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Application of continuous time random walks to dielectric relaxation with age-dependent transition rates

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Abstract. It is shown that the continuous time random walk (CTRW) method provides a simple and natural way of treating problems with age-dependent transition rates (ADTRs) that arise in many theories of non-exponential dielectric relaxation. In particular, ADTRs are especially suitable for analysing systems in which after any transition from one state to another there is initially an increased probability of a return transition to the original state. An extreme example of this is provided by a system of independent symmetric two-state dipoles having ADTRs, and for this system the CTRW method provides simple exact results. It follows from these results that the dielectric relaxation of such systems at short times is usually associated with a distribution of ADTRs. The results of calculations on some model systems are presented and discussed.

1. Introduction

In very many systems, mostly those with an appreciable degree of disorder, the dielectric and/or mechanical relaxation processes do not decay exponentially with time, or equivalently do not have a response of the Debye form in the frequency domain [1]. Instead, the response in the frequency domain can often be described by the Havriliak–Negami (henceforth HN) [2] function, whose asymptotic behaviour at high and low frequencies corresponds to Jonscher's 'universal' law [1]. Alternatively, the relaxation function in the time domain $F(t)$ is often fitted to the Kohlrausch–Williams–Watts stretched exponential relaxation function [3, 4]. Both of these lead to a response function $f(t)(= -\mathrm{d}F/\mathrm{d}t)$ that at short times decays algebraically, as t^{-n}, rather than exponentially with time. Such types of behaviour can always be attributed to the response of a large number of independent elements which each relax exponentially, with the appropriate distribution of relaxation times (DRT) [5, 6], but the required distribution has very specific and unrelated forms in the limits of short and long relaxation times, and its physical origin is far from clear. Alternatively, this behaviour has been attributed to processes with time-dependent transition rates (TDTRs), for which various physical mechanisms have been proposed [e.g. 7–10], or in some cases to a more complicated type of process [11]. One major objection to the use of TDTRs is that this is inconsistent with the superposition principle [12, 13]. We have recently shown that this objection can be overcome either by the use of age-dependent transition rates (ADTRs), i.e. rates that depend on how long the system has been in a given state rather than on the absolute time [14], or by the use of TDTRs for the system's response function rather than for its relaxation function [15]. The major problem in considering systems with ADTRs is that the methods developed so far for analysing their behaviour [14, 16–18] are much more

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complicated than those needed for TDTRs, since they involve functions that depend not only on the time t but also on the age a of the state, and the relationship between these two variables is far from simple. In the first part of this paper it is shown that there is a very simple and well known formalism available for the description of systems with ADTRs, namely the continuous time random walk (CTRW) method developed by Scher and Lax [19], henceforth referred to as SL. In particular, the ADTR method provides simple exact results for a system of independent two-state dipoles.

There is a close connection between TDTRs for the response function and ADTRs, and an examination of this will clarify which approach is more suitable for any given model system. By definition [20], the dielectric response function $f(t)$ describes the response of the system to a field that was applied instantaneously at time $t = 0$. For a system of dipoles, for instance, the only ones affected by such a field are those making a transition when it is applied, when the field causes the number of transitions in the direction of the field to exceed slightly the number occurring in the opposite direction and thus creates a net dipole moment or polarization $P(0)$ of the system. Thus, the TDTR for the response function describes the behaviour of the system as a function of the time that has elapsed since a transition, just as does the ADTR method. The difference between the two approaches is whether one starts again each time a transition takes place, as in the ADTR approach, or incorporates the effects of subsequent transitions in a TDTR. Which of these approaches is more suitable depends on the details of the system being considered. For the fractal time defect diffusion model of Shlesinger [10], if only a single relaxing transition is considered for each element then the TDTR approach for the response function is obviously the relevant one. However, if one allows for the possibility that the arrival of a defect may lead to only partial relaxation [21] and that defects such as free volume do not necessarily just disappear after causing a relaxation transition, then ADTRs could be more appropriate. In the theory of Ngai and his coworkers [9] it is assumed for instance that a polymer chain is initially free to move, but subsequently gets obstructed by entanglement with other chains. The question that arises here is whether a transition can only occur in chains that are free of such entanglements. If this is the case, each transition corresponds to the same initial state, and whether a TDTR or an ADTR is the more basic quantity for describing the transitions again depends on whether or not the first transition relaxes the system completely. On the other hand, if transitions can also occur in other configurations then there will initially be a distribution of transition rates corresponding to the relative probabilities of such configurations, and the calculations of the appropriate distributions of TDTRs or ADTRs is a complicated problem that does not seem to have been discussed in the literature. In the theories of Rose [7] and of Elliott and Owen [8], on the other hand, the time dependence of the transition rate is associated with the mechanical relaxation of the system surrounding the particle following its transition, and so the quantity that determines the transition rate is obviously the time that has elapsed since the previous transition, i.e. the age of the state. Hence, the ADTR approach is the most natural one, and the ADTR $v(t)$ should be directly related to the physical details of the process, while derivation of the TDTR for the response function from these details requires a complicated analysis of the probabilities of subsequent transitions taking place at different times after the first one. A similar conclusion applies for other systems in which after any transition from one state to another there is initially an increased probability of a return transition to the original state, as considered below. We conclude that ADTRs are certainly relevant to many of the models that have been proposed to explain non-exponential or non-Debye relaxation.

