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Pulse response functions of dielectric susceptibility

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As dielectric response in the time domain is becoming increasingly of experimental relevance and as such responses for quite a number of well-established susceptibility formulae are still unknown, we examine in this paper how pulse response functions may be calculated from susceptibility by use of various integral transform methods. We need to specialize some parameters in many cases to keep the mathematics sufficiently tractable. The asymptotic behaviour of pulse responses are then classified. Finally we comment on the adequacy of the Shin–Yeung response in the time domain.

1. Introduction

There exists in the literature a variety of formulae (see e.g. reference [1]) for the description of dynamical dielectric susceptibility $\hat{\chi}(\omega)$ of dielectric materials. Some are built directly from the step-response function (or time decay function of the polarization) $\Phi(t)$ such as in the Debye [2], Williams–Watts [3] and Dissado–Hill [4] models while others are modified either from the complex $\hat{\chi}(\omega)$ of the Debye formula $\chi(0)/(1 + i\omega\tau)$ where τ is the relaxation time constant, or simply from its loss part $\omega\tau/(1 + \omega^2\tau^2)$. On the other hand, Shin and Yeung [5] have discovered a very general expression for the dielectric susceptibility spectral shape function $\hat{F}(\omega) = \hat{\chi}(\omega)/\chi(0)$ from the solution of the non-linear differential equation

$$\mathscr{Q}(\mathscr{Q}(F)) = k\,\mathscr{Q}(F) \qquad (1)$$

where k is a parameter and $\mathscr{Q}$ is a differential operator defined by

$$\mathscr{Q}(F) = x\frac{\mathrm{d}^2}{\mathrm{d}x^2}(\ln F) + \frac{\mathrm{d}}{\mathrm{d}x}(\ln F)$$

where $x = \omega\tau$. It is demonstrated in that paper that the Debye, Cole–Cole [6], Davidson–Cole [7], Havriliak–Negami [8] and Nakamura–Ishida [9] complex dielectric susceptibility formulae as well as the Fuoss–Kirkwood [10], Jonscher [11] and Hill [12] dielectric loss formulae all satisfy Equation 1. The solution to Equation 1 has been obtained as

$$F(x) = \frac{N}{x^c}\operatorname{sech}^a(b\ln\theta x) \qquad (2)$$

where N is a normalization constant and the various parameters a, b, c and θ corresponding to the aforementioned spectral shape functions were worked out in [5]. In particular, Shin and Yeung [13] have recently suggested a new empirical dielectric loss formula which is a special case of Equation 2 with $b = \frac{1}{2}$ and has a real susceptibility integrable from Kramers–Kronig relations. There are however still several famous dielectric susceptibility formulae such as the Dissado–Hill, Williams–Watts, Kirkwood–Fuoss [14], Fröhlich [15] and Matsumoto–Higasi [16] formulae having forms at variance with Equation 2. Their common feature is that the susceptibility is derived subsequently from a pulse response function or distribution of relaxation times. Basically, the pulse response function represents the time domain properties of the dielectric material and is measured by the transient decay (or relaxation) current which can supplement the frequency domain properties provided by the dynamical dielectric measurements. There is increasing popularity in modern instrumentation with respect to dielectric studies to obtain frequency domain information via the use of hardware FFT on transient measurements. This in a way is making the pulse response function increasingly of direct experimental concern. Since Equation 2 is not sufficiently general to cover some well-known susceptibility formulae in the frequency domain, it will be useful and perhaps also illuminating to study their differences in the time domain.

Unfortunately, while systematic compilation of susceptibility formulae are fairly well done in the literature, there is little similar effort for the corresponding pulse response functions. This may be partly due to the necessity of involving complex mathematics in the derivation of many of those functions, and partly to the fact that in the past decades pulse responses are seldom measured. Hence the pulse response functions for quite a number of famous dielectric formulae are still unknown.

In this paper, we examine how pulse response functions may be worked out from susceptibility formulae by various integral transform methods. As the derivation details are lengthy and complex, only the final expressions are presented. In many cases, we need to specialize some parameters to make the derivation manageable. Our results are presented in Tables I and II together with some known responses. Then we discuss the asymptotic forms of the pulse response

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functions according to which a natural classification into three categories is possible. Lastly we examine the adequacy of the time domain behavior of the Shin–Yeung empirical formula [13] in the description of the susceptibility of glycerol.

