

A Model for Non-Debye Relaxation in Ionically Conducting Glasses*

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Abstract

A new model for dielectric relaxation in ionically conducting glasses is described. This is the "diffusion-controlled relaxation" model, in which non-Debye-like behaviour is naturally predicted, without the arbitrary assumption of a distribution of relaxation times. It is shown that the exact expression for the frequency dependence of the dielectric relaxation, obtained here for the first time, can account for the experimentally observed departures from Debye-like behaviour, together with certain aspects of the temperature and ionic composition dependences of the behaviour.

Relaxation processes in disordered materials very rarely follow a Debye-like behaviour, *i.e.* with a purely exponential dependence of a response function in the time domain ($\phi(t) = \exp(-t/\tau)$, with a single fixed value of relaxation time τ) or equivalently with a frequency-dependent susceptibility term of the form $\chi^*(\omega) = (1 + i\omega\tau)^{-1}$ (*i.e.* representing a perfect circle with the centre on the real axis in a complex plane or Cole–Cole plot of real and imaginary parts of χ^* , *i.e.* χ_1 and χ_2 respectively). Thus, non-exponential temporal decays and non-circular arcs in Cole–Cole plots (or equivalently broad asymmetric peaks in the loss function $\chi_2(\omega)$), *i.e.* non-Debye behaviour, are commonly observed in, for example, the behaviour of ionic dynamics in glasses [1]. Hence, it is essential to have a proper theoretical understanding of this rather general behaviour.

In general terms, non-Debye relaxational behaviour can be regarded as arising from an elongation of the time scale characteristic of the process in question, *i.e.* a single effective relaxation time is no longer sufficient to describe the entire relaxational behaviour. This situation can

always be represented by a particular distribution $g(\tau)$ of relaxation times if the net relaxational response can be regarded as being a superposition of independent responses each characterized by a particular value of τ and which act in parallel. However, this approach is only really valid if there is an underlying physical reason for the existence of the distribution $g(\tau)$, *e.g.* if τ is related to say the ionic jump distance, which in turn has a distribution of values. Alternatively, elongation of the time scale for relaxational behaviour can also arise if the relaxational process occurs in a series-like manner. This occurs, for example, if the individual relaxation processes are not independent but are coupled in some manner. The diffusion-controlled relaxation (DCR) model for ionic transport described in this paper is one such mechanism.

The DCR mechanism for ionic transport [2] takes as its basis the model originally proposed by Glarum [3] for dielectric relaxation in molecular liquids and which assumes that the relaxation is triggered by the arrival at a relaxational site of a "defect" diffusing from a neighbouring site. In the case of ionic transport, we adopt the ideas of Charles [4] for the microscopic motion of ions in a glass, and suppose that the "defect" in the Glarum approach is in fact a diffusing ion itself and that the arrival of such an ion at a site already occupied by an ion, thereby forming an "interstitialcy" [1], causes the triggering of a relaxation event (Fig. 1). In this paper, we analyse the theoretical behaviour expected for relaxation triggered by the diffusional motions of ions (the mechanisms in Figs. 1(a) and 1(b)). Elsewhere, we consider the consequences resulting from the intersite ionic hopping represented by the motions in Figs. 1(c) and 1(d) [5].

In the DCR model [2], we consider in fact two independent contributions to the relaxational behaviour. The first arises from the diffusion-triggered relaxation at an interstitialcy, as dis-

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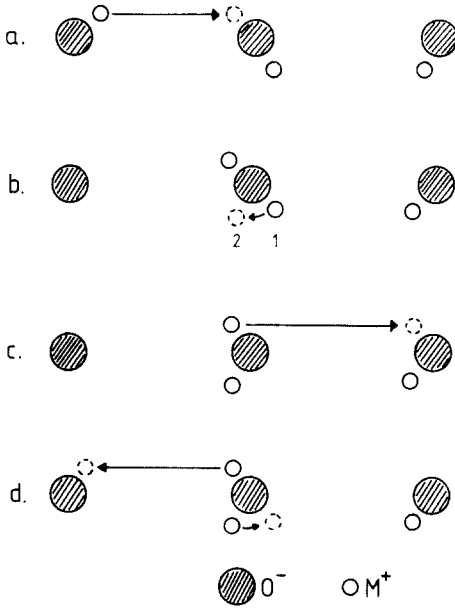


Fig. 1. Schematic representation of the DCR mechanism [2]: (a) diffusion and creation of a doubly occupied ("interstitialcy") site; (b) rotational relaxation of an ion 1 triggered by the arrival of another ion 2, giving rise to polarization; (c) subsequent diffusion, giving rise to d.c. conductivity; (d) reverse diffusion, *i.e.* intersite "hopping", giving rise to polarization conductivity only.

