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The physical significance of time-dependent transition rates

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Abstract. It is shown that physically significant time-dependent transition rates (TDTRS) for dielectric relaxation should be defined to refer to the decay of the system's response function, rather than that of its relaxation function. An examination of the stretched-exponential function in the time domain and of the Havriliak–Negami function in the frequency domain, to which experimental results are often fitted, shows that for most times the TDTRS must be proportional to the inverse of the time. This result is discussed in terms of the difference between global and local TDTRS.

1. Introduction

One widely used approach to the calculation of the response of the dielectric polarization $P(t)$ of a system on the removal of an applied electric field is to postulate a first-order differential equation for $P(t)$ and define a transition $W = -(1/P) dP/dt$ [1]. The relaxation function of the system $\Phi(t)$ is defined to be the ratio $P(t)/P(0)$ under these conditions, when the steady field was applied up to time $t = 0$. For systems in which $\Phi(t)$ decays exponentially with time, W is a constant and no problems arise as to its definition. However, for a large number of systems $\Phi(t)$ does not exhibit simple exponential decay [1–3]. Instead a time dependence of $\Phi(t)$ that can be fitted over a few decades of time to the Kohlrausch–Williams–Watts (KWW) [4, 5] stretched-exponential relaxation function $\exp(-[t/\tau]^\beta)$ is often observed. Alternatively, and often over a wider range of frequencies, the system's response in the frequency domain is often fitted to the empirical Havriliak–Negami (HN) function [6, 7] $1/[1 + (i\omega\tau)^\alpha]^\nu$, which incorporates Jonscher's 'universal' law [1]. Such types of behaviour can be described formally in terms of a time-dependent transition rate (TDTR) $W(t)$, which is related to the time-correlation function of the polarization ($P(t)P(0)$) [8]. In this paper we show that this transition rate has little basic physical significance, define a transition rate $w(t)$ that may have a simple physical meaning, and examine and discuss its relationship to the experimental results.

A number of theories of dielectric relaxation, such as the defect diffusion model [9–11] in its simplest form and the coupling models of Ngai and his co-workers [12] assume that the transition rate $W(t)$ for the polarization is associated with the relaxation of elements that start from a given well defined state at the time $t = 0$ when the steady electric field is removed. However, this is not in accord with the superposition principle, as has been noted by various authors [13, 14]. According to this principle, on which is based the universally used relationships between a system's response in the time domain and in the frequency domain [1], at every instant of time the field present then excites a different small fraction of the system, which immediately starts to relax in a way that is not influenced by the field. Hence, at time $t = 0$, the elements are in a distribution of states appropriate to thermal

equilibrium in the presence of the field. If one wants to consider elements in a definite state at time $t = 0$, the appropriate quantity is the response function $\phi(t)$, which describes the subsequent relaxation of that part of the system that was excited by the field present at time $t = 0$. The relaxation function is the sum of the responses of the fractions of this system that were excited by the field at all previous times and started relaxing immediately after they were excited, so that $\Phi(t)$ is given by $\int_0^\infty \phi(u) du$. Thus, if one wants to develop a microscopic theory for a TDTR, it should apply to that of the response function rather than that of the relaxation function. In particular, the defect triggering model [9–11] and the coupling theories of Ngai and his co-workers [12] would predict a stretched-exponential behaviour for the response function. A simple application of this result would lead to the relaxation function being described by an incomplete gamma function, in contradiction with the experimental results.

In this paper, we examine the form of the TDTR for the response function that would be required to account for the experimental results, and the implications of our findings. In section 2, we present a summary of the implications of the superposition principle, define the TDTR $w(t)$ appropriate to the response function, and also consider the relationship between the TDTRs and time-correlation functions of the polarization. Then, in section 3, we calculate the form of $w(t)$ appropriate to stretched-exponential decay of the relaxation function in the time domain and to the HN function in the frequency domain, and show that these types of behaviour require that for most times $w(t)$ be inversely proportional to the time t . The implications of this result, and in particular the need to distinguish between global and local response functions and TDTRs, are discussed in section 4, while our conclusions are summarized in section 5.

