Transport in ionic conducting glasses

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Abstract. The frequency-dependent conductivity of glasses is explained in a treatment spanning the range of frequencies, $0 < \omega < \nu_{ph} \approx 10^{12}$ Hz. A large spread of individual relaxation times is assumed. The connection between low frequency AC conduction and DC conduction is their common origin in non-local relaxation processes. This connection has already been exploited to derive results for $\sigma(\omega)$ in the electronic systems known as the 'Fermi glass' and the 'electron glass', which are in quantitative agreement with experiment. In these systems, quantitative expressions are available for the distribution of relaxation times, in contrast to the situation in ionic conducting glasses. In ionic conducting glasses, as in the electron glass, the effects of Coulomb interactions in the sequential correlation of individual transitions is critical at low frequencies when the relaxation is non-local. The framework of the calculations is given by percolation theory.

1. Introduction

1.1. General comments

The treatment given here allows relaxation between pairs of sites. The relaxation time for an ion hopping back and forth between two sites in any pair (over a barrier, E_i) is given approximately by (e.g. Pollak and Pike 1972, Dyre 1988)

$$\tau_i = \nu_{ph}^{-1} \exp[E_i/kT] \tag{1.1}$$

where ν_{ph} is a phonon frequency of order 10^{12} Hz. The pairs of sites are not assumed isolated (as in the case of Elliott 1988, Elliott and Owens 1989, where such pairs are assumed to be found in specific configurations on non-bridging oxygen ions) but can be interconnected to form a network which exists throughout the glass. The barriers encountered may be largely Coulombic, largely structural, or both together. The distribution of these barrier heights, E_i, is assumed given by $n(E_i)$. Because sequential correlations (described below) in hopping are assumed, this distribution is taken to be unaffected by the application of an external field. The form of $n(E_i)$ is unknown; knowledge of this distribution, as well as of any correlation between the barrier height and the site operation, r_i, would, within the framework of the theory developed here, allow a quantitative calculation of the dielectric relaxation at any frequency. Even without detailed knowledge of $n(E_i)$, it is possible to demonstrate that all known general features of dielecric relaxation may be obtained from this model by the application of a pair approximation at high frequencies and an application of percolation theory at low frequencies.

In a glass in which disorder may be strong enough to make transport along certain 'percolation' *paths* much easier than elsewhere, and in which a fairly smooth distribution of individual relaxation times exists, from the fastest local processes to the slowest local processes necessary to be included for macroscopic diffusion, these slowest processes then define not only the DC conductivity but provide the frequency scale of the variation of the low frequency AC conductivity as well.

At high frequencies, a distribution of relaxation times with an exponential dependence on random variables, i.e. E_i, is known to give non-Debye behaviour with $\sigma(\omega) \propto \omega^s$, $s < 1$. The departure of s from 1 arises from a non-uniform dependence of $n(E_i)$ on E_i. At low frequencies, relaxation of clusters of individual processes must be considered. Quasi-universal behaviour results from this model. The frequency dependence at low frequencies is normally supralinear, with the power a function of the dependence of cluster relaxation times on cluster size and of the distribution of cluster sizes.

The transition from AC to DC conduction is a transition from local to non-local relaxation (from pair processes in parallel to pair processes in series). Local relaxation can be described in the main by single-particle theories (but see section 2.4). The non-local relaxation at low frequencies has aspects of a many-particle theory. If percolation theory is utilized to describe the non-local relaxation, the result is automatically obtained that the transition occurs at a critical frequency, ω_c, proportional to the DC conductivity, whether σ_{dc} is activated, or (in electronic glasses) is given by $\ln\sigma_{dc} \propto -(T_0/T)^p$, with $p = 1/(d+1)$ in the 'Fermi glass' (variable range hopping, Mott 1969) or $p = 1/2$ in the electron glass (low temperature impurity conduction systems, Efros 1976, Hunt 1990a). In electronic systems (Hunt 1990a–d) quantitative agreement with experiment (Long *et al* 1988, Paalanen *et al* 1983) was obtained.