cussed above and shown in Figs. 1(a) and 1(b). The second contribution is assumed to take place in the absence of the DCR mechanism and can be thought to arise simply from the thermally activated motion of an ion in a singly occupied site from its locally stable position to a metastable position. The temporal response function $\phi(t)$ describing the decay in polarization after the sudden removal of a steady electric field can therefore be written as the product of two terms [2, 3]:

$$\phi(t) = \exp\left(-\frac{t}{\tau}\right) \{1 - P(t)\} \quad (1)$$

where the exponential term describes the diffusion-independent relaxation behaviour, characterized by a relaxation time τ (taken to be constant for simplicity for the time being), and $P(t)$ is the probability that a triggering ion has reached the relaxational site by time t . The original analysis of Glarum [3], followed by Elliott [2], is a simplified treatment, based on the assumption that only the triggering ion nearest to a site at $t=0$ was considered; subsequent work by Bordewijk [6] removed this restriction and he

showed that, for diffusive motion in one dimension,

$$1 - P(t) = \exp\left\{-\frac{2}{l_0} \left(\frac{Dt}{\pi}\right)^{1/2}\right\} \quad (2)$$

where D is the diffusion constant and l_0 is a length characterizing the spatial distribution of triggering ions (assumed to be random). Thus, the total decay function now becomes

$$\phi(t) = \exp\left(-\frac{t}{\tau}\right) \exp\left\{-\left(\frac{t}{\tau_1}\right)^{1/2}\right\} \quad (3)$$

where τ_1 is a characteristic diffusion time, given by

$$\tau_1 = \frac{\pi l_0^2}{4D} \quad (4)$$

The time (and hence the frequency dependence) of eqn. (3) has not been analysed previously.

By inspection, it can be seen that eqn. (3) predicts a non-exponential time dependence, *i.e.* non-Debye behaviour, of similar form to the Williams-Watts [7] function:

$$C(t) = \exp\left\{-\left(\frac{t}{\tau_{W-W}}\right)^{\beta_{W-W}}\right\} \quad (5)$$

where the exponent is given by

$$\beta_{W-W} = \frac{t/\tau + 2(t/\tau_1)^{1/2}}{t/\tau + (t/\tau_1)^{1/2}} \quad (6)$$

Thus, β_{W-W} is actually time dependent, and only at very long times is Debye-like behaviour, *i.e.* $\beta_{W-W}=1$, recovered. To date, however, very few time-dependent polarization studies have been performed for ionically conducting glasses, and consequently it is difficult to confirm experimentally relations such as that given by eqn. (3).

However, there have been many more studies of the frequency-dependent behaviour of the polarization and therefore, in order to test the DCR theory, it is necessary to ascertain the frequency dependence predicted by eqn. (3) by means of a Laplace transform. Although an analytic expression for the frequency dependence cannot be obtained in this way for the general Williams-Watts function (eqn. (5)) with $\beta_{W-W} \neq 0.5$ or 1.0, nevertheless it is fortuitous that such a transformation can be performed analytically

for eqn. (3). Thus, the frequency dependence predicted by the general DCR model is given here for the first time, namely

$$\chi^*(\omega) = \frac{1}{1+i\omega\tau} + \frac{i\omega\tau}{(1+i\omega\tau)^{3/2}} \left(\frac{\pi\tau}{4\tau_1} \right)^{1/2} \times \exp \left\{ \frac{\tau}{4\tau_1(1+i\omega\tau)} \right\} \operatorname{erfc} \left[\frac{\tau^{1/2}}{\{4\tau_1(1+i\omega\tau)\}^{1/2}} \right] \quad (7)$$

where the complex susceptibility $\chi^*(\omega) = (\varepsilon^* - \varepsilon_\infty)/(\varepsilon_0 - \varepsilon_\infty)$, and erfc refers to the complementary error function. Detailed quantitative analysis of eqn. (7) is complicated and will not be given here [8]; instead, in this paper, we give a qualitative discussion of eqn. (7).

The main interest lies in the frequency dependence exhibited by eqn. (7), and this can be ascertained approximately by comparison with the empirical Davidson–Cole [9] relation

$$\chi_{D-C}^*(\omega) = (1+i\omega\tau)^{-\beta_{D-C}} \quad (8)$$

By expanding both eqn. (7) and eqn. (8) to terms which are first order in $i\omega\tau$ and then comparing coefficients, eqn. (7) can be forced approximately into Davidson–Cole form, giving a value for the frequency exponent

$$\beta_{D-C} \approx 1 - \left(\frac{\pi\tau}{4\tau_1} \right)^{1/2} \quad (9)$$

It is interesting to note in passing that the approximate treatment introduced by Glarum [3] and used in our previous discussion of the DCR model [2] gave as the estimate for $\beta_{D-C} \approx 1/\{1 + (\pi\tau/4\tau_1)^{1/2}\}$ which, to a first approximation, is exactly the same as eqn. (9). Thus, although the detailed behaviour may differ between the exact treatment given here and the approximate analysis given previously, to a first approximation they give the same results; hence, the conclusions of our discussion of the DCR model given previously [2] remain essentially unchanged. It should be noted that in general $\beta_{D-C} \neq \beta_{W-W}$ except for the special case when both are equal to unity, *i.e.* the Debye case.

