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Analytical inversion of the Laplace transform without contour integration: application to luminescence decay laws and other relaxation functions

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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. The results are used for the determination of distributions of rate constants of several relaxation functions, including the stretched exponential and the compressed hyperbolic luminescence decay laws, and the asymptotic power law relaxation function.

KEY WORDS: Laplace transform, luminescence decay, relaxation function, kinetics, stretched exponential, asymptotic power law

AMS subject classification: 44A10 Laplace transform

1. Introduction

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

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

where $F(s) = 0$ for $s < 0$ by definition. A brief history of this important integral transform is presented by Deakin [4, 5].

The Laplace transform is a powerful tool for solving ordinary and partial differential equations, linear difference equations and linear convolution equations. 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 [6]. 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:

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

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 $\int_0^\infty H(k)\mathrm{d}k = 1$. In most situations (e.g., in the absence of a 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 of the dynamics of the luminescent systems [7–10], 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 equation (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

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

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

2. A step further

Performing the change of variable $t = c + i\omega$, equation (3) becomes

$$H(k) = \frac{\mathrm{e}^{ck}}{2\pi}\int_{-\infty}^{\infty} I(c + i\omega)\mathrm{e}^{ik\omega}\,\mathrm{d}\omega \tag{4}$$

or

$$H(k) = \frac{e^{ck}}{2\pi}\left[\int_{-\infty}^{\infty} I(c+i\omega)\ \cos(k\omega)d\omega + i\int_{-\infty}^{\infty} I(c+i\omega)\ \sin(k\omega)d\omega\right]. \tag{5}$$

Writing

$$I(c+i\omega) = \mathrm{Re}[I(c+i\omega)] + i\ \mathrm{Im}[I(c+i\omega)], \tag{6}$$

Equation (5) becomes

$$\begin{aligned} H(k) = \frac{e^{ck}}{2\pi}\Bigg\{&\int_{-\infty}^{\infty}[\mathrm{Re}[I(c+i\omega)\ ]\cos(k\omega) - \mathrm{Im}[I(c+i\omega)]\sin(k\omega)]d\omega \\ &+i\int_{-\infty}^{\infty}[\mathrm{Re}[I(c+i\omega)\ ]\cos(k\omega) + \mathrm{Im}[I(c+i\omega)]\sin(k\omega)]d\omega\Bigg\}. \end{aligned} \tag{7}$$

Given that $H(k)$ is a real function,

$$0 = \int_{-\infty}^{\infty}[\mathrm{Re}[I(c+i\omega)\ ]\cos(k\omega) + \mathrm{Im}[I(c+i\omega)]\sin(k\omega)]d\omega, \tag{8}$$

and equation (7) reduces to

$$H(k) = \frac{e^{ck}}{2\pi}\int_{-\infty}^{\infty}[\mathrm{Re}[I(c+i\omega)\ ]\cos(k\omega) - \mathrm{Im}[I(c+i\omega)]\sin(k\omega)]d\omega. \tag{9}$$

But, from equation (2),

$$\begin{aligned} \mathrm{Re}[I(c+i\omega)] &= \int_0^{\infty} e^{-ck}H(k)\ \cos(k\omega)\ dk \\ \mathrm{Im}[I(c+i\omega)] &= -\int_0^{\infty} e^{-ck}H(k)\ \sin(k\omega)dk, \end{aligned} \tag{10}$$

hence the integrand in equation (9) is of even parity, and equation (9) can be rewritten as

$$H(k) = \frac{e^{ck}}{\pi}\int_0^{\infty}[\mathrm{Re}[I(c+i\omega)\ ]\cos(k\omega) - \mathrm{Im}[I(c+i\omega)]\sin(k\omega)]d\omega. \tag{11}$$