Although a smooth variation in the distribution of relaxation times is sufficient to explain the general features of the experimental data, specific cases may be consistent with additional structure in the distribution of relaxation times.

A previous work (Hunt 1990e) showed that the fact that the ratio of the low frequency conductivity to the DC conductivity, σ_{dc}, scales with a critical frequency proportional to σ_{dc} is a consequence of percolation theory, the purpose of the current paper is to show that the low frequency conductivity derived using percolation theory agrees with the pair approximation at the critical frequency. This confirms the explanation of the Barton (1966)–Nakajima (1972)–Namikawa (1975) (B-N-N) relation as well as the shape of the α-peak.

1.2. The role of Coulomb interactions

At high frequencies, when relaxation is local between isolated pairs of sites, the role of Coulomb interactions is largely restricted to the distribution of barrier heights but at low frequencies, when relaxation is non-local, Coulomb interactions sequentially correlate individual transitions, making the relaxation a collective phenomenon and slowing the relaxation significantly. An exact many-body treatment of the Coulomb interaction is not proposed in this paper. It is proposed to treat the Coulomb interaction according to its effect on relaxation times of charged particles constrained to move on one-dimensional percolation paths.

In the electron glass it has been argued (Hunt 1990d) that the sequential correlation of the slowest transitions on the percolation path reduces the free energy. The increase in the interaction energy if the transitions are not correlated is sufficient to outweigh the

reduction in phase space (and resulting increase in $-TS$) if they are. The result obtained (Hunt 1990d), that $\Delta \mathcal{F} \approx NE_g - NkT \ln\{1 + eFr_0/kT\}$, with N the number of 'slowest' transitions in a linear chain and E_g a typical increase in interaction energy resulting from not correlating 'critical' transitions, is positive for all N if $kT < E_g$. It is not known with any certainty, but it is expected here that this effect should be even greater in ionic conducting glasses than in the electron glass, because in the latter the electrons can 'hop' variable distances, and thus past one another. The height of a potential barrier between two sites in the electron glass is immaterial; since electronic 'hopping' is actually phonon assisted tunnelling, what matters is the difference in energy between the initial and final configurations. In ionic conducting glasses, however, discrete ions are assumed to follow one another by hopping over barriers along one-dimensional paths of enhanced mobility. On these paths a similar general argument involving the free energy should apply. Alternatively, the Couloumb repulsion could be assumed to increase individual barrier heights significantly (slowing *exponentially* the individual transitions) if transitions were not sequentially correlated. If individual critical transitions are assumed to be sequentially correlated, the relaxation time of a cluster of N such critical transitions (with $\tau = \tau_c \propto 1/\omega_c$) will be enhanced proportional to the factor N. The enhancement of relaxation times has a critical influence in the low frequency dielectric behaviour, and must be added to single particle theories. Similar behaviour has been postulated due to Hubbard repulsion (intra-site Coulomb repulsion between electrons) by Richards (1977) and Shklovskii and Efros (1984) and termed the 'traffic jam effect'.

An additional feature is that 'faster' transitions on this path cannot admit charge transfer unrestrictedly, as the build up of charge between such faster transitions and blocking 'critical' transitions would also tend to increase the individual barrier heights. This increase in barrier heights would be evident in regions in which the charge density were increased. Thus at low frequencies (long times) the faster transitions are considered to be slowed to the critical transition rate. Although one might expect that the 'traffic jam' effect could reduce the barrier height of that critical transition causing the block, a self-consistent treatment can result in a slowing in the rate determining transition (Richards 1977). If sequential correlation is assumed, no charge redistribution (compared to the no field case) results and the effect only slows the 'faster' transitions, with a non-exponential reduction of the DC conductivity.

