2N_0}, \tag{15}$$

and *N_0* is the initial number of excited luminophores. Eq. (14) gives, upon expansion

$$I(t)=\beta^2\sum_{n=1}^{\infty}n(1-\beta)^{n-1}e^{-(n+1)k_1 t}, \tag{16}$$

hence the rate constant spectrum is infinite but discrete

$$H(k)=\beta^2\sum_{n=1}^{\infty}n(1-\beta)^{n-1}\delta\left[k-(n+1)k_1\right]. \tag{17}$$

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