Using equations (8) and (10), equation (11) can be rewritten for $k > 0$ either as

$$H(k) = \frac{2e^{ck}}{\pi}\int_0^{\infty}\mathrm{Re}[I(c+i\omega)]\cos(k\omega)d\omega, \tag{12}$$

or

$$H(k) = -\frac{2e^{ck}}{\pi}\int_0^{\infty}\mathrm{Im}[I(c+i\omega)\ ]\sin(k\omega)d\omega. \tag{13}$$

Writing

$$I(c+i\omega) = \rho(\omega)\, \mathrm{e}^{i\theta(\omega)}. \tag{14}$$

Equations (11), (12) and (13) become, respectively,

$$H(k) = \frac{\mathrm{e}^{ck}}{\pi} \int_0^\infty \rho(\omega) \cos\left[k\omega + \theta(\omega)\right] \mathrm{d}\omega, \tag{15}$$

$$H(k) = \frac{2\mathrm{e}^{ck}}{\pi} \int_0^\infty \rho(\omega) \cos\left[\theta(\omega)\right] \cos k\omega \,\mathrm{d}\omega = -\frac{2\mathrm{e}^{ck}}{\pi} \int_0^\infty \rho(\omega) \sin\left[\theta(\omega)\right] \sin k\omega \,\mathrm{d}\omega. \tag{16}$$

These relations allow a direct calculation of $H(k)$ from $I(t)$ dispensing contour integration. It is surprising that the mentioned equations are not found in textbooks, e.g., [1, 3] and monographs on the Laplace transform, e.g., [2], given their simplicity and usefulness. The author has initially derived them (for $c = 0$) from Fourier transform theory, only to find out, after a careful literature search, that they were already available in a more general form, but somewhat hidden in publications on the numerical inversion of Laplace transforms [11–15]. Nevertheless, the relations are also interesting for the analytical calculation of inverse transforms, as will be shown in the next sections.

3. Some simple examples

Consider the elementary case

$$I(t) = \frac{1}{t-a}, \tag{17}$$

whose inverse is $\exp(ak)$. Application of equation (12), for instance, with $c > a$, yields

$$H(k) = \frac{2(c-a)\,\mathrm{e}^{ck}}{\pi} \int_0^\infty \frac{\cos(k\omega)}{(c-a)^2+\omega^2}\, \mathrm{d}\omega = \mathrm{e}^{ak}. \tag{18}$$

A similar calculation for

$$I(t) = \frac{t}{t^2+1}, \tag{19}$$

allows to obtain (with $c = 1$)

$$H(k) = \frac{2\,\mathrm{e}^{k}}{\pi} \int_0^\infty \frac{(\omega^2+2)\cos(k\omega)}{\omega^4+4}\, \mathrm{d}\omega = \cos k. \tag{20}$$

The definite integrals become rapidly of difficult evaluation in closed form, even for simple cases. On the other hand, they allow to obtain very easily results that are not so direct with contour integration, and are also suited for numerical evaluation of the original functions (by numerical integration [11–15]). The analytical calculation of the PDF's of luminescence decays and other relaxation functions is discussed in the next section.

4. Application to luminescence decays and other relaxation functions

In the case of luminescence decay functions, physical reasons preclude the existence of singularities, and the constant c in equations (11)–(16) can always be set to zero.

(a) Exponential decay

$$I(t) = \mathrm{e}^{-t/\tau_0},$$
$$I(i\omega) = \mathrm{e}^{-i\,\omega/\tau_0},$$
$$H(k) = \frac{1}{\pi}\int_0^{\infty} \cos\left[\omega\left(k - \frac{1}{\tau_0}\right)\right]\mathrm{d}\omega = \delta\left(k - \frac{1}{\tau_0}\right). \tag{21}$$

(b) Stretched exponential (Kohlrausch)