2. The pulse response functions

In this work, the pulse response function $\phi(t)$ is defined in such a way that its Laplace transform $\mathscr{L}$ to $\mathrm{i}\omega$ is the spectral shape function $\hat{F}(\omega)$, i.e.

$$\hat{F}(\omega) = \mathscr{L}_{\mathrm{i}\omega}[\phi] = \int_0^\infty \mathrm{e}^{-\mathrm{i}\omega t}\phi(t)\,\mathrm{d}t \qquad (3)$$

Here $\hat{F}(\omega)$ is properly normalized so that $\hat{F}(0) = 1$. Note that the step response function $\Phi(t)$ can be expressed in terms of the pulse response function $\phi(t)$ by

$$\Phi(t) = \int_t^\infty \phi(t)\,\mathrm{d}t$$

which satisfies the boundary conditions that $\Phi(0) = 1$ and $\Phi(\infty) = 0$.

2.1. Pulse response functions from complex susceptibility

From Equation 3, the pulse response function is given by the inverse Laplace transform $\mathscr{L}^{-1}$ (or inverse Fourier transform $\mathscr{F}^{-1}$ as the spectral shape function must satisfy the Kramers–Kronig relations) as follows

$$\phi(t) = \mathscr{L}_t^{-1}[\hat{F}] = \mathscr{F}_t^{-1}[\hat{F}] = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{e}^{\mathrm{i}\omega t}\hat{F}(\omega)\,\mathrm{d}\omega \qquad (4)$$

Although it is usually a formidably difficult task to evaluate this integral analytically for many susceptibility formulae, we find it possible to obtain analytical results for some special cases of a given formula by making use of tables of Fourier transforms available in the literature (see e.g. reference [17]). Consider a special case of the Havriliak–Negami [8] formula $\hat{F}(\omega) = [1 + (\mathrm{i}\omega\tau)^{1-\alpha}]^{-\beta}$ with $\alpha = \frac{1}{2}$. Using Equation 4, we get

$$\phi(t) = \frac{2\beta}{\tau(2\pi)^{\frac{1}{2}}}\left(\frac{2t}{\tau}\right)^{\beta/2-1} \mathrm{e}^{t/2\tau} D_{-\beta-1}((2t/\tau)^{\frac{1}{2}})$$
$$= \frac{\beta}{\tau}\left(\frac{t}{\tau}\right)^{\beta/2-1}\left\{\frac{{}_1F_1\left(\frac{1+\beta}{2};\frac{1}{2};\frac{t}{\tau}\right)}{\Gamma\left(1+\frac{\beta}{2}\right)} - 2(t/\tau)^{\frac{1}{2}}\frac{{}_1F_1\left(1+\frac{\beta}{2};\frac{3}{2};\frac{t}{\tau}\right)}{\Gamma\left(\frac{1+\beta}{2}\right)}\right\}$$

where Γ, D_ν and ${}_1F_1(\ ;\ ;\ )$ are, respectively, the gamma, parabolic cylinder and confluent hypergeometric functions (see [18] for their definitions). It is noted that the present $\hat{F}(\omega)$ is also a special case of Equation 2 with $a = \beta$, $b = 1/4$, $c = a/4$ and $\theta = \mathrm{i}$.

If we apply Equation 4 to the Nakamura–Ishida formula [9] $\hat{F}(\omega) = 1/[1 + \mathrm{i}^\beta\omega\tau]$, $0 < \beta \le 1$ then we get

$$\phi(t) = \frac{1}{\tau}\exp\left\{-\frac{t}{\tau}\sin\frac{\beta\pi}{2} - \mathrm{i}\left(\frac{(\beta-1)\pi}{2} + \frac{t}{\tau}\cos\frac{\beta\pi}{2}\right)\right\}$$

which is in general complex unless $\beta = 1$. This result is physically unacceptable because the formula itself has the innate defect of not fulfilling the Kramers–Kronig relation. Hence, we shall discard further analysis of it in this paper.

2.2. Pulse response functions from loss part

Very often there are many empirical formulae on the loss part of the dielectric constant only, i.e., the imaginary part F'' of the spectral shape function $\hat{F}(\omega) \equiv F'(\omega) - \mathrm{i}F''(\omega)$. It is therefore better to derive the pulse response function directly from F'' via the Fourier Sine transform $\mathscr{F}^{\mathrm{s}}$:

$$\phi(t) = \frac{2}{\pi}\mathscr{F}_t^{\mathrm{s}}[F''] = \frac{2}{\pi}\mathscr{Im}\{\mathscr{L}_{-\mathrm{i}t}[F'']\} = \frac{2}{\pi}\int_0^\infty \sin\omega t\,F''(\omega)\,\mathrm{d}\omega \qquad (5)$$

Here we are able to apply Equation 5 to special cases of the following dielectric loss expressions.

