Improved computational methods for the calculation of Kohlrausch–Williams/Watts (KWW) decay functions*

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Convergence-accelerating methods have been applied to series expansions for the stable-law density

$$Q_\alpha(z)=\frac{1}{\pi}\int_0^\infty \mathrm{e}^{-u^\alpha}\cos(zu)\,\mathrm{d}u$$

which is, in turn, simply related to the spectral density of the Kohlrausch–Williams/Watts (KWW) decay function $\phi(t)=\mathrm{e}^{-(t/\tau)^\alpha}]$. N.m.r. relaxation parameters such as NOEF, T_1 and $T_{1\rho}$ are computed for polycarbonate and polydimethylsiloxane using the new series and the results compared to experiment and to earlier computations which employed a decomposition of the KWW function into a sum of exponential terms.

(Keywords: convergence acceleration; series expansions; stable-law density)

INTRODUCTION

The non-exponential character of molecular relaxation in glasses and polymers is well known, and several empirical model functions have been suggested to describe quantitatively the observed frequency and time dispersion. Some of the best known and most widely used examples, such as the Cole–Cole[1] (CC), Cole–Davidson[2] (CD) and combined Havriliak–Negami[3] (HN) functions, are closed-form expressions in the frequency domain which are convenient and popular for fitting and modelling experimental (frequency) data. Theories of molecular motion, on the other hand, highlight the central role of time correlation functions of molecular positions and orientations. In the case of dielectric and n.m.r. relaxation in isotropic systems, the time evolutions of specific molecular vectors are required, and some experiments are directly related to the autocorrelation function

$$\phi_{20}(t)\equiv\langle P_2(0)P_2(t)\rangle \tag{1}$$

where $P_2(t)=\frac{1}{2}\{1-3\cos^2[\theta(t)]\}$ is the second Legendre polynomial, $\theta(t)$ is the polar angle of the molecular vector at time t, and the angular brackets denote an equilibrium ensemble average taken at time $t=0$. The time dependences of other spherical harmonics are also usually needed, but subscripts on the correlation functions are ignored in the following discussion with attention centred on the time/frequency behaviour only. In Debye's original theory, $\phi(t)$ is found to be the simple exponential $\phi(t)=\mathrm{e}^{-t/\tau}$.

N.m.r. relaxation parameters are directly related to the Fourier transform of $\phi(t)$. The spectral density $j(\omega)$ corresponding to the molecular motion is defined[4] as the Fourier transform

$$j(\omega)\equiv\int_0^\infty \phi(t)\mathrm{e}^{-\mathrm{i}\omega t}\,\mathrm{d}t \tag{2}$$

with the understanding that $\phi(t)$ is real and symmetric in time. The CC, CD and HN functions are, of course, models of $j(\omega)$ and not $\phi(t)$. But as Shore and Zwanzig[5] point out, when one attempts to find the time correlation function $\phi(t)$ corresponding, for example, to the Cole–Cole function

$$j_{\mathrm{CC}}(\omega)=\frac{\tau}{1+(\mathrm{i}\omega\tau)^{1-\alpha}} \tag{3}$$

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it is found that $\phi(t)$ diverges at $t=0$. Thus, while these empirical $j(\omega)$ models are useful for fitting data, they have unphysical properties, which in turn suggests the difficulty in finding a satisfactory model for the underlying physical phenomenon.

Hoffman[6] developed the site model of relaxation with Pfeiffer to explain non-exponential dielectric response in crystalline solids in terms of a simple physical picture of the local crystal-field hindrance to internal rotations. The present article is concerned with the Kohlrausch–Williams/Watts[7] (KWW) model of relaxation in amorphous liquids and glasses

$$\phi_{\mathrm{KWW}}(t)=\mathrm{e}^{-(t/\tau)^{\alpha}} \qquad 0<\alpha\leqslant 1 \tag{4}$$

which Shlesinger and Montroll[8] derived from a model based on hindered defect diffusion. As is the case with the CC, CD and HN models, the early time behaviour of the KWW is unphysical in that a jump occurs at $t=0$. However, this aspect of the KWW is related to the neglect of inertia, and therefore corresponds to an obvious physical simplification which is easily removed[5]. This difficulty at early times is, of course, also shared by Debye's original result, a point recently discussed by Powles[9].