1.3. Comparison with other theories

In a new theory (Elliott 1988, Elliott and Owens 1989) called diffusion controlled relaxation, the enhancement over Debye in the conductivity at high frequencies is assumed to come from the effect of an interaction between the DC, assumed diffusive, transport, characterized by an activated relaxation, and much faster Debye type relaxation at two-site centres of non-bridging oxygens (NBOs). This approach seems to us invalid, as through Coulomb interactions a very slow (DC) process is deemed capable of speeding up a very rapid process (AC relaxation). The reason for this inconsistency would seem to be the fact that Elliott only considers the possibility that the arrival of a 'diffusing' ion in the vicinity of an NBO may trigger the relaxation of a metallic ion, but he does not consider the possibility that the prior existence of such a potentially 'diffusing ion' at such a site in the identical configuration will block the relaxation of the 'polarizable' ion in the case when the field is reversed.

Work by Elliott and Henn (1990) based on a pair approximation considers the tendency of $s = d(\ln\sigma)/d(\ln\omega)$ to approach 1 with reduction in temperature. Formulations of s in terms of the upper limit cut-off, ν_{ph}, usually yield a temperature independent s. However, it was recently shown (Hunt 1990c, f) that expressions of s based on the critical frequency, ω_c, yield $s = 1 - n(kT/E')^p$, with E' a characteristic energy defining the loss peak (α-peak) frequency, and n a number which varies from system to system.

A cluster approach to the Fermi glass developed by Boettger and Bryksin (1985) is known to yield results incompatible with experiment in one-dimensional systems (Bernasconi *et al* 1980, Hunt 1990b) as well as in three-dimensional systems (Hunt 1990c). The failure in one dimension can be rectified by modifying their broken bond network to short resistances much smaller than the maximally valued resistances; in three dimensions an error arises from omission of the enhancement of relaxation times of compound processes on large clusters. This defect is shared by a work of the author (Hunt 1987) as well as Zvyagin (1980).

Other approaches, developed from a treatment by Scher and Lax (1973), have been termed the continuous time random walk (CTRW) (Dyre 1988, Niklasson 1987, Odagaki and Lax 1981). There the concept of fractal time, as well as of percolation networks involving fractal dimensionalities, has been proposed as bearing on conduction. It is believed here that the CTRW is physically incorrect. Specific criticisms include the treatment of clusters and the lack of distinction between systems with strong Coulomb interactions and those in which the Coulomb interaction may be neglected.

The CTRW (as Boettger and Bryksin) assumes that conduction takes place on the infinite, percolation, cluster at low frequencies, and on large clusters at frequencies above the so-called critical frequency. It has been shown (Hunt 1990c, e) however, that cluster relaxation times grow with cluster size. The particular enhancement is system dependent and may be proportional to the first or to the second power of the cluster length. Since processes with relaxation times inversely proportional to the frequency, ω, make the largest contribution to the real part of the conductivity, the size of the most important clusters is a function of the frequency of the applied field. This continuous dependence of the scale of the relaxation on ω is not a feature of the CTRW model. The association of percolation with some finite frequency is correct, insofar as the connection of all bonds with relaxation times less than the critical relatxation time, $\tau_c \propto 1/\omega_c$ forms an infinite network; the neglect of the enhancement of relaxation times, however, misses the fundamental physics. In particular, charge transport over infinite distances (percolation) actually occurs in the limit of infinite time, or zero frequency, as the relaxation times of infinite clusters diverge. Thus, there is no universal dependence of the conductivity on percolation exponents in the limit $\omega \rightarrow \omega_c$, but there is a universal dependence in the limit $\omega \rightarrow 0$.