(a) *For the Jonscher formula* [11] *with* $n = m$,

$$F''(\omega) = \frac{\sin(n\pi)}{2}\frac{(\theta\omega\tau)^n}{(1+\theta\omega\tau)}.$$

We obtain

$$\phi(t) = \frac{1}{\theta\tau}\sin\left(\frac{t}{\theta\tau}\right) + \frac{\Gamma(n)\sin(n\pi)}{\pi\theta\tau}\left(\frac{t}{\theta\tau}\right)^{-n} \times \mathscr{Im}\left[\mathrm{e}^{\mathrm{i}\left(\frac{n\pi}{2}-\frac{t}{\theta\tau}\right)}{}_1F_1\left(-n;1-n;\frac{\mathrm{i}t}{\theta\tau}\right)\right]$$

and the real part of the spectral shape function

$$F'(\omega) = \frac{1-\cos(n\pi)x^n}{2(1+x)} + \frac{1-x^n}{2(1-x)}$$

where $x = \theta\omega\tau$. When we put $n = \frac{1}{2}$ and $\theta = 1$, the present case is further reduced to a special case of the Fuoss–Kirkwood loss $F''(\omega) = \alpha/2\,\mathrm{sech}(\alpha\ln(\omega\tau))$ with $\alpha = \frac{1}{2}$. The corresponding $\phi(t)$ becomes

$$\tau\phi(t) = \left(\frac{\tau}{2\pi t}\right)^{1/2} + \sin\left(\frac{t}{\tau}\right) - 2^{\frac{1}{2}}\sin\left(\frac{t}{\tau}+\frac{\pi}{4}\right) \times C\left(\frac{t}{\tau}\right) + 2^{\frac{1}{2}}\cos\left(\frac{t}{\tau}+\frac{\pi}{4}\right)S\left(\frac{t}{\tau}\right)$$

where C and S are the Fresnel cosine and sine integrals respectively.

(b) *For the Hill formula* [12] *with* $s = 1$,

$$F''(\omega) = \frac{\pi\Gamma\left(\frac{1-n+m}{2}\right)}{\Gamma\left(\frac{m}{2}\right)\Gamma\left(\frac{1-n}{2}\right)}\frac{(\omega\tau)^m}{[1+(\omega\tau)^2]^{(1-n+m)/2}}$$

We obtain

$$\phi(t) = \frac{-m}{\tau(1+n)}\left(\frac{t}{\tau}\right) \times {}_1F_2\left(1+\frac{m}{2};\frac{3+n}{2},\frac{3}{2};\left(\frac{t}{2\tau}\right)^2\right) + \frac{\Gamma\left(\frac{1-n+m}{2}\right)\Gamma\left(\frac{1+n}{2}\right)}{\tau\Gamma\left(\frac{m}{2}\right)\Gamma(1-n)}\left(\frac{t}{\tau}\right)^{-n} \times {}_1F_2\left(\frac{1-n+m}{2}; 1-\frac{n}{2},\frac{1-n}{2};\left(\frac{t}{2\tau}\right)^2\right)$$

where ${}_1F_2(\,;\,,\,;\,)$ is a generalized hypergeometric function. We may concisely express $\phi(t)$ in terms of a single Meijer's **G**-function (see [18] for the definition) so that

$$\phi(t) = \frac{\pi^{\frac{1}{2}}}{\tau\Gamma\left(\frac{m}{2}\right)\Gamma\left(\frac{1-n}{2}\right)} \times \mathbf{G}^{21}_{13}\left(\left(\frac{t}{2\tau}\right)^2 \middle| \begin{matrix}\frac{1-m}{2}\\ \frac{-n}{2},\frac{1}{2},0\end{matrix}\right)$$

Putting the above $\phi(t)$ into Equation 3, we get the complex spectral shape function

$$\hat{F}(\omega) = \frac{m}{(1+n)(1+x^2)} \times {}_2F_1\left(1,\frac{1+n-m}{2};\frac{3+n}{2};\frac{1}{1+x^2}\right) + \left(\tan\frac{n\pi}{2}-\mathrm{i}\right)\frac{\pi}{B\left(\frac{m}{2},\frac{1-n}{2}\right)} \times \frac{x^m}{(1+x^2)^{(1-n+m)/2}}$$

where $x = \omega\tau$ and $B(\,,\,)$ and ${}_2F_1(\,,\,;\,;\,)$ are the Beta and Gaussian hypergeometric functions, respectively.