This paper reports a new method for the computation of the real and imaginary parts of the spectral density $j(\omega)$ defined by equation (2). N.m.r. applications use only the real part of $j(\omega)$, which is defined in the customary notation[4] by

$$J(\omega)=\mathrm{Re}[j(\omega)]=\int_0^{\infty}\phi(t)\cos(\omega t)\,\mathrm{d}t \tag{5}$$

When $\phi(t)$ is the KWW function of equation (4), our earlier studies combined parameters and introduced a standard notation[10,11]

$$Q_\alpha(z)=\frac{1}{\pi}\int_0^{\infty}\mathrm{e}^{-u^{\alpha}}\cos(zu)\,\mathrm{d}u \tag{6}$$

where $z=\omega\tau$.

SERIES EXPANSIONS FOR $Q_\alpha(z)$

A converging series for $Q_\alpha(z)$ for values of α in the range $0<\alpha\leqslant 1$ is found by expanding the exponential in equation (6) and integrating term by term

$$Q_\alpha(z)=\frac{1}{\pi}\sum_{n=1}^{\infty}(-1)^{n+1}\frac{\Gamma(1+n\alpha)}{n!z^{1+n\alpha}}\sin(\pi n\alpha/2) \tag{7}$$

If instead of expanding the exponential in equation (6) we expand the cosine we are led to a series which is formally divergent for values of α in (0, 1), but is nevertheless useful because it is an asymptotic series[12] in that range. This series has the form

$$Q_\alpha(z)=\frac{1}{\pi\alpha}\sum_{n=1}^{\infty}(-1)^{n+1}\frac{\Gamma\left(\dfrac{2n-1}{\alpha}\right)}{(2n-2)!}z^{2(n-1)} \tag{8}$$

which is useful for calculating values of $Q_\alpha(z)$ for small z.

We have found earlier[11] that equations (7) and (8) are inadequate for convenient computation of $Q_\alpha(z)$ at a number of intermediate z values (e.g. for $\alpha=0.4$, from $z=0.002$ to 0.004; for $\alpha=0.6$, from $z=0.05$ to 0.1). This difficulty can be overcome by numerically integrating a transformed form of the original expression in equation (6) to complement the remaining values of $Q_\alpha(z)$ obtained from the series in equations (7) and (8). We now find that a modified Euler transformation of the convergent series of equation (7) gives very satisfactory results for these values of z. A detailed specification of the transformed series requires that we define the difference operator Δ, which is the discrete analogue of a derivative. For example, if $f(n)$ is a function defined on the set of integers then the shift operator is defined by

$$\Delta f(n)=f(n+1)-f(n) \tag{9}$$

Higher powers of Δ are defined in an obvious way, e.g.

$$\Delta^2 f(n)=\Delta[\Delta f(n)]=f(n+2)-2f(n+1)+f(n) \tag{10}$$

and so forth.

In what follows we define the function $f(n)$ and an angle θ by

$$f(n)=\frac{\Gamma(1+n\alpha)}{\Gamma(1+n)},\quad \theta=\tan^{-1}\left[\frac{\sin(\pi\alpha/2)}{z^{\alpha}+\cos(\pi\alpha/2)}\right] \tag{11}$$

These functions allow us to write an alternative series for $Q_\alpha(z)$ as

$$Q_\alpha(z)=\frac{1}{\pi z^{1-\alpha}}\sum_{n=0}^{\infty}(-1)^n\frac{\sin[\beta n-(n+1)\theta]}{(1+2z^{\alpha}\cos\beta+z^{2\alpha})^{(n+1)/2}}\Delta^n f(0) \tag{12}$$

A derivation of this equation can be found in the Appendix. In the next section we apply equations (7), (8) and (10) to the computation of n.m.r. parameters for two polymers.