The CTRW treatment may thus not escape the difficulty of the original treatment of Scher and Lax (1973) namely that it should give a frequency-independent conductivity at low frequencies. In the original CTRW in one dimension, the cause of this difficulty lay in the assumed homogeneity of the chain, which led to equal probabilities of hopping in either direction. Even if inhomogeneities of the percolation cluster are included, these inhomogeneities lead to a lowest order quadratic dependence on ω of $\sigma(\omega) - \sigma_{dc}$, a dependence which is never observed (e.g. Jonscher 1977; Long *et al* 1988; Goetze 1991). It is hard to see how assuming transport on the percolation cluster at all finite frequencies less than ω_c can give a physically meaningful frequency dependence for $\sigma(\omega) - \sigma_{dc}$, other than the quadratic dependenced of Boettger and Bryksin (1985).

The error in associating universality with ω_c is explicit when Niklasson (1987) states that the exponent, s, on ω^s above the loss peak is related to percolation. In fact s is given by the distribution of pair relaxation times and varies strongly from system to system.

2. Calculations

The calculations given are for the real part of $\sigma(\omega)$; the imaginary part can of course be obtained by dispersion relations.

2.1. The pair approximation

The polarization current, I_{ij} of a pair of sites between which an ion can jump by hopping over a barrier is given in the model of Pollak and Pike (1972) and Anderson *et al* (1972) as

$$I_{ij} = i\omega\alpha_{ij} = e\Delta f r_0 \left[(\omega^2\tau_{ij} + i\omega)/(1 + \omega^2\tau_{ij}^2)\right] \tag{2.1}$$

where $\alpha_{ij} \propto r_0^2$ is the polarizability of the pair, r_0 is the physical extent of the pair and Δf is the change in occupation of one member of the pair induced by the application of the electric field F given by

$$\Delta f \approx eFr_0/kT \tag{2.2}$$

to lowest order in the field. For ionic conduction, r_0 is of the order of one interatomic spacing and is not considered a random variable in the model of Pollak and Pike. Of course, if this model is assumed to be consistent with the DC conductivity as well some variation in pair lengths, r_0, must be allowed. Nevertheless this variation should be relatively small except in the dilute limit. This is because in the picture of random barriers there is no point in making the hop of a given ion much larger than the typical separation of these ions, as it would only encounter more barriers over which it must hop.

The usual assumption (e.g. Pollak and Pike 1972, Dyre 1988) is that the values, τ_{ij}, depend on barrier heights, E_{ij}, as

$$\tau_{ij} \approx \nu_{ph}^{-1} \exp[E_{ij}/kT] \tag{2.3}$$

with ν_{ph} a 'phonon' frequency, roughly 10^{12} Hz. E_{ij} is a random variable, ensuring a large spread in the values of the τ_{ij} even if the spread in the values of E_{ij} is not too large. The conductivity is then

$$\sigma(\omega) = \sigma_{dc} + (e^2/kT)r_0^2\omega\int[\omega\tau(E) + i]n(E)dE/[1 + \omega^2\tau^2(E)] \tag{2.4}$$

with $n(E)$ the volume density of pairs with barrier height, E. This procedure of treating pair currents is valid so long as the main contribution to $\sigma(\omega)$ comes from pairs which may be treated independently from the remainder of the system. This latter condition is satisfied as long as the remainder of the system responds much more slowly to the electric field than the pairs considered (valid at relatively high frequencies); i.e. if the density of pairs with $\tau \leqslant 1/\omega$ is not so large that clusters of pairs satisfying this condition form. The DC conductivity is added separately for reasons which will be made clear.

It is known that only those pairs with $\tau \approx 1/\omega$ contribute to $\text{Re}\sigma(\omega)$. Thus one has

$$\text{Re}\sigma(\omega) = \sigma_{dc} + \omega r_0^2(e^2/kT)N'[kT\ln\nu_{ph}/\omega]. \tag{2.5}$$

Here $N'[kT\ln(\nu_{ph}/\omega)]$ is an integral over the probability density $n(E_i)$, and gives the

concentration of pairs in a (small) energy range about $kT \ln(\nu_{ph}/\omega) = E$ (such that $\omega\tau$ is of order 1 throughout the range of energies).