2. The theory of time-dependent transition rates

In this paper, it is convenient to restrict our attention to the response of the dielectric polarization $P(t)$ to an applied electric field $E(t)$, but similar considerations apply to the response of the mechanical strain to an applied stress, for instance.

The superposition principle, on which are based the standard connections between results in the frequency and time domains [1], requires that in the presence of a weak perturbation, whose energy is much less than the thermal energy $k_B T$, the response of the system is the linear superposition of its responses to the application of the perturbation at each time in the past. According to linear-response theory [15, 16], these responses each decay with time just as they would in the absence of the perturbation, and this leads to the fluctuation-dissipation theorem, since the decay of an excitation in the absence of a field will be the same whether it was produced by the applied field or by a thermal fluctuation. Incidentally, it is worth noting that according to this theory one cannot speak of field-induced transitions, as these take place at the same time (thermally stimulated) rate whether or not a weak field, with associated energy $\ll k_B T$, is applied. Rather, the effect of the field is to give a preferred direction to the transitions, and this leads to a net polarization, whose subsequent relaxation in the absence of a field is described by the system's relaxation function or response function.

We start by summarizing the results that follow from the superposition principle, using essentially the notation of Kubo [15]. It is convenient to use a normalized response function $\phi(t)$ and for the sake of simplicity we assume that there is no instantaneous response, so that the dielectric susceptibility at infinite frequency is zero. In that case, we can define $\phi(t)$ by writing the response to a field $E_0\delta(t)$ as

$$P(t) = \chi_s E_0 \phi(t) \quad (1)$$

where χ_s is the static susceptibility. Thus, in accordance with the superposition principle, the response to a general field $E(t)$ is

$$P(t) = \chi_s \int_{-\infty}^t E(u) \phi(t-u) du. \quad (2)$$

For the special case of a steady field E_0 being applied up to time $t = 0$ and then removed, it follows that

$$P(t) = \chi_s E_0 \int_t^{\infty} \phi(x) dx. \quad (3)$$

In this case

$$P(0) = \chi_s E_0. \quad (4)$$

The system's relaxation function $\Phi(t)$ is most conveniently defined for this situation, in which

$$P(t) = P(0)\Phi(t). \quad (5)$$

Hence, the relaxation and response functions are related by the basic equation

$$\Phi(t) = \int_t^{\infty} \phi(x) dx \quad (6)$$

and it follows that

$$\phi(t) = -d\Phi/dt. \quad (7)$$

This establishes the connection between our notation and that commonly used in analysing dielectric relaxation [16].

Another interesting special case is that a periodic field, $E(t) = E_0 \exp(-i\omega t)$, for which it follows from equation (2) that

$$P(t) = \chi(\omega) E(t) \quad (8)$$

where

$$\chi(\omega) = \chi_s \int_0^{\infty} \phi(x) \exp(i\omega x) dx. \quad (9)$$

This establishes the standard connection between results obtained in the frequency domain and those obtained in the time domain [1].

We now consider the analysis of the time dependence of the polarization following the removal of a steady applied field in terms of transition rates. Such a description is not the simplest one to derive formally [8], but seems attractive since it can be related to simple concepts such as rate equations. For systems in which the relaxation function decays exponentially with time, one can write

$$dP/dt = -W_0 P(t) \quad (10)$$

where W_0 is just the inverse of the relaxation time. For systems in which the relaxation function is not so simple, but can be approximated by a stretched-exponential function of time, for instance, one possible approach is to replace the constant transition rate W_0 by a time-dependent transition rate (TDTR) $W(t)$, and so to write

$$dP/dt = -W(t)P(t). \quad (11)$$

It has been shown [8] that this TDTR is related to the correlation function of the system's dipole moment, so there is no formal problem in defining it. However as we discussed in section 1, it is not valid to calculate $W(t)$ on the assumption that all the relaxing elements in the system were in the same well defined state when the steady field was removed. Instead, they will be in a distribution of states corresponding to the thermal equilibrium situation in the presence of the field, so that the application of any simple model to the calculation of $W(t)$ is quite complicated. This fundamental difficulty can be avoided if one considers only elements that were affected by an impulse field applied at time $t = 0$, since these could all be in the same initial state. Accordingly, we now introduce the TDTR for the response to an impulse field, which we denote by $w(t)$. These two rates describe the decay of the relaxation function and of the response function respectively, i.e.