(c) *For the Shin–Yeung formula* [5] *with* $b = \frac{1}{2}$ [13],

$$F''(\omega) = \frac{\pi\Gamma(a)}{2\Gamma\left(\frac{a}{2}-c\right)\Gamma\left(\frac{a}{2}+c\right)}\frac{x^{a/2-c}}{(1+x)^a}$$

where $x = \theta\omega\tau$. To make the parameters compatible with Hill's and Jonscher's expressions, we take $a = 1-n+m$ and $c = (1-n-m)/2$ so that

$$F''(\omega) = \frac{\pi}{2}B(m, 1-n)\frac{x^m}{(1+x)^{1-n+m}}$$

and the real part has been obtained [13] from a Hilbert transform as

$$F'(\omega) = \frac{-\pi x^m}{2B(m,1-n)\sin(m\pi)} \times \left[\frac{\cos m\pi}{(1+x)^{1-n+m}} + \frac{1}{(1-x)^{1-n+m}}\right] + \tfrac{1}{2}[{}_2F_1(1,1-n;1-m;x) + {}_2F_1(1,1-n;1-m;-x)]$$

The corresponding pulse response function is found by Equation 5 to be

$$\phi(t) = \frac{-m}{n\theta\tau}\mathscr{Im}\left[\mathrm{e}^{-\frac{it}{\theta\tau}}{}_1F_1\left(n-m;1+n;\frac{it}{\theta\tau}\right)\right] + \frac{\Gamma(n)}{\theta\tau B(m,1-n)}\left(\frac{t}{\theta\tau}\right)^{-n} \times \mathscr{Im}\left[\mathrm{e}^{\mathrm{i}\left(\frac{n\pi}{2}-\frac{t}{\theta\tau}\right)}{}_1F_1\left(-m;1-n;\frac{it}{\phi\tau}\right)\right]$$

which becomes identical to the one for the Jonscher expression when we set $n = m$.

2.3. Pulse response functions from distribution of relaxation time

Occasionally, there are dielectric susceptibility formulas based on the distribution function $g(\tau)$ of relaxation time τ which is related to the spectral shape function by

$$\hat{F}(\omega) = \int_0^\infty \frac{g(\tau)\,\mathrm{d}\tau}{1+\mathrm{i}\omega\tau}$$

from which we can find the pulse response function

$$\phi(t) = \int_0^\infty \frac{g(\tau)\mathrm{e}^{-t/\tau}}{\tau}\mathrm{d}\tau \qquad (6)$$

Here we apply this equation to the following distribution functions.

(a) *Kirkwood–Fuoss distribution function* [14],

$$g(\tau) = \frac{\tau_0}{(\tau+\tau_0)^2}$$

We obtain $\phi(t) = \dfrac{1}{\tau_0}\left\{\left(\dfrac{t}{\tau_0}+1\right)\mathrm{e}^{t/\tau_0}E_1\left(\dfrac{t}{\tau_0}\right) - 1\right\}$

where the exponential integral

$$E_1(x) \equiv \int_x^\infty \frac{\mathrm{e}^{-y}}{y}\mathrm{d}y.$$

Furthermore, we get the complex spectral shape function by Equation 3

$$\hat{F}(\omega) = \mathscr{L}_{\mathrm{i}\omega}[\phi] = \frac{1}{1-\mathrm{i}x} - \frac{\pi x}{2(1-\mathrm{i}x)^2} + \frac{\mathrm{i}x}{(1-\mathrm{i}x)^2}\ln x$$

where $x = \omega\tau_0$.

(b) *Matsumoto–Higasi distribution function* [16],

$$g(\tau) = \frac{p}{\tau_1^p - \tau_2^p}\tau^{p-1} \quad \text{for } \tau_2 < \tau < \tau_1$$
$$= 0 \quad \text{otherwise.}$$

We obtain

$$\phi(t) = \frac{p}{(1-p)(\tau_1^p - \tau_2^p)} \times \left\{ \frac{1}{\tau_2^{1-p}} {}_1F_1\left(1-p; 2-p; \frac{-t}{\tau_2}\right) - \frac{1}{\tau_1^{1-p}} {}_1F_1\left(1-p; 2-p; \frac{-t}{\tau_1}\right) \right\}$$

and

$$\hat{F}(\omega) = \frac{p}{(1-p)(\tau_1^p - \tau_2^p)} \times \left[\frac{\tau_2^p}{(1+\mathrm{i}\omega\tau_2)} {}_2F_1\left(1,1; 2-p; \frac{1}{1+\mathrm{i}\omega\tau_2}\right) - \frac{\tau_1^p}{(1+\mathrm{i}\omega\tau_1)} \times {}_2F_1\left(1,1; 2-p; \frac{1}{1+\mathrm{i}\omega\tau_1}\right) \right].$$

Originally, Matsumoto and Higasi had obtained the expressions of $\phi(t)$ and $\hat{F}(\omega)$ for the values of $p = \pm 1/3$, $\pm 1/2$ and $\pm 2/3$ only.