The real part of equation (2.4) can also be written

$$\text{Re}\sigma(\omega) = \sigma_{dc} + (r_0^2/R)\int \omega^2 \tau^2 n(E)dE/(1 + \omega^2\tau^2) \tag{2.6}$$

if one writes for τ

$$\tau = RC = (e^2/kT)R. \tag{2.7}$$

Here C gives the charge generated per unit change of the potential difference between the two sites of a pair. This interpretation is consistent with the derivation of Pollak and Pike (1972), in which the factor arises from the expansion to first order of an occupation function. It also implies that the pair is singly occupied, a condition which can be made to hold for any frequency if transitions along the percolation paths are sequentially correlated. Equation (2.6) is essentially identical to the pair approximation for electronic glasses where it is possible to define R and C unambiguously (Miller and Abrahams 1960, Pollack 1974). It will be seen, however, that pairs with short relaxation times, which would thereby be assigned a low resistance value, can only be characterized by this resistance at high frequencies. At low frequencies, transport through such pairs can be blocked through Coulomb repulsion by bottlnecks further along the (percolation) conducting path. This particular objection should not apply to transitions with τ_c, however, as slower transitions are excluded from the percolation path. Thus the identification

$$\tau_c = R_c(e^2/kT) \tag{2.8}$$

is made for any frequency. Taking all pairs as approximately the same length is consistent with assuming that the capacitance of each is e^2/kT; the variation with frequency of the charge passed by a particular pair is attributed to a change in the resistance.

For small ω the pair approximation breaks down. Individual processes exist with τ_{ij} ranging smoothly from very small values all the way up to values commensurate with σ_{dc} (justifying the use of percolation theory in the calculation of σ_{dc}) and somewhere in the neighbourhood of a critical frequency, $\omega_c \propto \sigma_{dc}$, at least, the pair approximation must break down. This critical frequency, ω_c is defined such that the 'sub-lattice' composed of all pair processes with rates $w_{ij} \geq \omega_c$ form a macroscopic continuous path.

2.2. The DC conductivity

We write the DC conductivity as being

$$\sigma_{dc} \propto \exp(-E_0/kT) \tag{2.9}$$

where

$$\int_0^{E_0} n(E)dE = \alpha(d)/r_0^3 \tag{2.10}$$

defines E_0 by expressing the condition that some well-defined fraction, $\alpha(d)$ of bonds linking nearest neighbours in dimension d must be connected before a continuous network of infinite size linking nearest neighbours can exist. The integration is therefore cut off at the (lowest possible) maximum energy (corresponding to a maximum τ) which must be included in order to assure percolation. The expression for the DC conductivity will depend on the cluster structure. It is assumed here that d-dimensional clusters

($d \leqslant 3$) can be constructed in d-dimensional surfaces. The separation of the surfaces (if $d < 3$) is given by a length ℓ'. Using the assumption of equation (2.8) relating τ_c and R_c allows us to express σ_{dc} in terms of a critical resistance, R_c, as

$$\sigma_{dc} = r_0/\ell^{d-1}\,\ell'^{(3-d)}R_c = (e^2 r_0/kT\ell^{d-1}\ell'^{(3-d)}\tau_c)$$
$$= (e^2 \nu_{ph} r_0/kT\ell^{d-1}\ell'^{(3-d)})\exp(-E_0/kT). \tag{2.11}$$

An argument for the choice of the lengths, r_0, ℓ, and ℓ', is now given. The length r_0 in the numerator is assumed to give the linear separation of the largest 'resistances' on the current carrying path. The length ℓ in the denominator is assumed to give the separation of pairs with τ_c within the d-dimensional surface in which the percolation cluster is embedded. The quantities ℓ and ℓ' are given by $[N'(kT\ln\nu_{ph}/\omega_c)] = [N'(E_0)] = \ell^{-d}\ell'^{(d-3)}$.