$$d\Phi/dt = -W(t)\Phi(t) \quad (12)$$

and

$$d\phi/dt = -w(t)\phi(t). \quad (13)$$

Hence, it follows from equation (7) that $W(t)$ and $w(t)$ are connected by the equation

$$w(t) = W(t) - (1/W) dW/dt. \quad (14)$$

Incidentally, the use of $w(t)$ also overcomes the various objections in the literature to the use of the TDTR $W(t)$ [13, 14], and gives a definite physical meaning to the origin of time for $w(t)$, namely the moment when the instantaneous field was applied to the system.

The question still arises as to whether any TDTR has a basic physical significance. It is certainly possible that the environment of a dipole gradually changes with time [12] or that defects start to move towards it [9-11], and that this leads to an effective relaxation rate that decreases as time progresses. If a definite initial state for the elements is postulated, the corresponding TDTR is that associated with the response function, $w(t)$. However, the form predicted for $w(t)$ by these theories leads to a stretched-exponential decay with time of the response function rather than of the relaxation function, which would not seem to be in accordance with the experimental results. We return to this point in section 4, after first presenting in the next section the form of $w(t)$ required to account for the types of response function that are usually observed in experiments.

Finally, before doing this, we consider briefly the relationship between the above analysis, which was based purely on the superposition principle, and linear-response theory [15, 16]. According to the latter, the relaxation function can be expressed in terms of field-free correlation functions of the system's dipole moment [16], and in particular, for fields and moments in the z direction, the relaxation function

$$\Phi(t) = \langle P_z(0)P_z(t) \rangle / \langle P_z(0)P_z(0) \rangle \quad (15)$$

where $\langle \rangle$ denotes a configurational average. This would seem to suggest that the relaxation function has some fundamental significance, and so perhaps that $W(t)$ would also have. However, the configurational average must be taken over a system in thermal equilibrium, and so refer to an equilibrium renewal process [17], in which the distribution of initial states is that appropriate to thermal equilibrium. On the other hand, as noted above, microscopic models usually treat systems undergoing ordinary renewal processes, in which the initial state is such that a transition took place and the system subsequently started relaxing at time $t = 0$. The relationship between these two types of process is essentially the same as that discussed above between the relaxation function and the response function, and so between the TDTRs $W(t)$ and $w(t)$.

3. The empirical form of the time-dependent transition rate

Since we have shown that it is the TDTR $w(t)$ associated with the response function that may be of physical significance, it is of interest to examine its form for two types of response to which the experimental results on dielectric polarization are often fitted. Such an examination will provide a basis for the discussion, in the next section, of the relationship between TDTRs and the experimental results.

The first example that we consider is that in which the relaxation function is described by the KWW stretched-exponential function [4, 5], so that

$$\Phi(t) = \exp(-[t/\tau]^\beta). \quad (16)$$

In this case

$$w(t) = (1 - \beta)\tau/t + \beta\tau[t/\tau]^{\beta-1} \quad (17)$$

and the first term on the left-hand side is the dominant one for

$$[t/\tau]^{\beta-1} < (1 - \beta)/\beta. \quad (18)$$

On the other hand, the experimental data are usually only fitted to equation (16) for $0.99 > \Phi(t) > 0.01$, and for most of this time range the inequality (18) holds true. For $\beta = \frac{1}{2}$, for instance, $\Phi(t)$ is in the required range for $0.0001 < t/\tau < 21$, while the first term in $w(t)$ dominates for $t/\tau < 1$. Thus, for most of the times of interest $w(t)$ is inversely proportional to the time.