2.4. Summary of pulse response functions

Having obtained pulse response functions by various integral transforms, we tabulate in Tables I and II our results together with those known from the literature for the following often-quoted formulae.

(a) *Debye* [2]: $\dfrac{1}{1 + \mathrm{i}x}$

(b) *Cole–Cole* [6]: $\dfrac{1}{1 + (\mathrm{i}x)^{1-\alpha}}$ for $0 \leq \alpha < 1$

with the special case $\alpha = 1/2$ and $\hat{F}(\omega) = 1/[1 + (\mathrm{i}x)^{1/2}]$

(c) *Davidson–Cole* [7]: $1/(1 + \mathrm{i}x)^{\beta}$ for $0 < \beta \leq 1$

(d) *Williams–Watts* [3]:

$$\sum_{n=1}^{\infty} \frac{(-1)^{n-1}\Gamma(n\beta + 1)}{\Gamma(n+1)} \left(\frac{1}{\mathrm{i}x}\right)^{n\beta}$$

for $0 < \beta < 1$

(e) *Dissado–Hill* [4]:

$$\frac{\Gamma(1-n+m)\, {}_2F_1(1-n, 1-m; 2-n; 1/(1+\mathrm{i}x))}{\Gamma(2-n)\Gamma(m)(1+\mathrm{i}x)^{1-n}}$$

(f) *Fröhlich* [15]: $$\frac{1}{\ln(\tau_1/\tau_2)} \left\{ \ln\left[\frac{\tau_1(1+\omega^2\tau_2^2)^{1/2}}{\tau_2(1+\omega^2\tau_1^2)^{1/2}}\right] - \mathrm{i}(\tan^{-1}\omega\tau_1 - \tan^{-1}\omega\tau_2) \right\}$$

In the above formulae, x stands for $\omega\tau$.

TABLE I Pulse response functions for complex dielectric formula

Formula	Pulse response function $\phi(t)$
Debye	$\frac{1}{\tau} e^{-t/\tau}$
Cole–Cole	$\frac{1}{\tau} \sum_{n=1}^{\infty} \frac{(-1)^n \left(\frac{t}{\tau}\right)^{-n(1-\alpha)-1}}{\Gamma(n(\alpha-1))}$, for $t > \tau$
	$\frac{1}{\tau} \sum_{n=0}^{\infty} \frac{(-1)^n \left(\frac{t}{\tau}\right)^{n(1-\alpha)-\alpha}}{\Gamma((n+1)(1-\alpha))}$, for $t < \tau$
	$(\pi\tau t)^{-\frac{1}{2}} - \frac{1}{\tau} e^{t/\tau} \mathrm{Erfc}[(t/\tau)^{\frac{1}{2}}]$, for $\alpha = 1/2$
Davidson–Cole	$\frac{1}{\tau\Gamma(\beta)} \left(\frac{t}{\tau}\right)^{\beta-1} e^{-t/\tau}$
Williams–Watts	$\frac{\beta}{\tau}\left(\frac{t}{\tau}\right)^{\beta-1} e^{-(t/\tau)^{\beta}}$
Kirkwood–Fuoss	$\frac{1}{\tau}\left\{\left(\frac{t}{\tau}+1\right) e^{t/\tau} E_1\left(\frac{t}{\tau}\right) - 1\right\}$
Fröhlich	$\frac{e^{-t/\tau_1} - e^{-t/\tau_2}}{t \ln(\tau_1/\tau_2)}$ $\tau_2 < \tau_1$
Havriliak–Negami (with $\alpha = 1/2$)	$\frac{2\beta}{\tau(2\pi)^{\frac{1}{2}}}\left(\frac{2t}{\tau}\right)^{\beta/2-1} e^{t/2\tau} D_{-\beta-1}((2t/\tau)^{\frac{1}{2}})$
Matsumoto–Higasi	$\frac{p}{(1-p)(\tau_1^p - \tau_2^p)}\left\{\frac{1}{\tau_2^{1-p}} {}_1F_1\left(1-p; 2-p; \frac{-t}{\tau_2}\right) - \frac{1}{\tau_1^{1-p}} {}_1F_1\left(1-p; 2-p; \frac{-t}{\tau_1}\right)\right\}$
Dissado–Hill	$\frac{\Gamma(1-n+m) e^{-t/\tau}\left(\frac{t}{\tau}\right)^{-n} {}_1F_1\left(1-m; 2-n; \frac{t}{\tau}\right)}{\tau\Gamma(1-n)\Gamma(2-n)\Gamma(m)}$