In section 2 of this paper we present the CTRW formalism for a system in which all the elements have the same ADTR $v(t)$, and start with the analysis for a general system.

For an ADTR, the distribution of waiting times that is the basic constituent of the CTRW method does not arise from an average over a set of constant transition rates, as in SL [19], but is rather a basic property of the system associated with the time dependence of $v(t)$. For a system of conducting particles such as ions, the subsequent analysis of the conductivity, and hence of the dielectric relaxation, is the same as for the systems considered by SL, provided that there is no correlation between successive steps. However, such correlation can be important; for instance, computer simulations [22, 23] have recently shown that in ionic conduction there is initially a preference for the ion to return to the site that it originally left. In the remainder of this paper, we consider the extreme case of correlation between successive transitions, namely a system of two-state dipoles, for which each transition is the reverse of the previous one. For such a system, the property that determines the relationship between the dipole moment at time t, $m(t)$, and its initial value, $m(0)$, is not the total number of transitions that have taken place in time t but whether this number is odd or even. As shown in the second part of section 2, this property enables us to derive from the CTRW formalism a simple exact expression for the system's response function and for its frequency-dependent dielectric susceptibility in terms of the ADTR $v(t)$. The application of our analysis to a system of two-state dipoles whose dielectric properties are described by the HN function is considered in section 3. We show that while the low-frequency (or long-time) behaviour of this function is compatible with the existence of a single ADTR, the high-frequency (or short-time) behaviour can only be explained if there is a distribution of ADTRs, and the relevant formulae are derived for this case. Then, in section 4, the results are presented of calculations for systems of two-state dipoles with distributions of some simple ADTRs, chosen so that the results at both short and long times are similar to those observed experimentally. The extension of our methods to systems of multistate dipoles with different ADTRs for transitions between the states is considered in section 5, where we also discuss the differences between a distribution of ADTRs and the distribution of constant relaxation times of the DRT method. Finally, a summary of our results is presented in section 6.

2. The response of systems with a single age-dependent transition rate

We consider the relaxation of a set of independent charged elements (such as dipoles or ions) which we refer to as particles, and which can make transitions between discrete states. In this section, we consider systems such that in the absence of an applied electric field the transition rate out of each state is the same function $v(t)$ of the time t since entering the state (i.e. of the age of the state) for all the states. This is the simplest case to analyse, and the extension to systems with more than one rate $v(t)$ will be treated in the following sections.

2.1. The response of a general system

By the definition of the ADTR $v(t)$, the probability $\phi(t)$ that a particle will not make a transition out of its original state for at least time t after entering it satisfies the equation

$$\mathrm{d}\phi/\mathrm{d}t = -v(t)\phi(t) \tag{1}$$

with the initial condition that $\phi(0) = 1$. Thus $\phi(t)$, which is the basic quantity of the CTRW formalism [19], is given by

$$\phi(t) = \exp\left[-\int_0^t v(y)\,\mathrm{d}y\right]. \tag{2}$$

The difference between an ADTR and the usual CTRW formalism lies not in the definition of $\phi(t)$ but in its interpretation. In the usual CTRW approach $\phi(t)$ arises from an average over a lot of possible constant transition rates, but in the ADTR approach it is directly associated with the single ADTR $v(t)$.