If Coulomb interactions could be neglected, the appropriate length in the numerator of equation (2.11) would also be ℓ since ℓ gives the typical separation of pair processes with τ_c on the percolation path. We choose r_0 instead of ℓ because of the so-called 'traffic jam effect'. Due to Coulomb repulsion smaller 'resistances' can only pass charge when the blocking, 'resistance' has done so; when the DC conductivity is considered they must be assigned resistances equal to R_c as well (if C is constant). Thus an effective resistance of the percolation path is increased roughly by a factor ℓ/r_0 by such a 'traffic jam effect', and the DC conductivity is reduced by the Coulomb repulsion.

2.3. Low frequency conductivity

At very low frequencies, $\omega < \omega_c = \nu_{ph}\exp(-E_0/kT)$, clusters of processes form in which the transport of charge is correlated over large distances. If one considers instead the temporal evolution of clusters a long time after the application of a DC field, the frequency dependent conductivity may be obtained by a simple Fourier inversion, or equivalently by the substitution $t \to 1/\omega$ (Pollak 1987).

We will argue that the current density, $j(t)$, after a time t has elapsed is given by

$$j(t) = \sigma_{dc}F + CV_0(\ell/r_0)\upsilon n(t)$$
$$= \sigma_{dc}F + K(d)C(Fr_0)(\ell/r_0)(r_0/\tau_c)[\ell^{-d}\ell'^{(d-3)}N(t)^{1+d-d_f}]^{-1} \tag{2.12}$$

where $CV_0(\ell/r_0)$ is a cluster polarization charge, υ is its average velocity, and $n(t)$ is the volume concentration of contributing clusters at time t. In this equation d is the dimension of the surface on which transport occurs, d_f is the fractal dimensionality of clusters in that surface, $K(d)$ is a numerical constant which depends on the dimension, $C = e^2/kT$, and $N(t)$ is the number of slowest rates, τ_c, in a one-dimensional path of length $N(t)\ell$. The justification for this expression follows.

If the slowest individual transitions are sequentially correlated it can easily be seen that after a time $t > \tau_c$, equilibrium can be reached only in clusters of length $N\ell \leqslant (t/\tau_c)\ell$. In each unit of time equal to τ_c, the typical size of clusters which have reached equilibrium grows to length ℓ. This cluster growth can be represented by a polarization current, $q\upsilon$ (charge times velocity), while the (on the average) continuous cluster growth provides a source and sink of charge allowing the flow of a steady state (DC) current within the clusters. The result for the polarization current

$$I = q\upsilon = (CFr_0)(\ell/r_0)(r_0/\tau_c) \tag{2.13}$$

arises because in each length r_0, the typical capacitance C generates a charge

$q = CV_0 = CFr_0$, while a total of ℓ/r_0 pairs can be found, on the average, between two slowest rates. The average velocity, v, of the individual ions is the hopping length, r_0, divided by the transition time, τ_c. The concentration of one dimensional paths (with length between $N\ell$ and $[N + \Delta N]\ell$) is given by an integral over the probability density, $n_N dN$, and is approximately equal to the product of n_N and an appropriate width of acceptable paths, taken to be small on a relative scale, but proportional to N. The probability density, $n_N dN$, has been shown to be (the derivation by Hunt (1990c) is based on the statistics of Stauffer 1979 and is given in the appendix)

$$n_N dN \propto K(d)\ell^{-d}\ell'^{(d-3)}N(t)^{-(2+d-d_f)}dN. \tag{2.14}$$

The concentration of contributing clusters is proportional to $N^{-(1+d-d_f)}$, as in equation (2.12). The numerical factor $K(d)$ depends only on the dimensionality of the subspace containing the clusters. Substituting $N(t) = t/\tau_c$ into equation (2.12) and transforming to the frequency domain

$$\begin{aligned}\mathrm{Re}\sigma(\omega) &= \sigma_{dc} + K(d)(e^2 r_0/kT\ell^{d-1}\ell'^{(3-d)}\tau_c)(\omega/\omega)_c)^{1+d-d_f} \\ &= \sigma_{dc}[1 + K(d)(\omega/\omega_c)^{1+d-d_f}].\end{aligned} \tag{2.15}$$