The other example that we consider is that in which the results in the frequency domain are represented by the HN function [6], so that

$$\chi(\omega) = \chi_s/[1 + (i\omega\tau)^\alpha]^\gamma. \quad (19)$$

In this case, $\Phi(t)$, $\phi(t)$ and $w(t)$ have to be evaluated by numerical integration, using the representation of the HN function as a superposition of relaxation times τ with the distribution function given by HN [6], namely

$$g(\ln[\tau]) = (1/\pi)(\tau/\tau_H)^{\alpha\gamma} \sin(\gamma\theta)/[(\tau/\tau_H)^{2\alpha} + 2(\tau/\tau_H)^\alpha \cos(\alpha\pi) + 1]^{\gamma/2} \quad (20)$$

where θ is given by

$$\tan(\theta) = \sin(\gamma\theta)/[(\tau/\tau_H)^\alpha + \cos(\gamma\theta)] \quad 0 \leq \theta \leq \pi. \quad (21)$$

Incidentally, because of the complicated form of the integrand, we found it more efficient to use a fixed-point integration formula such as Simpson's rule rather than formulae that choose different points for different values of the frequency or the time.

Before presenting the results of our calculations for a set of typical values of the parameters, we note two quite general features of these results, which are also shared by the Dissado-Hill function [18] and by Jonscher's 'universal' law [1]. These concern the asymptotic forms of $\phi(t)$ at long and short times, and make use of Tauberian theorems to relate the response in the frequency and the time domains. In general, if as $\omega \rightarrow \infty$, $\phi(\omega) \sim (\omega\tau_H)^{n-1}$, where $0 < n < 1$, then as $t \rightarrow 0$, $\phi(t) \sim (t/\tau_H)^{-n}$ and so $w(t) \sim n/(t/\tau_H)$. Similarly, if as $\omega \rightarrow 0$, $\phi(\omega) \sim 1 - (\omega\tau_H)^m$, where $0 < m < 1$, then as $t \rightarrow \infty$, $\phi(t) \sim (t/\tau_H)^{-(1+m)}$ and so $w(t) \sim (1+m)/(t/\tau_H)$. For the HN function, $\phi(\omega)$ has the above limiting forms, which $1 - n = \alpha\gamma$ and $m = \alpha$.

We now present in figure 1 the results of our calculations of $W(t)$ and $w(t)$ for a typical set of parameters, namely $\tau_H = 2.92$, $\alpha = 0.81$ and $\gamma = 0.51$, the values which according to Alvarez *et al* [19] give the best fit to $\exp(t^{1/2})$. From a comparison of the continuous line, which refers to $w(t)$, with the dashed line representing a function proportional to $1/t$, we see that $w(t)$ is inversely proportional to t for most of the time range, with only slight deviations from a straight line in the region of the crossover between the two asymptotic forms of the behaviour. This arises because the straight lines corresponding to these forms intercept the line $\log(T/\tau_H) = 0$ at two points with a distance between them of $\log(n) - \log(1+m)$. From the dotted line, which represents $W(t)$, we note that $W(t)$ is also proportional to $1/t$ at long times, rather than to $t^{-1/2}$ as for the corresponding stretched-exponential function. This is in accord with the results of Alvarez *et al* [19], *inter alia*, that the stretched exponential can only be fitted to the HN function over a limited range of times or frequencies. Very similar results are obtained with other values of the HN parameters.