TABLE II Pulse response functions for special cases of dielectric loss models

Model (special case)	Parameters of Equation 2	Pulse response function $\phi(t)$
Fuoss–Kirkwood ($\alpha = 1/2$)	$a = 1,\ b = 1/2$ $c = 0,\ \theta = 1$	$\frac{1}{(2\pi\tau t)^{\frac{1}{2}}} + \frac{1}{\tau}\left[\sin\left(\frac{t}{\tau}\right) - 2^{\frac{1}{2}}\sin\left(\frac{t}{\tau} + \frac{\pi}{4}\right)C\left(\frac{t}{\tau}\right) + 2^{\frac{1}{2}}\cos\left(\frac{t}{\tau} + \frac{\pi}{4}\right)S\left(\frac{t}{\tau}\right)\right]$
Jonscher ($n = m$)	$a = 1,\ b = 1/2$ $c = \frac{1}{2} - n$	$\frac{1}{\theta\tau}\sin\left(\frac{t}{\theta\tau}\right) + \frac{\Gamma(n)\sin(n\pi)}{\pi\theta\tau}\left(\frac{t}{\theta\tau}\right)^{-n} \times \mathscr{Im}\left[e^{i\left(\frac{n\pi}{2} - \frac{t}{\theta\tau}\right)}{}_1F_1\left(-n; 1-n; \frac{it}{\theta\tau}\right)\right]$
Hill ($s = 1$)	$a = \frac{1 - n + m}{2},\ b = 1$ $c = \frac{1 - n - m}{2},\ \theta = 1$	$\frac{\pi^{\frac{1}{2}}}{\tau\Gamma\left(\frac{m}{2}\right)\Gamma\left(\frac{1-n}{2}\right)}\mathbf{G}^{21}_{13}\left(\left(\frac{t}{2\tau}\right)^2 \middle\vert \begin{matrix}\frac{1-m}{2} \\ \frac{-n}{2}, \frac{1}{2}, 0\end{matrix}\right)$
Shin–Yeung ($b = \frac{1}{2}$)	$a = 1 - n + m,\ b = \frac{1}{2}$ $c = \frac{1 - n - m}{2}$	$\frac{-m}{n\theta\tau}\mathscr{Im}\left[e^{-\frac{it}{\theta\tau}}{}_1F_1\left(n - m; 1 + n; \frac{it}{\theta\tau}\right)\right]$ $+ \frac{\Gamma(n)}{\theta\tau B(m, 1-n)}\left(\frac{t}{\theta\tau}\right)^{-n}\mathscr{Im}\left[e^{i\left(\frac{n\pi}{2} - \frac{t}{\theta\tau}\right)}{}_1F_1\left(-m; 1-n; \frac{it}{\theta\tau}\right)\right]$

3. Discussion

In Section 2.1 we obtained a generally complex pulse response for the Nakamura–Ishida formula unless $\beta = 1$, in which case it reduces to the Debye formula. Nakamura and Ishida have remarked that their formula does not satisfy the Kramers–Kronig relations. Our result explicitly demonstrates that causality is not observed and hence confirms their conclusion.

In the course of this work we also obtained some complex susceptibility expressions in closed form by transforming from pulse response functions. These correspond to the Hill formula with $s = 1$, the Kirkwood–Fuoss distribution of relaxation times and the Matsumoto–Higasi distribution, and are found in Sections 2.2(b), 2.3(a) and 2.3(b), respectively.

