The significance of temperature-dependent distributions of activation energies

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Abstract.   While the response to an electric field of many disordered systems can be accounted for by postulating that the system contains independent particles with transition rates having a distribution of energy barriers or activation energies, in order to account for the temperature dependence of the experimental results it is often assumed that this distribution depends on temperature. In this paper, the question is examined of the minimum temperature dependence of the energies of the rates for the individual particles that is required to produce such temperature-dependent distributions for the system. This permits the clarification of the meaning of a temperature-dependent distribution of activation energies, and also shows that standard techniques such as the measurement of thermally stimulated depolarization currents often cannot determine whether or not such a distribution exists.

1. Introduction

In many physical systems, especially those possessing an appreciable amount of disorder, the experimental results for properties such as the mechanical or dielectric response and the ionic conductivity [1, 2] cannot be attributed to a single type of process with a given relaxation time τ. Such a process would lead, for instance, to the electric polarization $P(t)$ on the removal of a steady field or the mechanical stress $G(t)$ on the removal of a steady strain exhibiting a simple exponential decay with time. Instead, the response of these two properties can often be described in the time domain by the Kohlrausch–Williams–Watts (KWW) [3, 4] stretched exponential function, $\exp[-(t/\tau)^\beta]$, or in the frequency domain by the Havriliak–Negami (HN) [5] function $[1 + (i\omega\tau)^\alpha]^{-\gamma}$. Numerous explanations have been advanced for this type of response, and also for the observed frequency dependence of the ionic conductivity, such as Ngai's [6] coupling model and Shlesinger's [7] generalized trigger diffusion model. One quite popular type of model attributes the experimental results to the existence of different particles, such as molecules or ions, relaxing in parallel with a distribution of relaxation times (DRT) that can be associated with a distribution $h(E_a)$ of activation energies E_a. This model has been used, *inter alia*, to account for the dielectric response [8, 9] and the ionic conductivity [9–12] of different systems, and has also been used to account for the results of nuclear magnetic resonance in ionic conductors [11], while detailed statistical arguments have been advanced for a DRT that leads to relaxation functions of the KWW form [13].

In order to account for the experimental results at different temperatures, it is usually necessary to assume that the above distribution of activation energies (DAE) is a function of the temperature T [8–11], i.e. that it is of the form $h(E_a, T)$. Such a temperature-dependent

distribution certainly seems possible physically, as we discuss in section 3, and it raises no problems as long as one is only interested in the isothermal macroscopic properties of the system. However, if one is interested in the properties of a particular set of particles when the temperature changes, as for instance in experiments involving the thermally stimulated depolarization of molecules that were polarized at a given starting temperature [14, 15], the global DAE is not sufficient, and one needs to know how the activation energy for a given set of molecules changes with the temperature. This question assumes, of course, that a physical meaning can be attached to temperature-dependent activation energies, an assumption that we make for the present and will discuss below in section 3. In this paper, we examine the minimum changes in the activation energies of the transitions of the individual particles that will lead to an observed distribution $h(E_a, T)$, and discuss the consequences of our results. The motivation for such an approach is that one does not expect that a gradual change in the temperature will lead to a sudden change in the environment of any given particle and so in the activation energy that is required for it to make a transition.

In section 2 of this paper, we present the formalism for associating a global temperature-dependent distribution of activation energies for the system with the temperature dependence of the activation energies of the individual particles. In particular, we find that for the double-exponential DAE together with a fixed pre-exponential factor that is often used [8–10], it is not possible to distinguish between this DAE and a distribution of pre-exponential factors (DPF) for the transition rates with a single activation energy. In section 3, we first show that a temperature-dependent activation energy should really be regarded as a temperature-dependent energy barrier, and then consider briefly the physical motivation for such distributions. The main question that we consider in this section is whether it is possible to obtain conclusive experimental evidence for the presence of a distribution of temperature-dependent energy barriers. Finally, our conclusions are summarized in section 4.

2. Temperature-dependent distributions

It is instructive to start by considering the more general problem of a system in which the energies E, whether they be the energies of eigenstates of the system or the activation energies E_a for transitions between states, are functions of temperature. In such systems, the states or transitions obviously cannot be identified by their energies, and so we will associate with each of them a parameter x, having a distribution $g(x)$ that is independent of temperature. This parameter is chosen to be such that for each value of x there is a unique associated energy $E(x, T)$, and we write the inverse of this relationship in the form

$$x = X(E, T). \tag{1}$$

Then, since the range of x corresponding to energies between E and $E + dE$ is $|\partial X(E, T)/\partial E| dE$, one readily finds that

$$g(x)|\partial X(E, T)/\partial E| = h(E, T). \tag{2}$$

In order to show how the parameter x can have some physical significance, we consider first a crystal in which we choose for this parameter the wavenumber k, and in which the energy of the state associated with this wavenumber is

$$E(k) = \hbar^2 k^2/[2m'(T)] \tag{3}$$

where $m'(T)$ is a temperature-dependent effective mass. In this case, the distribution $g(\mathbf{k})$ for a crystal in d dimensions is just

$$g(\mathbf{k}) = Ak^{d-1} \tag{4}$$

where A is a normalizing constant, and hence it follows from equation (2) that

$$h(E, T) = (A/2)[2m'(T)/\hbar^2]^{d/2} E^{d/2-1} \tag{5}$$

which corresponds to the standard result in the case of three-dimensional systems [16].