NUMERICAL RESULTS AND N.M.R. APPLICATIONS

A Fortran program was written to use the equations given above to compute $Q_\alpha(z)$. As a general check of the program the results shown in *Figure 1* compare the earlier tabulated values[11] of $zQ_\alpha(z)$ with some results produced by the new program for $\alpha=0.1$ and 0.5 over a wide range of z. Agreement to four decimal places is found between the values calculated by our program and those calculated

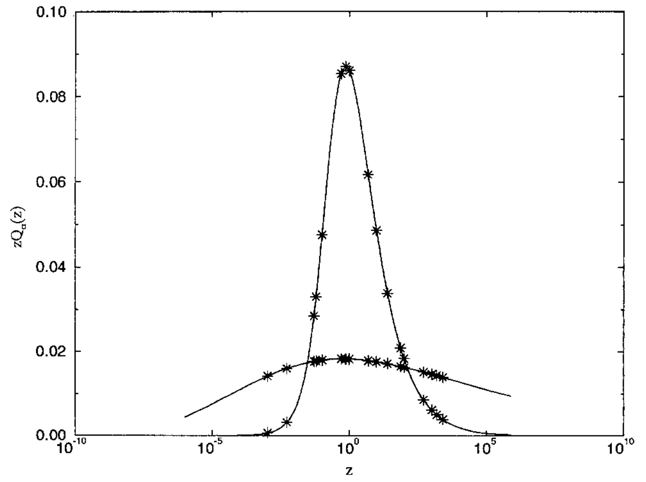

Figure 1 Comparisons between accurate values (*) of $zQ_\alpha(z)$, as tabulated to six-place accuracy in ref. 11, and (solid line) those calculated from the present algorithm for (a) $\alpha=0.1$ and (b) $\alpha=0.5$

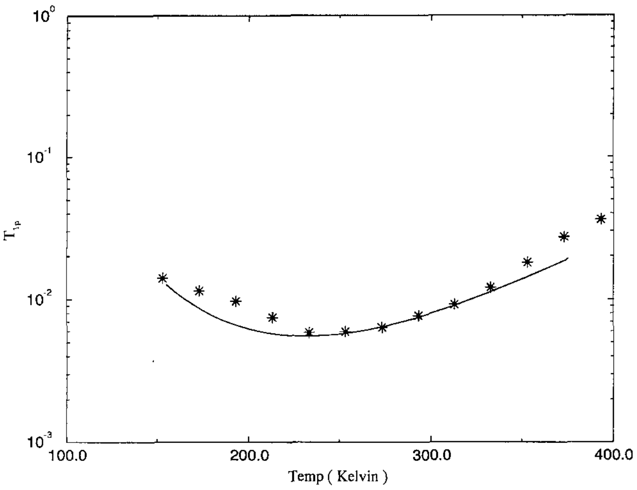

Figure 2 A comparison of experimentally obtained values of $T_{1\rho}$ for polycarbonate (∗), plotted as a function of temperature, against values obtained from equation (13) using the KWW function (solid line). The values obtained from the analysis in ref. 13 are indistinguishable from those obtained from the present formalism