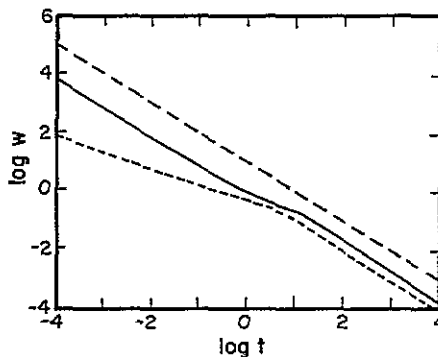


Figure 1. The logarithms of the TDTRs as functions of $\log(t)$ for the HN function with $\tau_H = 2.92$, $\alpha = 0.81$ and $\gamma = 0.51$, which corresponds approximately to $\exp(-t^{1/2})$. The continuous line shows the TDTR $w(t)$ for the response function and the dotted line the TDTR $W(t)$ for the relaxation function, while the dashed line shows, for comparison, a function proportional to $1/t$.

Our conclusion from the above results is that the TDTR $w(t)$ has the same very specific form at most values of the time both for systems in which the dielectric relaxation is described in the time domain by a stretched-exponential function and for those in which the response in the frequency domain is described by the HN function.

4. Discussion

While the TDTR $w(t)$ for the dielectric response function could in principle be of physical significance, the results presented in the previous section indicate that, for a system having a scaling time τ , at most times these rates are inversely proportional to t/τ , with a constant of proportionality that lies between zero and unity at short times and between unity and two at long times. It is certainly far from simple to devise a theory of TDTRs having such properties, and most microscopic theories using TDTRs so not satisfy these requirements. The natural conclusion would seem to be that such rates do not have any fundamental physical meaning, and that one should look for some different approach to the calculation of a system's dielectric response. Incidentally, one such possible approach is provided by the theory of Dissado *et al* [18], which predicts (cf equation (10) of that paper) that at long times there is an effective transition rate inversely proportional to the time. However, an approach in terms of TDTRs is also possible, since the above conclusion concerning the TDTRs is only partially correct. While the TDTR $w(t)$ deduced directly from the experimental results as in the previous section may not be very meaningful, there can be a function $w(t)$ of the form predicted by the various theories that corresponds to the experimental results. The reason for this is that the TDTR was calculated in section 3 from the observed global response of the system, and so is only meaningful if all the elements in the system have exactly the same response function. Otherwise a distinction has to be made between the global TDTRs, derived from the macroscopic properties of the system, and the local TDTRs of the individual elements. Such a distinction corresponds to the difference between the global response function of the whole system and the local response functions of which it is the sum.

In order to clarify this distinction and hence the possible meaning of a TDTR $w(t)$, it is useful to start by considering an alternative approach to the explanation of non-exponential relaxation, namely one that attributes it to a distribution of relaxation times (DRTs). In this approach, the observed relaxation or response functions are attributed to a superposition of processes with constant transition rates $1/\tau$ occurring in parallel with a distribution $g(\tau)$ of the relaxation times τ [20]. While this is always possible formally, there is not yet a good explanation of why the same form of $g(\tau)$ is observed in a variety of different systems. The alternative approach that we suggest is to attribute the response to a superposition of processes having a distribution of TDTRs $w(t)$ for their response functions, all of similar form but with different values of the parameters because of the inhomogeneity of the system. Incidentally, such a superposition is made more plausible by the recent experimental evidence that glasses are microscopically quite inhomogeneous [21, 22]. The form of these TDTRs and response functions need not be the same as those for the macroscopic system, just as it is not for the DRT approach. The number of possible forms of response functions or TDTRs $w(t)$ and distributions of parameters that can fit the experimental results is very large, and the problem is to find appropriate combinations that are sufficiently general and physically plausible.

5. Conclusions

Our main conclusion is that time-dependent transition rates $w(t)$ can in principle be usefully defined only for the dielectric response function, and not for the relaxation function as in many popular approaches. For the response function, the experimental results indicate that, for a system having a scaling time τ , at most times these rates are inversely proportional

to t/τ , with a constant of proportionality that lies between zero and unity at short times and between unity and two at long times. Such a behaviour is not predicted by any of the current theories. However, if allowance is made for the difference between global and local response functions, the requirement that the $w(t)$ appropriate to each element have the same generic form, with different values of the parameters because of the inhomogeneity of the system, could well provide an explanation for the observed non-exponential relaxation.

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