We now turn to the main subject of this paper, namely disordered systems involving transitions over energy barriers and so having temperature-dependent distributions $h(E_a, T)$ of activation energies E_a. These systems are often modelled [8–13] by a set of independent entities (which we will call particles for convenience) each relaxing in parallel, with a distribution of relaxation times (DRT) τ such that at temperature T after a disturbance from equilibrium each particle relaxes exponentially in time towards some ground state with a relaxation time

$$\tau = \tau_0 \exp(E_a/k_B T) \tag{6}$$

where k_B is the Boltzmann constant and in the simplest cases the pre-exponential factor τ_0 is assumed to be constant. Rather than treat a general temperature-dependent DAE, we consider here the special case for which the normalized distribution of activation energies $h(E_a, T)$ has the form

$$h(E_a, T) = cH[(E_a - E_0)f(T)] \tag{7}$$

where $H(y)$ is a normalized distribution. Since both distributions are normalized,

$$1 = \int_{-\infty}^{\infty} h(E_a, T) \, dE = [c/|f(T)|] \int_{-\infty}^{\infty} H(y) \, dy = c/|f(T)| \tag{8}$$

and so

$$c = |f(T)|. \tag{9}$$

For this type of distribution, it is natural to choose as the parameter that identifies the different particles

$$x = [E_a - E_0]f(T) \tag{10}$$

in which case

$$g(x) = h(E_a, T)/|f(T)| = H(x). \tag{11}$$

We note that a similar idea, but with a very different motivation, was used by MacDonald [9].

The first DAE of this type that we consider is the double-exponential DAE [8–10], which has often been invoked to explain the observed frequency dependence of the electrical susceptibility or of the ionic conductivity,

$$h(E_a, T) = \begin{cases} A \exp[-a(E_0 - E_a)/k_B T] & E_a \leqslant E_0 \\ A \exp[-b(E_a - E_0)/k_B T] & E_a \geqslant E_0 \end{cases} \tag{12}$$

where E_0, a and b are constants that are independent of T, and $A = ab/[(a + b)k_B T]$ is the normalizing constant. This distribution leads at high and low frequencies to the same power-law dependence of the response on the frequency as the HN function [8], and the temperature dependence of $h(E_a, T)$ is required in order to obtain the time–temperature superposition, i.e. that the form of frequency dependence is independent of temperature, which is often found at least approximately [1, 2]. For this distribution, $f(T) = 1/(k_B T)$, and so the parameter x given by equation (10) has the temperature-independent distribution

$$g(x) = \begin{cases} B \exp(ax) & x \leqslant 0 \\ B \exp(-bx) & x \geqslant 0 \end{cases} \tag{13}$$

where $B = ab/(a+b)$. However, it then follows that the relaxation time for a given particle x is

$$\tau(x, T) = \tau_0 \exp[E_0/k_B T] \exp(x). \tag{14}$$

Thus, while the relaxation times were assumed, usually on physical grounds, to arise from a DAE, they in fact are indistinguishable from a DRT with a single activation energy E_0 and a DPF $\tau_0 \exp(x)$. This result, which we discuss in section 3, is of particular interest for the analysis of measurements of thermally stimulated depolarization currents (TSDC).

The other typical DAE that we consider is a physically very plausible one for a disordered system and one which has also been invoked to explain experimental results for ionic conduction [9, 11], namely a Gaussian distribution of activation energies with standard deviation σ:

$$h(E_a, T) = [2\pi\sigma^2]^{-(1/2)} \exp[-(E_a - E_0)^2/(2\sigma^2)]. \tag{15}$$

Since there is no *a priori* reason why σ should not be a function of temperature, we write $\sigma = \sigma(T)$. This distribution is then of the form of equation (7), with $f(T) = 1/\sigma(T)$, so the states are identified by the parameter

$$x = (E_a - E_0)/\sigma(T) \tag{16}$$

for which $g(x)$ is just the normal distribution. In the simplest case of a $\sigma(T)$ that decreases linearly with increasing temperature

$$\sigma(T) = \sigma_0 - ak_B T \tag{17}$$

one then readily finds that

$$\tau(x, T) = \tau_0 \exp[E_0/k_B T] \exp([\sigma_0 x]/k_B T) \exp(-ax). \tag{18}$$

In this case, the pre-exponential factor of a particle with apparent activation energy $E_0 + \sigma_0 x$ is just $\tau_0 \exp(-ax)$, which is just the well-known compensation law [14, 15, 17] or Meyer–Neldel rule [18]. Incidentally, MacDonald [9] found that the best fit of his truncated Gaussian distribution to the experimental results of Birge *et al* [19] for the a.c. conductivity of the ionic conductor $(KBr)_{0.5}(KCN)_{0.5}$ involved a standard deviation that decreases with temperature, although he did not attempt to fit it to the form of equation (17).