The significance of the fact that eqn. (7) can be recast approximately in the Davidson–Cole form is that eqn. (8) predicts that Cole–Cole plots of real and imaginary components of the susceptibility or dielectric constant (or modulus) etc. would be skewed, as is generally found experimentally for ionically conducting glasses [1], and

that correspondingly the loss peak curves of $\chi_2(\omega)$ would be broader and more asymmetric than predicted for a pure Debye-like response. The high frequency side of the peak is predicted to behave as $\chi_2(\omega) \propto \omega^{-\beta_{D-C}}$ for the Davidson–Cole function, eqn. (8) [10]. Since the real part of the a.c. conductivity is related to the dielectric loss by $\sigma_1(\omega) \propto \omega\chi_2(\omega)$, it is predicted that the frequency dependence of the a.c. conductivity should behave approximately as

$$\sigma_1(\omega) = A\omega^s$$

where

$$s = 1 - \beta_{D-C} \approx \left(\frac{\pi\tau}{4\tau_1} \right)^{1/2} = \left(\frac{D\tau}{l_0^2} \right)^{1/2} \quad (10)$$

Thus the DCR model can account for the widespread observation of a power law frequency-dependent conductivity in ionic glasses.

Very recently, Jain and Mundy [11] have presented experimental a.c. conductivity data for a number of borate and germanate glasses which show very unusual behaviour, namely a minimum in the temperature dependence of s . This behaviour cannot readily be understood on the basis of most existing theories for the a.c. conductivity in amorphous materials. However, the DCR model does predict such a minimum in $s(T)$ under certain conditions; the temperature dependence arises from the fact that both τ and D in eqn. (10) are themselves temperature dependent, *i.e.*

$$\tau = \tau_0 \exp \left(\frac{W}{kT} \right) \quad (11a)$$

and

$$D \propto T\sigma_{dc} \propto T\sigma_0 \exp \left(-\frac{E_a}{kT} \right) \quad (11b)$$

As a consequence, eqn. (10) predicts that a minimum in $s(T)$ occurs when $W - E_a = kT$ [2]. It is commonly found experimentally that E_a and W , the activation energy for the loss peak corresponding to diffusion-independent local motions, are almost equal.

Thus far, the theoretical treatment has assumed that one-dimensional diffusive motion on a regular lattice triggers the relaxation. We believe that this circumstance is approximately obeyed in practice in ionically conducting glasses, at least at intermediate ion concentrations x , since a percolation conducting pathway through the structure is established at $x \approx 10\text{--}15\text{ at.}\%$ which is one dimensional in character. Such percolation pathways may be viewed as comprising the channels bordered by non-bridging anion sites in the modified continuous random network model proposed by Greaves [12]. However, at very low (or very high) ion concentrations, the transport is more likely to be three dimensional in character. In such a case, Bordewijk [6], Shlesinger and Montroll [13] and Klafter and Shlesinger [14] have shown that eqn. (2) becomes instead the pure exponential function

$$1 - P(t) = \exp\left(-\frac{t}{\tau_2}\right)$$

where τ_2 is a constant involving D and l_0 . Thus, $\phi(t)$ from eqn. (1) becomes a simple exponential function, with a single relaxation time

$$\frac{1}{\tau_0} = \frac{1}{\tau} + \frac{1}{\tau_2}$$

i.e. in three dimensions Debye-like behaviour is recovered. There is, in fact, experimental support for this theoretical prediction. Simmons *et al.* [15] found that the electrical relaxation behaviour of borosilicate glasses containing very low (about 400 ppm) concentrations of Na^+ ions became more Debye like than at higher concentrations.

It must be admitted that the assumption that the DCR process in ionic glasses involves one-dimensional diffusive motion on a regular lattice may be an oversimplification. There is some evidence that percolation clusters near criticality are in fact "fractal" structures. Diffusion on such fractal networks also leads to stretched-exponential (Williams-Watts) temporal decay [14] but, since the exponent is no longer necessarily equal

to $\frac{1}{2}$ (depending on the details of the fractal lattice), an analytic expression for the frequency dependence of the complex dielectric constant (or susceptibility) cannot in general be obtained.

Finally, brief mention should be made of the factors determining the magnitude of the susceptibility $\chi^*(\omega)$ (or $\epsilon^*(\omega)$), since the discussion so far has centred solely around the frequency-dependent behaviour. The illustration of the local ionic environment shown in Fig. 1 is very schematic and is intended only to represent the ionic motions believed to be important in determining the dielectric relaxation in ionic glasses. The association of a given ion with a single conjugate non-bridging anion site is almost certainly an oversimplified picture, except at very low ion concentrations. The magnitude of the dielectric relaxation will be determined, of course, by the number of ions—cations and anions—present at a given site and which take part in the relaxation process. However, the general mechanism described in this paper, which leads to the predicted frequency dependence, is unaffected by such details.

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