In one dimension (e.g. the electron glass)

$$\sigma(\omega) = \sigma_{dc}[1 + K(1)(\omega/\omega_c)]. \tag{2.16}$$

Application of the Kramers–Kronig dispersion relations to $\mathrm{Re}\sigma(\omega)$ throughout the entire frequency range results in

$$\mathrm{Im}\sigma(\omega) = K(d)\sigma_{dc}[A(d)(\omega/\omega_c) - B(d)(\omega/\omega_c)^{1+d-d_f}] + \ldots \quad (d > 1)$$
$$\propto \sigma_{dc}[(\omega/\omega_c)\ln(\omega/\omega_c)] \qquad (d = 1) \tag{2.17}$$

where higher order terms have been neglected. Here the proportionality symbol implies that constants of order unity have been neglected. A and B are numerical constants and are dimensionally dependent with $A > B$.

From equation (2.17) one gets immediately

$$\mathrm{Re}\varepsilon(\omega) = \mathrm{Im}\sigma(\omega)/\omega = K(\sigma_{dc}/\omega_c)[A - B(\omega/\omega_c)^{d-d_f}] \tag{2.18}$$

or in one dimension,

$$\mathrm{Re}\varepsilon(\omega) \propto (\sigma_{dc}/\omega_c)\ln(\omega_c/\omega) \tag{2.19}$$

where the latter expressions hold for $\omega \ll \omega_c$. As a consequence

$$\sigma_{dc} \propto \omega_c \varepsilon(0)/K'(d) \tag{2.20}$$

with $K'(d) = K(d)A(d)$, except in one dimension. The result can be identified as the B–N–N relation, if it can be shown that the loss peak frequency in $\mathrm{Im}\varepsilon(\omega)$ is the same frequency as the critical frequency, ω_c. To demonstrate this, we must show: (i) that the upper limit of applicability of the low frequency result is ω_c, (ii) that the lower limit of applicability of the pair approximation is also ω_c, (iii) that the two expressions yield essentially the same result at ω_c. We examine here $\mathrm{Re}\sigma(\omega)$, as it relates directly to $\mathrm{Im}\varepsilon(\omega)$.

As the low frequency result for $\sigma(\omega)$ is evidently an expansion in the variable ω/ω_c, the upper limit in frequency of applicability of a formula including only the first term must obviously scale with ω_c.

It has already been argued on physical grounds that an absolute lower limit of applicability of the pair approximation is ω_c. But in a range of frequencies near ω_c, the pair approximation needs to be modified, reflecting the onset of cooperative behaviour, i.e. multiple hopping (this regime has been defined in a similar context for variable range hopping systems by Pollak (1974), although without the emphasis on cooperative behaviour).

2.4. Multiple hopping regime

The pair approximation is

$$\text{Re}\sigma(\omega) = \sigma_{dc} + \omega r_0^2(e^2/kT)N'[kT\ln(\nu_{ph}/\omega)]. \tag{2.21}$$

For frequencies of the order of, but somewhat larger than ω_c, no clusters with large numbers of τ's equal to τ_c exist, but clusters with one τ_c and many smaller τ's can form. A total of ℓ/r_0 charges can each be transported a distance r_0 each time one charge with a blocking $\tau = \tau_c$ hops. This approximate result reflects the fact that the typical spatial separation of all transitions with $\tau < \tau_c$ is of the order of r_0, while the typical separation of those transitions with $\tau = \tau_c$ is of the order of ℓ by definition. (Of course this treatment is approximate because not all faster transitions will be linked with those transitions with $\tau = \tau_c$.) This 'traffic jam' effect tends to increase the number of charges hopping in phase with the field by the factor ℓ/r_0, but the distance which each charge hops is unaffected. Therefore, in the vicinity of ω_c the pair approximation must be increased by the factor ℓ/r_0, or

$$\text{Re}\sigma(\omega) = \omega r_0\ell(e^2/kT)N'[kT\ln(\nu_{ph}/\omega)]. \tag{2.22}$$