3. Discussion

We now turn to the physical significance of the above results, and consider first the meaning of a temperature-dependent activation energy. Strictly speaking, if the activation energy is defined by an Arrhenius law such as equation (6), then it is nonsense to speak of a temperature-dependent activation energy, and this temperature dependence should be absorbed in the pre-exponential factor, as in equations (14) and (18). However, the physical motivation for an Arrhenius law is often the difference between the free energy of the initial state and that of either the final state or of some intermediate state through which the system must pass during the transition. The above energy barriers can certainly depend on the temperature, and so if one uses temperature-dependent distributions one should really use the term distributions of energy barriers rather than distributions of activation energies. Since the latter term has become so accepted in the literature, we will continue to use it, but with the above interpretation.

The second point that we consider is the possible physical justification for the existence of a specific DAE. The physical motivation for the Gaussian distribution [9, 11] used in equation (15) is simply that in any disordered system one expects to find a distribution

of energy barriers, and according to the central-limit theorem (if it is applicable here) this distribution should be Gaussian. However, at least for dielectric relaxation in insulators [9], this Gaussian distribution does not usually fit the isothermal results as well as the double-exponential DAE used in equation (12) does, since (as mentioned above) only this latter leads to a form similar to the HN function, which is widely used to describe experimental results in the frequency domain. A physical motivation for this temperature-dependent distribution has been suggested by Wang and Bates [10], in terms of the thermal fluctuations that change the activation energy for transitions of the individual particles. In this theory, the distribution should be of quite general validity, and they in fact apply it to ionic solids in which the ions are situated in double-well potentials.

The main question of interest is the possibility of observing experimentally a DAE, and in particular a temperature-dependent one of the form of equation (7). The results of isothermal experiments can always be represented formally in terms of a DRT, whether or not the processes involved are in fact the relaxation in parallel of independent particles. Thus the results of isothermal experiments at different temperatures can always be expressed in terms of a temperature-dependent DRT, whatever the physical processes that are involved. However, isothermal experiments provide no indication as to the temperature dependence of the individual relaxation times, if these are assumed to have some physical significance. Thus, the best hope of obtaining direct experimental evidence for a DAE is by means of experiments that monitor the effects of changes of temperature on the individual elements of the system, such as TSDC experiments. In fact, it has been claimed in the past [20, 21] that these experiments permit an unequivocal distinction to be made between systems with a DAE and those having a fixed activation energy and a DPF. However, the above results were based on the assumption of a temperature-independent DAE with a fixed pre-exponential factor, which is often not compatible with the isothermal results for the dielectric susceptibility at different temperatures. Our analysis shows that for the frequently observed temperature-dependent double-exponential DAE of the form of equation (12), it is not possible to conclude from experiments of the TSDC type whether the states in a system have the above DAE and a fixed pre-exponential factor or a single activation energy and a DPF that could arise, for instance, from a distribution of tunnelling distances or other subsidiary processes. Similarly, in systems with a Gaussian distribution for the DAE, it is not possible to determine by these methods whether the pre-exponential factor is fixed and the standard deviation of the distribution is temperature dependent or whether the distribution is fixed and the pre-exponential factor depends on the activation energy according to the compensation rule. The reason for this is that, at least for relaxation experiments, for the system as a whole (i.e. for an ensemble) the free-energy differences and pre-exponential factors for transitions are not independent variables. While this result is trivial for isothermal experiments, in which only the relaxation times τ are important for the DRT and not which term in equation (6) for τ is the variable, the main novel point of our analysis is to show that this is also true for relaxation experiments at variable temperatures. However, it is just possible that one could distinguish between these possibilities by experimental techniques which involve energy differences rather than relaxation times, if these can be performed at varying temperatures.

4. Conclusions

The main conclusion from our analysis is that, even when the system's response is measured under conditions of varying temperature, one often cannot distinguish experimentally between different physical models that lead to a temperature-dependent distribution of

relaxation times. In particular, one cannot distinguish between the double-exponential DAE with a fixed pre-exponential factor that is often used to describe experimental results and a distribution of these factors with a single constant activation energy. Of course, this does not necessarily detract from the value of models involving DAEs for the correlation of experimental results on different systems, for instance, but it indicates that the standard types of experiment, such as TSDC, cannot be used to test the validity of different types of model.

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