For the stretched exponential (or Kohlrausch) decay law

$$I(t) = \exp\left[-\left(\frac{t}{\tau_0}\right)^{\beta}\right], \tag{22}$$

One has,

$$I(i\omega) = \exp\left[-\left(\frac{i\omega}{\tau_0}\right)^{\beta}\right] = \exp\left[-\left(\frac{\omega}{\tau_0}\right)^{\beta}\cos\left(\frac{\beta\pi}{2}\right)\right] \times \exp\left[-i\left(\frac{\omega}{\tau_0}\right)^{\beta}\sin\left(\frac{\beta\pi}{2}\right)\right]. \tag{23}$$

and therefore, from equation (15),

$$H(k) = \frac{1}{\pi}\int_0^{\infty} \exp\left[-\left(\frac{\omega}{\tau_0}\right)^{\beta}\cos\left(\frac{\beta\pi}{2}\right)\right] \times \cos\left[k\omega - \left(\frac{\omega}{\tau_0}\right)^{\beta}\sin\left(\frac{\beta\pi}{2}\right)\right]\mathrm{d}\omega. \tag{24}$$

Performing the change of variable $u = \omega/\tau_0$ it is finally obtained that

$$H(k) = \frac{\tau_0}{\pi}\int_0^{\infty} \exp\left[-u^{\beta}\cos\left(\frac{\beta\pi}{2}\right)\right]\cos\left[k\tau_0 u - u^{\beta}\sin\left(\frac{\beta\pi}{2}\right)\right]\mathrm{d}u. \quad (25)$$

From equation (16) alternative forms are ($k > 0$)

$$H(k) = \frac{2\tau_0}{\pi}\int_0^{\infty} \exp\left[-u^{\beta}\cos\left(\frac{\beta\pi}{2}\right)\right]\cos\left[u^{\beta}\sin\left(\frac{\beta\pi}{2}\right)\right]\cos(k\tau_0 u)\mathrm{d}u, \quad (26)$$

and

$$H(k) = \frac{2\tau_0}{\pi}\int_0^{\infty} \exp\left[-u^{\beta}\cos\left(\frac{\beta\pi}{2}\right)\right]\sin\left[u^{\beta}\sin\left(\frac{\beta\pi}{2}\right)\right]\sin(k\tau_0 u)\mathrm{d}u. \quad (27)$$

Any normalised linear combination of equations (26) and (27) is also a valid solution. $H(k)$ can be expressed by elementary functions only for $\beta = 1/2$ [3, 16, 17],

$$H(k) = \frac{\mathrm{e} - 1/(4k\tau_0)}{\sqrt{4\pi k^3 \tau_0}} \quad (28)$$

and is variously called Smirnov [16] and Lévy [17] PDF.

Pollard's relation [18], which is the only previously known integral form for $H(k)$,

$$H(k) = \frac{\tau_0}{\pi}\int_0^{\infty} \exp(-k\tau_0 u)\exp\left[-u^{\beta}\cos(\beta\pi)\right]\sin\left[u^{\beta}\sin(\beta\pi)\right]\mathrm{d}u. \quad (29)$$

was obtained from the Bromwich integral (complex inversion integral) by defining a special contour. Equation (25) can of course also be obtained by contour integration [10], but not so directly.

(c) Compressed hyperbola (Becquerel)

For the compressed hyperbolic decay [10]

$$I(t) = \frac{1}{\left[1 + (1-\beta)\,\frac{t}{\tau_0}\right]^{1/(1-\beta)}}, \quad (30)$$

one has, successively,

$$I(i\omega) = \frac{1}{\left[1 + (1-\beta)\,\frac{i\omega}{\tau_0}\right]^{1/(1-\beta)}} = \left[1 + \left(\frac{(1-\beta)\,\omega}{\tau_0}\right)^2\right]^{-1/(2(1-\beta))}$$

$$\times \exp\left[-i\frac{\arctan\left(\frac{(1-\beta)\,\omega}{\tau_0}\right)}{1-\beta}\right], \quad (31)$$

$$H(k) = \frac{1}{\pi} \int_0^{\infty} \left[1 + \left(\frac{(1-\beta)\,\omega}{\tau_0} \right)^2 \right]^{-1/(2(1-\beta))} \cos \left[k\omega - \frac{\arctan\left(\frac{(1-\beta)\,\omega}{\tau_0}\right)}{1-\beta} \right] \mathrm{d}\omega, \tag{32}$$