Following SL [19], we denote by $\psi(t)\,dt$ the probability that the first transition from a state takes place between times t and $t+dt$ after entering it, so that

$$\psi(t) = -d\phi/dt = v(t)\phi(t) \tag{3}$$

and its Laplace transform

$$\hat{\psi}(u) = 1 - u\hat{\phi}(u) \tag{4}$$

where $\hat{g}(u)$ denotes the Laplace transform of the function $g(t)$. Let $r_n(t)\,dt$ be the probability that the nth transition takes place between times t and $t+dt$, and $p_n(t)$ the probability that exactly n transitions take place up to time t, with the initial conditions

$$r_n(t) = \delta(t-0+)\delta_{n,0}. \tag{5}$$

Then the basic equations are

$$r_{n+1}(t) = \int_0^t r_n(y)\psi(t-y)\,dy \tag{6}$$

and

$$p_n(t) = \int_0^t r_n(y)\phi(t-y)\,dy. \tag{7}$$

Following SL, we define the generating functions

$$r(t,z) = \sum_0^\infty z^n r_n(t) \qquad p(t,z) = \sum_0^\infty z^n p_n(t). \tag{8}$$

On taking the Laplace transforms of equations (5)–(8) and using equation (4), one readily finds, as in SL, that

$$\hat{r}(u,z) = 1/[1 - z\hat{\psi}(u)] \tag{9}$$

and hence that

$$\hat{p}(u,z) = \hat{\phi}(u)/[1 - z + zu\hat{\phi}(u)]. \tag{10}$$

2.2. *Analysis of systems of two-state dipoles*

The usual applications of the CTRW formalism are to random walks of mobile particles with no correlation between successive steps, where the electrical conductivity is derived from the mean square distance travelled by a particle in time t in the absence of a field. In that case, the analysis presented above refers to systems in which there is no correlation between the probability of a jump after a given waiting time t and the distance jumped, so that the conductivity depends only on the mean number of steps taken in time t, and so on $\partial\hat{p}(u,z)/\partial z$ evaluated at $z = 1$ [19]. The opposite extreme case of complete correlation between successive steps is provided by a system in which each charged particle can only jump back and forth between a pair of states. Such a system is formally equivalent to a system of dipoles each having two possible states, with dipole moments $\pm p$. For this system, the moment at time t is determined by the probability of an even number of steps being taken in time t minus the probability that an odd number of steps is taken in this time, and the Laplace transform of this probability is just $\hat{p}(u,z)$ with $z = -1$. Thus the

moment $m(t)$ of a dipole which started with moment $m(0)$ at time $t = 0$ has the Laplace transform

$$\hat{m}(u) = m(0)\hat{p}(u, -1) = m(0)\hat{\phi}(u)/[2 - u\hat{\phi}(u)]. \tag{11}$$

The above equation applies to a dipole with symmetric transition rates between the two states, and the extension of the analysis to the case of asymmetric rates, and so to the properties of general two-level systems [24], will be discussed in section 5. For the present, we restrict our attention to systems of independent symmetric two-state dipoles, and consider the application of the above result to the calculation of the dielectric properties of such a system. In order to do this, we first summarize the definition of the dielectric response function.

In an approach and notation similar to that of Kubo [20], the basic quantity used in describing the dielectric response is the normalized response function $f(t)$ which describes the system's response to an impulse field. The polarization $P_i(t)$ at time t after the application of such a field is just

$$P_i(t) = \chi_s E_0 f(t) \qquad \text{for } E(t) = E_0\delta(t) \tag{12}$$

where χ_s is the static susceptibility of the system. It follows from the superposition principle and equation (12) that the polarization $P(t)$ produced by a field $E(t)$ is

$$P(t) = \chi_s \int_{-\infty}^{t} E(s) f(t - s)\,\mathrm{d}s. \tag{13}$$

If a constant field E_0 is applied from $t = -\infty$ until $t = 0$ and is then removed, the resulting polarization $P_c(t)$ defines the relaxation function $F(t)$ according to

$$P_c(t) = \chi_s E_0 F(t) = P_c(0) F(t). \tag{14}$$

Hence, $F(t)$ is related to the response function $f(t)$ by

$$F(t) = \int_t^{\infty} f(s)\,\mathrm{d}s \tag{15}$$

or equivalently

$$f(t) = -\mathrm{d}F/\mathrm{d}t \tag{16}$$

while from equations (14) and (15) together with the definition of the static susceptibility