The pulse response functions $\phi(t)$ for the various dielectric formulae discussed take very different functional forms, with some depending on higher transcendental functions that are not easily visualized. One way to understand these pulse responses systematically is provided by their asymptotic behaviour in the short time and long time limits. These are calculated in Tables III and IV, and generally follow a power law or approach a constant. As far as asymptotic behaviour is concerned, pulse response functions are thus seen to fall into three classes, or progressive generality:

Class I: $\phi(t \to 0) =$ constant and $\phi(t \to \infty) = 0$;

Class II: $\phi(t \to 0) \sim t^{-n}$ and $\phi(t \to \infty) = 0$;

Class III: $\phi(t \to 0) \sim t^{-n}$ and

$$\phi(t \to \infty) \sim t^{-(m+1)};$$

where the power-law exponent parameters n and m lie between 0 and 1.

It is found that the pulse response functions of the Debye model and the two distribution-of-relaxation models, to wit, the Fröhlich and Matsumoto–Higasi models all fall in Class I. These models were known to be of limited applicability in fitting many dielectric data and many modifications had been suggested. Amongst those modifications, the $\phi(t)$'s of the Davidson–Cole, Williams–Watts, and Havriliak–Negami formulae belong to Class II but they are still restrained in the low-frequency region which corresponds to the long time limit of the pulse response functions. We have also tentatively classified the Kirkwood–Fuoss formula into Class II even though the short time limit of its pulse response is logarithmic instead of a simple power. Currently, a highly successful dielectric model is called the *universal model* of Jonscher [11], who, by analysis of the dielectric data of a wide range of materials, found that the dielectric loss formula is characterized by the double slopes in the graph of $\log F''(\omega)$ against $\log \omega$. Specifically, $F''(\omega)$ follows ω^m at the low-frequency region and $\omega^{-(1-n)}$ at the high-frequency region. In the time domain, the pulse response function $\phi(t)$ follows $t^{-(m+1)}$ at long time limit and t^{-n} at short time limit and so it is categorized into a distinct Class III. The Cole–Cole and Dissado–Hill formulae of Table III and all those listed in Table IV belong to this class.

Class III behaviour is given physical rationale by Dissado and Hill who suggested that the dominant physical mechanisms in those two time regions are the slow *dipolar flip-flop* process and the fast *dipolar tunnelling* process, respectively. Based on these mechanisms, they have derived a pulse response function $\phi(t)$ of the form $e^{-t/\tau}t^{-n}{}_1F_1(;;t/\tau)$ from which they have obtained a closed form expression for the complex dielectric susceptibility formula. The spectral shape function $\hat{F}(\omega)$ of their model is a Gaussian hypergeometric function of $1/(1 + i\omega\tau)$ for which it is difficult to separate the real $F'(\omega)$ and loss $F''(\omega)$ parts analytically. As mentioned in the Introduction (Section 1), this function is not directly related to Equation

TABLE III Asymptotic forms of pulse response functions for various complex dielectric models

Model	Short time limit $t \to 0$	Long time limit $t \to \infty$	Class
Debye	$\frac{1}{\tau}$	0	I
Cole–Cole	$\frac{1}{\tau\Gamma(1-\alpha)}\left(\frac{t}{\tau}\right)^{-\alpha}$	$\frac{(1-\alpha)}{\tau\Gamma(\alpha)}\left(\frac{t}{\tau}\right)^{-(2-\alpha)}$	III
Cole–Cole ($\alpha = \frac{1}{2}$)	$\frac{1}{\tau\pi^{\frac{1}{2}}}\left(\frac{t}{\tau}\right)^{-1/2}$	$\frac{1}{2\tau\pi^{\frac{1}{2}}}\left(\frac{t}{\tau}\right)^{-3/2}$	III
Davidson–Cole	$\frac{1}{\tau\Gamma(\beta)}\left(\frac{t}{\tau}\right)^{-(1-\beta)}$	0	II
Williams–Watts	$\frac{\beta}{\tau}\left(\frac{t}{\tau}\right)^{-(1-\beta)}$	0	II
Kirkwood–Fuoss	$\frac{1}{\tau}\ln\left(\frac{\tau}{t}\right)$	0	II[a]
Fröhlich	$\frac{1/\tau_2 - 1/\tau_1}{\ln(\tau_1/\tau_2)}$	0	I
Havriliak–Negami	$\frac{\beta\pi^{\frac{1}{2}}2^{\beta+1}}{\tau\Gamma\left(\frac{1-\beta}{2}\right)}\left(\frac{t}{\tau}\right)^{\beta/2-1}$	0	II
Matsumoto–Higasi	$\frac{p}{(1-p)(\tau_1^p - \tau_2^p)}\left\{\frac{1}{\tau_2^{1-p}} - \frac{1}{\tau_1^{1-p}}\right\}$	0	I
Dissado–Hill	$\frac{\Gamma(1-n+m)\left(\frac{t}{\tau}\right)^{-n}}{\tau\Gamma(1-n)\Gamma(2-n)\Gamma(m)}$	$\frac{\Gamma(1-n+m)\sin(m\pi)}{\tau\pi\Gamma(1-n)}\left(\frac{t}{\tau}\right)^{-1-m}$	III

[a] Nominal classification.