$$H(k) = \frac{\tau_0}{\pi\,(1-\beta)} \int_0^{\infty} \left(1+u^2\right)^{-1/(2(1-\beta))} \cos\left(\frac{k\tau_0 u - \arctan u}{1-\beta} \right) \mathrm{d}u, \tag{33}$$

and from equation (16),

$$H(k) = \frac{2\tau_0}{\pi\,(1-\beta)} \int_0^{\infty} \left(1+u^2\right)^{-1/(2(1-\beta))} \cos\left(\frac{\arctan u}{1-\beta} \right) \cos\left(k\tau_0 u\right) \mathrm{d}u, \tag{34}$$

$$H(k) = \frac{2\tau_0}{\pi\,(1-\beta)} \int_0^{\infty} \left(1+u^2\right)^{-1/(2(1-\beta))} \sin\left(\frac{\arctan u}{1-\beta} \right) \sin\left(k\tau_0 u\right) \mathrm{d}u. \tag{35}$$

Equations (33)–(35) are alternative forms of the Gamma PDF,

$$H(k) = \frac{\tau_0}{1-\beta} \frac{(k\tau_0/(1-\beta)^{\beta/(1-\beta)} \exp\left(-(k\tau_0/(1-\beta))\right)}{\Gamma\left(1/(1-\beta)\right)}. \tag{36}$$

(d) Asymptotic power law

The asymptotic power law [19, 20]

$$I(t) = \frac{1}{1+(t/\tau_0)^{\alpha}} \tag{37}$$

with $\alpha < 1$, was suggested as an alternative to the stretched exponential relaxation function, for the description of peptide folding kinetics [20], and indeed also successfully fitted experimental data spanning seven orders of magnitude [20]. However, this equivalence does not hold for excited state kinetics: equation (37) is not a valid luminescence decay law over the entire time range, given that $\int_0^{\infty} \mathrm{I(t)}\, \mathrm{d}t$ is divergent for $\alpha < 1$.

It is interesting to compute the inverse Laplace transform of equation (37), i.e., the respective PDF of rate constants. Application of equation (12) yields

$$H(k) = \frac{2\tau_0}{\pi} \int_0^{\infty} \frac{u^{\alpha} \cos\left(\alpha\pi/2\right) + 1}{u^{2\alpha} + 2u^{\alpha}\cos\left(\alpha\pi/2\right) + 1} \cos\left(k\tau_0 u\right) \mathrm{d}u, \tag{38}$$

and equivalent expressions can be obtained from equations (11) and (13). A more complex expression for $H(k)$ is available [21]. Series expansion of equation (37) in powers of τ_0/t, followed by termwise Laplace inversion, allows to express $H(k)$ in terms of the generalized Mittag–Leffler function $E_{\alpha,\beta}(\mathrm{x})$[21],

$$H(k) = \tau_0 \left(\tau_0 k\right)^{\alpha-1} E_{\alpha,\alpha}\left(-\left(\tau_0 k\right)^{\alpha}\right), \tag{39}$$

where

$$E_{\alpha,\beta}(x) = \sum_{n=0}^{\infty} \frac{x^n}{\Gamma(\alpha n + \beta)}. \tag{40}$$

For $\alpha = 1/2$ equation (38) reduces to

$$H(k) = \tau_0 \left[\frac{1}{\sqrt{\pi \tau_0 k}} - \exp(\tau_0 k)\,\mathrm{erfc}\left(\sqrt{\tau_0 k}\right) \right]. \tag{41}$$

5. Conclusions

Laplace transforms find applications in several areas of physical and chemical relevance, including time-resolved luminescence and other relaxation phenomena. In this work, relations that allow a direct (i.e., dispensing contour integration) calculation of the original function from its transform were re-derived and applied to the analytical calculation of the distributions of rate constants of the stretched exponential and compressed hyperbolic luminescence decay laws, and also to the asymptotic power law relaxation function.

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