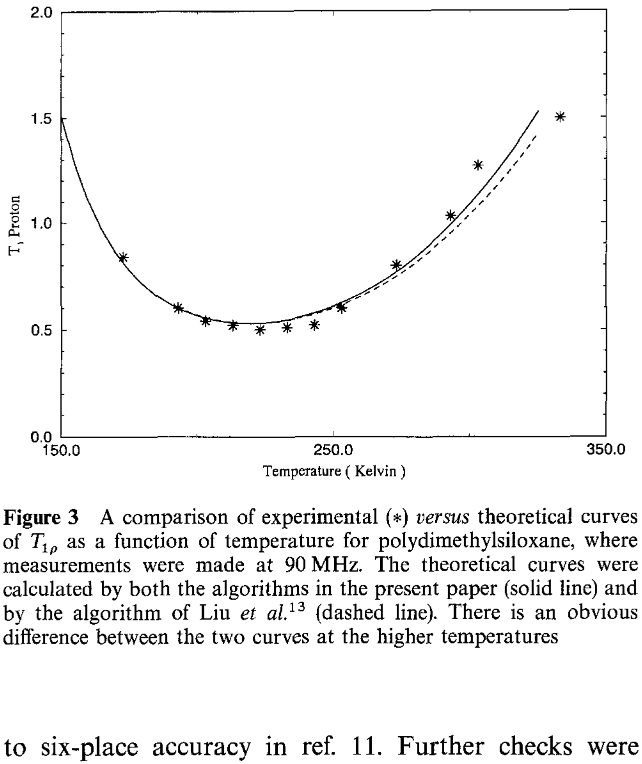

Figure 3 A comparison of experimental (∗) *versus* theoretical curves of $T_{1\rho}$ as a function of temperature for polydimethylsiloxane, where measurements were made at 90 MHz. The theoretical curves were calculated by both the algorithms in the present paper (solid line) and by the algorithm of Liu *et al.*[13] (dashed line). There is an obvious difference between the two curves at the higher temperatures

to six-place accuracy in ref. 11. Further checks were made for a large number of values of z and α in the physically interesting range $0.1 < \alpha \leqslant 1$. Our program also allows for the calculation for values of z larger and smaller than found in the tables in ref. 11. Equations (7) and (8) may be used to generate $Q_\alpha(z)$ for very small values of z (down to 1×10^{-20}) and for small values of α (of the order of 0.1), but quadruple precision is required in the program.

Figure 2 shows an application of our program in a computation of the proton $T_{1\rho}$ of polycarbonate. The equation for $T_{1\rho}$ is[13]

$$T_{1\rho}^{-1} = \tfrac{2}{3}\gamma^2 S[1.5J(2\omega_e) + 2.5J(\omega_H)] \qquad (13)$$

where γ is the gyromagnetic ratio, S is the intermolecular second moment, $\omega_e = \gamma H_{rf}$, ω_H is the Larmor frequency and $J(\omega)$ is the spectral density which is modelled by the KWW function with $\alpha = 0.14$ as indicated in equations (5) and (6). The computed value of $T_{1\rho}$ agrees almost exactly with that reported in ref. 13 which is based on an approximate representation of $\phi(t)$ as a sum of exponential terms. An example in which the two algorithms yield slightly different results is shown in *Figure 3*, which compares values of $T_{1\rho}$ for polydimethylsiloxane measured at 90 MHz against values predicted by a KWW formula. The value of $T_{1\rho}$ calculated from the algorithm of Liu *et al.*[13] is shown as a dashed line, while the results of the present algorithm are presented as a solid line.

Copies of the programs are available from the authors at General Electric. They can be contacted by e-mail at bendler@crd.ge.com.

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APPENDIX

Derivation of the generalized Euler transformation

Quite often the results of a physical calculation are expressed in terms of an infinite series. However, having in hand a formal series and being able to derive usable numerical results from it are not always synonymous. A common example of this difficulty occurs in the evaluation of many types of lattice sums that arise in solid-state physics, but other examples abound in the physical sciences[14]. To overcome the practical problems posed by slowly converging series one often has recourse to so-called convergence-accelerating techniques. A review of many of these methods is to be found in a recent monograph by Brezinski and Zaglia[15].

One of the earliest and most easily implementable of these techniques is known as the Euler transformation[12,15]. This transforms a series in which successive terms alternate in sign into a second series of this type which often has a dramatically improved convergence rate.