TABLE IV Asymptotic forms of pulse response functions for special cases of dielectric loss models

Model	Short time limit $t \to 0$	Long time limit $t \to \infty$	Class
Fuoss–Kirkwood ($\alpha = \frac{1}{2}$)	$\frac{1}{\tau(2\pi)^{\frac{1}{2}}}\left(\frac{t}{\tau}\right)^{-1/2}$	$\frac{1}{2\tau(2\pi)^{\frac{1}{2}}}\left(\frac{t}{\tau}\right)^{-3/2}$	III
Jonscher ($n = m$)	$\frac{\sin(n\pi/2)}{\theta\tau\Gamma(1-n)}\left(\frac{t}{\theta\tau}\right)^{-n}$	$\frac{n\sin\frac{1+n}{2}\pi}{\theta\tau\Gamma(1-n)}\left(\frac{t}{\theta\tau}\right)^{-1-n}$	III
Hill ($s = 1$)	$\frac{\Gamma\left(\frac{1-n+m}{2}\right)\Gamma\left(\frac{1-m}{2}\right)}{\tau\Gamma(m/2)\Gamma(1-n)}\left(\frac{t}{\tau}\right)^{-n}$	$\frac{2\Gamma\left(\frac{1-n+m}{2}\right)\sin\frac{m+1}{2}\pi}{\tau\Gamma\left(\frac{m}{2}\right)\Gamma\left(\frac{1-n}{2}\right)}\left(\frac{t}{\tau}\right)^{-m-1}$	III
Shin–Yeung ($b = \frac{1}{2}$)	$\frac{\Gamma(n)\sin\frac{n\pi}{2}}{\theta\tau B(m, 1-n)}\left(\frac{t}{\theta\tau}\right)^{-n}$	$\frac{m\Gamma(1-n+m)\sin\frac{1+m}{2}\pi}{\theta\tau\Gamma(1-n)}\left(\frac{t}{\theta\tau}\right)^{-m-1}$	III

2, and hence it will be of interest to examine how it differs numerically from expressions compatible with Equation 2. The recent Shin–Yeung empirical formula [13] is one such expression corresponding to $b = \frac{1}{2}$ in Equation 2, and has a Class III pulse response. As regards this paper, we shall compare the pulse response functions of the Shin–Yeung and Dissado–Hill formulae with power-law exponent parameters $n = 0.48$ and $m = 0.68$ obtained from the dielectric susceptibility of glycerol [19]. The responses are plotted in Fig. 1. It is found that the Dissado–Hill curve is slightly lower at both short-time and long-time regions but the difference is not very significant. On this basis, and on the basis of an earlier comparison [13]

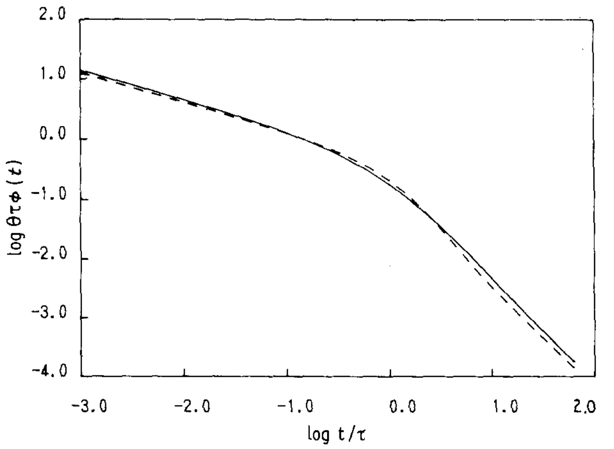

Figure 1 Logarithmic graph of pulse response functions $\phi(t)$ for the Shin–Yeung (solid line) and Dissado–Hill (dash line) susceptibility formulae with power-law exponent parameters $n = 0.48$ and $m = 0.68$ for glycerol. The horizontal axis is $\log t/\tau$ while the vertical one is $\log \theta\tau\phi(t)$ where $\theta = 1$ in the Dissado–Hill case.

with the Jonscher formula in the frequency domain, we believe that the recent Shin–Yeung formula provides an adequate alternative description of dielectric response.

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