$$\hat{f}(0) = F(0) = 1. \tag{17}$$

The connection between our previous analysis, and in particular equation (11), and the dielectric response function $f(t)$ is based on the fact that, as discussed in the introduction, $f(t)$ describes the response of the dipoles that made a transition at time $t = 0$; the field applied then causes the number of transitions in the direction of the field to exceed slightly the number occurring in the opposite direction and thus creates a net dipole moment or polarization $P(0)$ of the system. These dipoles are just the ones considered in the analysis presented in the first part of this section, so that $P(t)$ relaxes in the same way that $m(t)$ did there. Hence, $f(t)$ is proportional to $m(t)$, while the dielectric susceptibility $\chi(\omega)$ at frequency ω is just $\chi_s \hat{f}(\mathrm{i}\omega)$. Thus, it follows from equations (11) and (17) that

$$\hat{f}(u) = [2\hat{\phi}(u)/\hat{\phi}(0)]/[2 - u\hat{\phi}(u)] \tag{18}$$

where the factor $2/\hat{\phi}(0)$ ensures that $\hat{f}(0) = 1$. Hence, from equation (13),

$$\chi(\omega) = \chi_s\{[2\hat{\phi}(u)/\hat{\phi}(0)]/[2 - u\hat{\phi}(u)]\}_{u=\mathrm{i}\omega}. \tag{19}$$

The above equations, in conjunction with equation (2), provide expressions for the dielectric response function $f(t)$ and the dielectric susceptibility $\chi(\omega)$ in terms of the fundamental quantity of our approach, namely the age-dependent transition rate $v(t)$.

A simple example of the application of the above results is provided by a system with a constant transition rate, $v(t) = 1/b$. In that case,

$$\hat{\phi}(u) = b/(1 + ub) \tag{20}$$

so that

$$f(t) = (2/b)\exp(-2t/b) \tag{21}$$

and

$$\chi(\omega) = \chi_S/(1 + i\omega b/2). \tag{22}$$

These are just the results that would be obtained from an analysis in terms of rate equations with constant transition rates, and correspond to dipoles having a relaxation time $\tau = b/2$.

3. General properties of systems of dipoles

We now consider how ADTRs can be used to describe the observed dielectric properties of materials. In very many cases, the dielectric susceptibility $\chi(\omega)$ can be fitted by the HN function [2],

$$\chi(\omega) = \chi(0)/[1 + (i\omega\tau)^{\alpha}]^{\gamma} \tag{23}$$

in which case the dielectric response function $f(t)$ and its Laplace transform $\hat{f}(u)$ have the following asymptotic forms, with $m = \alpha$ and $n = 1 - \alpha\gamma$:

(i) as $t \to 0$ or $u \to \infty$ $\quad \hat{f}(u) \sim A(u\tau_0)^{n-1}$ and $f(t) \sim A'(t/\tau_0)^{-n}$

$$0 < 1 - n = \gamma\alpha \leqslant 1 \tag{24}$$

(ii) as $u \to 0$ or $t \to \infty$ $\quad \hat{f}(u) \sim B[1 - (u\tau_0)^m]$ and $f(t) \sim B'(t/\tau_0)^{-(1+m)}$

$$0 < m = \alpha \leqslant 1. \tag{25}$$

These asymptotic forms are identical with those of Jonscher's [1] 'universal' dielectric response. It is worth noting that the above asymptotic forms for $f(t)$ are not valid if m is an integer or if $n = 1$, while for Debye relaxation, equation (22), $m = \alpha = 1$ and $n = 0$ so that $\alpha\gamma = 1$.