Specifically, let $\{a_n\}$ be a sequence of positive terms, and let S be the sum

$$S=\sum_{n=0}^{\infty}(-1)^n a_n \tag{A1}$$

The Euler transformation converts this into the equivalent

$$S=\sum_{n=0}^{\infty}\frac{(-1)^n}{2^{n+1}}\Delta^n a_0 \tag{A2}$$

where the difference operator has been defined in the text. A dramatic illustration of the effectiveness of the Euler transformation is provided by the case in which $a_n=(1-10^{-6})^n$, for which $S=0.50000025$. A direct sum of the first 10^6 terms in equation (A1) gives a value equal to 0.68394006, which in most cases is a completely unsatisfactory approximation to the true value. On the other hand, just two terms of the transformed series suffice to reproduce the value of S to the number of digits shown. A parenthetical but relevant remark is that the transformed series in equation (A2) is not necessarily more quickly convergent than that in equation (A1), as evidenced by the series defined by $a_n=(0.1)^n$ for which equation (A1) yields far quicker convergence than does the transformed equation (A2).

When $\alpha \leqslant 1$ equation (7) gives a convergent, but not necessarily useful, Fourier series representation for $Q_\alpha(z)$. Calculating the sum of this series can be problematic, either because of slow convergence or because of the erratic behaviour of the partial sums. To overcome this difficulty we derive a transformation for a Fourier series, analogous to the Euler transformation in equation (7), which can often accelerate the convergence of such series. This type of transformation can be applied in many other fields, exemplified by the Dubner–Abate method for numerical inversion of Laplace transforms[16]. Our starting point in the derivation is the general definition

$$S(x,\beta)=\sum_{n=0}^{\infty}(-1)^n a_n x^n \mathrm{e}^{\mathrm{i}n\beta} \tag{A3}$$

in which x is real. Equation (7) for $Q_\alpha(z)$ can be identified with this form of the series by writing

$$Q_\alpha(z)=-\mathrm{Im}\left[S\left(\frac{1}{z^\alpha},\frac{\pi\alpha}{2}\right)\right] \tag{A4}$$

where the a_n are

$$a_n=\frac{1}{\pi z}\frac{\Gamma(1+n\alpha)}{\Gamma(1+n)} \tag{A5}$$

and 'Im' means 'the imaginary part of'.

To derive the generalized transformation we first define a shift operator E which converts a function $b(n)$ into $b(n+1)$. That is to say, E is defined by the property

$$\mathrm{E}b(n)=b(n+1) \tag{A6}$$

The definition in equation (9) indicates that that difference operator Δ is formally related to E by

$$\Delta=\mathrm{E}-1 \tag{A7}$$

or $\mathrm{E}=\Delta+1$. Equation (A3) can be rewritten in terms of the operator E as

$$S(x,\beta)=\sum_{n=0}^{\infty}(-1)^n x^n \mathrm{e}^{\mathrm{i}n\beta}\mathrm{E}^n \mathrm{a}_0=\frac{1}{1+x\mathrm{E}\mathrm{e}^{\mathrm{i}\beta}}a_0 \tag{A8}$$

where we have used the fact that the series can be thought of as being geometric. The last term in equation (A8) can be re-expanded to yield an equivalent expression in terms of Δ. This allows us to write for $S(x,\beta)$

$$S(x,\beta)=\frac{1}{1+x\mathrm{e}^{\mathrm{i}\beta}(1+\Delta)}a_0=\sum_{n=0}^{\infty}(-1)^n\frac{x^n\mathrm{e}^{\mathrm{i}\beta n}}{(1+x\mathrm{e}^{\mathrm{i}\beta})^{n+1}}\Delta^n a_0 \tag{A9}$$

Notice that the original Euler transformation can be recovered from this formula by setting $\beta=0$ and $x=1$. If x and the a_n are real, equation (A9) can be decomposed into real and imaginary parts as

$$S(x,\beta)=\sum_{n=0}^{\infty}(-1)^n\frac{x^n}{(1+2x\cos\beta+x^2)^{(n+1)/2}} \times\{\cos[n\beta-(n+1)\theta]+\mathrm{i}\sin[n\beta-(n+1)\theta]\}\Delta^n a_0 \tag{A10}$$

in which

$$\theta=\tan^{-1}\left(\frac{x\sin\beta}{1+x\cos\beta}\right) \tag{A11}$$

Equations (A10) and (A11) together with equation (A4) imply our result given in equation (12) in the text.