In order to see how ADTRs can account for the above asymptotic behaviour, we now examine some general properties that follow from the results of section 2. Physically, and in accordance with equation (2), one expects that for a single ADTR,

$$\phi(t) \to 1 \text{ and } m(t) \to m(0) \qquad \text{as } t \to 0. \tag{26}$$

It then follows from Tauberian theorems [25] that

$$u\hat{\phi}(u) \to 1 \qquad \text{as } u \to \infty \tag{27}$$

and so, from equation (18), that

$$\hat{f}(u) \sim A/u \tag{28}$$

where $A = 2/\hat{\phi}(0)$. This result does not agree with equation (24) unless $n = 0$ there, in which case the short-time behaviour is just of the Debye form, i.e. that of a system with a constant transition rate. It follows that the behaviour of general systems at short times cannot be described by a single ADTR $v(t)$. On the other hand, as $u \to 0$ or $t \to \infty$,

the requirement from equation (25) that $\hat{m}(u) \sim Bm(0)[1 - (u\tau_0)^m]$ is consistent with equation (11) if $\hat{\phi}(u) \sim 2B[1 - (u\tau_0)^m]$, a form that is in principle quite possible.

In view of the above conclusion regarding the short-time behaviour, it is of interest to derive expressions for the dielectric responses $f(t)$ and $\chi(\omega)$ when one has a distribution of ADTRs $v(t)$. For this purpose, it is convenient to define the function

$$h_v(t) = \int_0^t v(y)\,dy \tag{29}$$

so that for a single rate $v(t)$ the CTRW functions of interest are

$$\phi_v(t) = \exp[-h_v(t)] \tag{30}$$

and

$$\hat{\phi}_v(u) = \int_0^\infty \exp[-h_v(t) - ut]\,dt. \tag{31}$$

If one has a distribution $g[v(t)]$ of ADTRs $v(t)$, one might be tempted to write, for instance,

$$\langle\hat{\phi}(u)\rangle = \int g(v)\left\{\int_0^\infty \exp[-h_v(t) - ut]\,dt\right\}dv. \tag{32}$$

However, this $\langle\hat{\phi}(u)\rangle$ is not relevant to the calculation of $f(t)$ or $\chi(\omega)$ for a system of dipoles from equations (18) and (19). Instead, the response function $f(t)$ or $\hat{f}(u)$ of each type of dipole with a given $v(t)$ must be calculated separately before an average is taken over the distribution of the $v(t)$, so that $\hat{\phi}(u)$ in equations (18) or (19) cannot just be replaced by $\langle\hat{\phi}(u)\rangle$. Thus, for a distribution of ADTRs

$$\hat{f}(u) = C\int g(v)[2\hat{\phi}_v(u)/\hat{\phi}_v(0)]/[2 - u\hat{\phi}_v(u)]\,dv. \tag{33}$$

We note that if $u\hat{\phi}_v(u) \to 0$ as $u \to 0$, which will normally be true, then $C = 1$ since $\hat{f}(0) = 1$ and $g(v)$ is a probability density.

4. Results of calculations for some model systems

In order to demonstrate the application of the above analysis, we now present the results of calculations for a series of model systems with specific forms of ADTR $v(t)$. On physical grounds, we expect that for any given dipole $v(t)$ will be finite as $t \to 0$, while we are interested in a $v(t)$ that leads to the desired behaviour in the long-time or low-frequency limits. The simplest such ADTR having these properties is

$$v_c(t) = a/(c + t) \tag{34}$$

for which

$$\phi_c(t) = (1 + t/c)^{-a}. \tag{35}$$

It is necessary that $a > 1$ in order that $\hat{\phi}_c(0)$ be finite. Incidentally, the corresponding distribution of waiting times is of the form recently studied by Bettin *et al* [26], and has the physically reasonable property that the transition rate decreases as time progresses. It is possible to add a small constant term k to $v(t)$ if one wants a finite transition rate as $t \to \infty$, but this will only affect the results appreciably at frequencies of order of magnitude not greater than k, and we choose not to consider such low frequencies. Initially, we present

the results for a single value of c, namely $c = 1$, and after that we consider a distribution of ADTRs $v(t)$ with different values of the parameter c. We note that

$$\hat{\phi}_c(i\omega) = \int_0^\infty \exp(-i\omega t)(1 + t/c)^{-a}\,dt = c\hat{\phi}_1(ic\omega) \tag{36}$$

so that, from equation (19),

$$\chi_c(\omega)/\chi_c(0) = \chi_1(c\omega)/\chi_1(0). \tag{37}$$

In all cases, we write

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega) \tag{38}$$

and present the results for $\chi''(\omega)/\chi(0)$, since the frequency dependence of the imaginary part of the susceptibility, which always exhibits a maximum at some frequency, is a more sensitive test of the results than is the monotonically decreasing real part.

4.1. Results for a single ADTR

In order to evaluate $\hat{\phi}_1(i\omega)$, we wrote

$$(1 + t)^{-a} = [1/\Gamma(a)] \int_0^\infty \exp[-(1 + t)x]x^{a-1}\,dx \tag{39}$$

and interchanged the order of integration over t and x to obtain

$$\hat{\phi}_1(i\omega) = [1/\Gamma(a)] \int_0^\infty [\exp(-x)x^{a-1}/(x + i\omega)]\,dx \tag{40}$$

a form that is much more amenable to numerical integration. From equation (40), it is at once apparent that $\hat{\phi}_1(i\omega) \sim 1/i\omega$ as $\omega \to \infty$, just as for Debye relaxation; this result is expected since $v(t) \to a/c$, a constant, as $t \to 0$. At low frequencies, on the other hand, one readily finds (on substituting $y = x/\omega$) that

$$\hat{\phi}_1(0) - \hat{\phi}_1(i\omega) = [i\omega^{a-1}/\Gamma(a)] \int_0^\infty [y^{a-2}\exp(-\omega y)/(y + i)]\,dy. \tag{41}$$

If $a < 2$, the integral is dominated by the values of the integrand for small values of y, and so is virtually independent of ω as $\omega \to 0$. Thus one should choose $a = 1 + m$ in order to obtain the results of equation (25). Accordingly, we performed calculations for $a = 1.5$, 1.8, and 2.2, where the third value was deliberately chosen to be greater than two, since for such values of a term of order ω will dominate one of order ω^{a-1} as $\omega \to 0$.

In figures 1 and 2, we show $\chi''(\omega)/\chi(0)$ and $\log[\chi''(\omega)/\chi(0)]$ respectively as functions of $\log(\omega)$. The results shown in figure 1 look quite reasonable, while from figure 2 we see that at high frequencies $\chi''(\omega)/\chi(0)$ is proportional to $1/\omega$ for all the systems, while at low frequencies the slope of $\log[\chi''(\omega)/\chi(0)]$ as a function of $\log(\omega)$ is close to 0.5 for $a = 1.5$, to 0.8 for $a = 1.8$, and to unity for $a = 2.2$, in accordance with the above predictions.

4.2. Results for a distribution of ADTRs

In order to obtain the behaviour at short times or high frequencies given by equation (24), we require a distribution of ADTRs, as noted above. In order to find the appropriate distribution of the parameter c, we note that $v(t) \to a/c$ as $t \to 0$, while according to equations (21) and (22) a constant $v(t) = a/c$ would lead to a Debye relaxation with relaxation time $\tau = c/(2a)$. Now a distribution of relaxation times $g(\tau) = A(\tau/\tau_0)^{\beta-1}$ leads to a response function $f(t)$ proportional to $(t/\tau_0)^{\beta-1}$ and to a susceptibility $\chi(\omega)$ proportional to $(i\omega\tau_0)^{-\beta}$

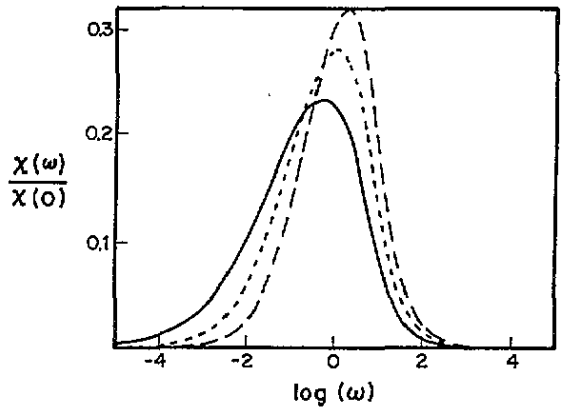

Figure 1. The susceptibility $\chi''(\omega)/\chi(0)$ at frequency ω as a function of $\log(\omega)$ for a single ADTR $v(t) = a/(1+t)$. The continuous line is for $a = 1.5$, the dotted line for $a = 1.8$, and the broken line for $a = 2.2$.

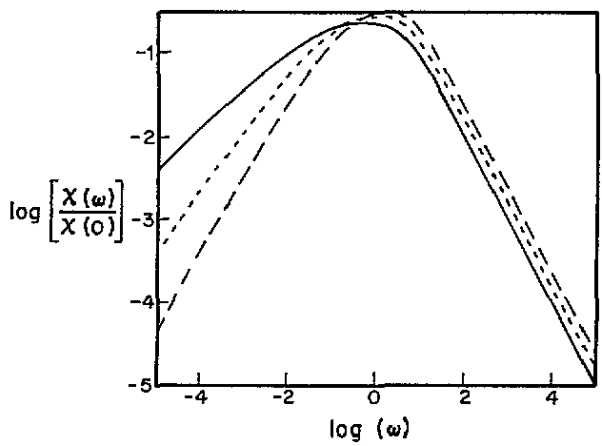

Figure 2. $\log[\chi''(\omega)/\chi(0)]$ as a function of $\log(\omega)$ for a single ADTR $v(t) = a/(1+t)$. The continuous line is for $a = 1.5$, the dotted line for $a = 1.8$, and the broken line for $a = 2.2$.

[27]. Accordingly, in order to obtain results similar to those of equation (24), we chose a distribution of the parameter c

$$g(c) = \beta c^{\beta-1} \qquad 0 < c < 1. \tag{42}$$

The values of $\chi''(\omega)/\chi(0)$ were then calculated from equations (33) and (37) by numerical integration of the results of section 4.1, and the results for a typical value of β, $\beta = 0.6$, are presented in figures 3 and 4, which correspond to figures 1 and 2 for a single value of c. From the log–log plot in figure 4, we see that while the above distribution of ADTRs did not affect the frequency dependence of $\chi''(\omega)/\chi(0)$ at low frequencies, it did lead as expected to the proportionality of $\chi''(\omega)/\chi(0)$ to $\omega^{-\beta}$ at high frequencies for all three values of the parameter a. Similar results were obtained for other values of the exponent β.

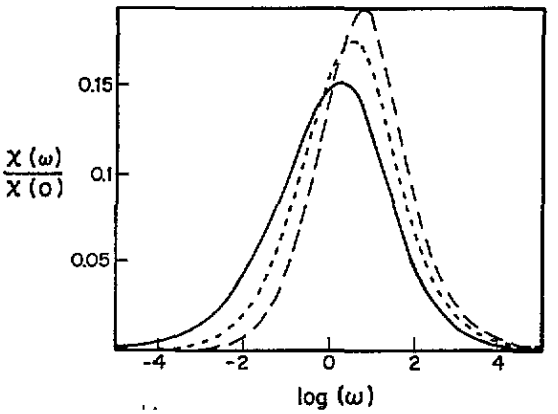

Figure 3. The susceptibility $\chi''(\omega)/\chi(0)$ at frequency ω as a function of $\log(\omega)$ for a distribution of ADTRs $v(t) = a/(c+t)$ with $g(c) = \beta c^{\beta-1}$, $0 < c < 1$, and $\beta = 0.6$. The continuous line is for $a = 1.5$, the dotted line for $a = 1.8$, and the broken line for $a = 2.2$.

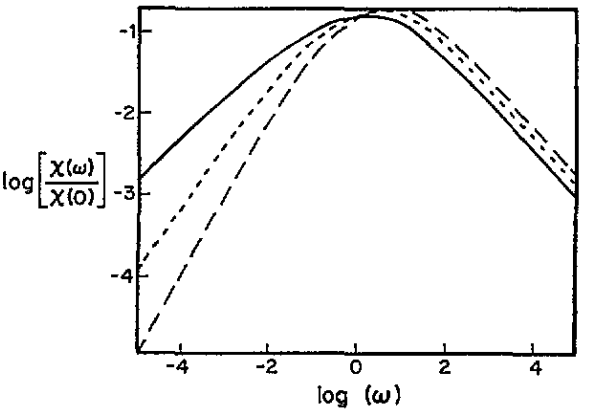

Figure 4. $\log[\chi''(\omega)/\chi(0)]$ as a function of $\log(\omega)$ for a distribution of ADTRs $v(t) = a/(c+t)$ with $g(c) = \beta c^{\beta-1}$, $0 < c < 1$, and $\beta = 0.6$. The continuous line is for $a = 1.5$, the dotted line for $a = 1.8$, and the broken line for $a = 2.2$.

5. Discussion

The results presented in section 4.2 show that even a simple distribution of ADTRs $v(t)$ can lead to results for the dielectric susceptibility at both high and low frequencies similar to that observed experimentally. The first point that we now consider is how our methods can be applied to more complicated systems of dipoles than the system of symmetric two-state dipoles considered so far. For this purpose, we examine a system of dipoles with N possible states, which we label by j, $1 \leqslant j \leqslant N$, and arbitrary ADTRs between them that are the same for all the dipoles; a two-level system with asymmetric transition rates [24] is a simple special case of such a system. In the application of our method, the probability $\phi(t)$ of a waiting time of at least t in equations (1) and (2) must then be replaced by the corresponding quantity $\phi(t; j)$ for state j, and $\psi(t)$ of equation (3) by $\psi(t; j, j')$, the probability density that a transition takes place from state j' to state j after time t. Similarly, $r_n(t)$ and $p_n(t)$ of equations (5) and (7) must be replaced by the corresponding probabilities $r_n(t; j, k)$ and $p_n(t; j, k)$ that a dipole initially in state k will after n steps arrive at or be in state j, and

equations (6) and (7) will be replaced by a set of simultaneous equations involving these quantities. This formalism is similar to that of the multistate CTRW [28], and the main difference is once again that the total polarization at time t is determined for a system of dipoles by the appropriate sum (in an obvious notation) of the generating functions $p(t, z; j, k)$ with $z = 1$, rather than by the derivatives of these functions. The analysis in this case is so much more complicated, especially if one considers distributions of ADTRs as in section 4.2, that we preferred to present in this paper just the analysis for a system of two-state symmetric dipoles. For that system exact results could be derived fairly simply, while there is no obvious reason to expect that the general features of dielectric relaxation for systems of this type differ appreciably from those of more complicated systems of dipoles.

Another possible extension of our method, as indicated in the introduction, is to the study of ionic transport in systems where an ion that hops from one site to another has initially an increased probability of returning to the original site [22, 23]. This is a very much more complicated problem than that of a system of two-state dipoles, and is at present being investigated.

Although the main aim of this paper was to show how the CTRW method provides a natural way of treating ADTRs, it is of interest to consider finally the implications of our analysis and results for the value of the concept of ADTRs. In sections 3 and 4 we saw that, at least for a system of two-state dipoles, it is necessary to assume a distribution of ADTRs in order to account for the short-time or high-frequency behaviour of the HN response that is often observed. The question that naturally arises is whether and why such a distribution of ADTRs may be preferable to the distribution of constant relaxation times used in the DRT method. We note here just one significant aspect of the difference between the two approaches. The DRT method requires one distribution for short relaxation times, which govern the short-time behaviour of the system, and an entirely different distribution for the long relaxation times that determine its long-time behaviour, while the ADTR method only requires a distribution for the short-time behaviour. It has been suggested [29] that the short-time behaviour of many systems is associated with local motions and the immediate environment of a particle; even for the longitudinal vibrations of a polymer chain, the higher-frequency modes correspond approximately to the optical modes of a linear chain, and so are much more sensitive to the local disorder than the low-frequency acoustic-type vibrations. Since in a disordered system one certainly expects the existence of short-range disorder, a distribution of rates for the description of this behaviour is not unexpected, and its universal form is associated with a power law distribution of relaxation times τ for short values of these times which corresponds to a Levy distribution of relaxation frequencies $\nu = 1/\tau$ for large values of ν. The long-time behaviour, on the other hand, can well be of the same form for all the dipoles, as in the model systems that we considered.

6. Conclusions

The main conclusion from our analysis is that the CTRW method of SL [19] provides a natural framework for treating age-dependent transition rates. These ADTRs are expected to be of particular significance in systems where there is an increased probability that after making a transition a particle will return to its original site rather than making its subsequent transition to some other site. An extreme example of such correlations is provided by systems of symmetric two-state dipoles, where all the transitions are of this form, and for these the CTRW formalism leads to very simple exact formulae for the dielectric response function and the dielectric susceptibility in terms of this transition rate. A comparison of these formulae with the typical dielectric behaviour of real systems indicates that a

distribution of such rates is usually required in order to account for the short-time high-frequency behaviour, but (in contrast to the approach based on a distribution of relaxation times) another independent distribution is not needed in order to explain the long-time low-frequency behaviour of the systems. These results are confirmed by the results of our calculations on some model systems.

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