Evaluated at $\omega = \omega_c$, $kT\ln(\nu_{ph}/\omega)$ gives by definition E_0. $N'[E_0]$ is, by definition $\ell^{-d}\ell^{d-3}$, so that,

$$\text{Re}\sigma(\omega_c) = \sigma_{dc} + \omega_c r_0\ell e^2/kT\ell^d\ell'^{(3-d)} = \sigma_{dc} + \sigma_{dc}. \tag{2.23}$$

Comparing this result with the result for $\text{Re}\sigma(\omega_c)$ (equation 2.16) arrived at from the low frequency treatment,

$$\text{Re}\sigma(\omega_c) = \sigma_{dc}[1 + K(d)(\omega_c/\omega_c)^{1+d-d_f}] = \rho_{dc}[1 + K(d)] \tag{2.24}$$

demonstrates their essential equivalence, proving that the treatment discussed here is consistent with the B–N–N relation with the identity $\omega_c = \nu_{ph}\exp[-T_0/T]$ (and $\sigma_{dc} \propto \exp[-T_0/T]$).

Note that the 'traffic jam effect' enhances the low frequency conductivity.

3. Conclusions

The pair approximation for the high frequency conductivity of glasses is based on the assumption of a wide spread of individual transition rates. It is demonstrated here that the pair approximation breaks down in the vicinity of the loss peak frequency, ω_c, in the imaginary part of the dielectric constant. A cluster theory for the low frequency conductivity based on the statistical distribution of clusters given by percolation theory is theoretically consistent with the pair approximation and the two results are guaranteed to join fairly smoothly at ω_c. The growing importance of Coulomb interactions with reduction of the frequency can be treated within the framework of percolation theory.

The B–N–N relationship, $\sigma_{dc} = B\omega_c\varepsilon(0)$, is a consequence of the applicability of percolation theory (as long as $\varepsilon(\omega)$ does not diverge in the limit of zero frequency). The two different sequences of glasses reported by Namikawa (1975), correspond to two different values of B; it is natural, though unconfirmed, to assume that these two values correspond to the two possibilities mentioned here, that the 1D percolation paths are constructed randomly throughout the bulk, or that they are constructed within two-dimensional layers. The third possibility, that these paths are structurally confined to lie strictly along independent one-dimensional channels, is inconsistent with the B–N–N relation as in this case the frequency dependent dielectric constant diverges in the limit of zero frequency. Nevertheless such a divergence has been observed in the electron glass (Paalanen *et al* 1983) and possibly in ionic glasses as well (see Mansingh *et al* 1972).

The non-analytic frequency dependence of $\sigma(\omega)$ on ω^s at high frequencies is a direct result of the wide spread of transition rates; the departure of s from 1 is dependent (as argued by Pollak and Pike (1972)) on the exact form of the distribution, and certainly not (as claimed by Dyre 1988) on an artificial cut-off at some large τ, or low rate. Non-analytic behaviour at low frequencies results from enhanced relaxation times of large clusters of individual transitions due to sequential correlations (resulting from Coulomb repulsion). When transport may be considered restricted to one-dimensional channels (deep in the glass regime, due to a wide spread in transition rates), this formulation in which the relaxation time of a cluster is proportional to its linear extent should be adequate. Fractal time seems unnecessary; the non-analyticity at low frequencies derives from the non-integral dependence on N of the volume density of chains of length N. This number is related to the fractal structure of randomly generated large clusters, at least in the treatment reported here. Although powers of the frequency compatible with the results derived here, $1 + d - d_f \approx 1.6(3 - d) \approx 1.8(2 - d)$ are seen, it has not been reported that the values of these powers are universal. On the other hand it will be difficult to reconcile the apparent universality of the constant B in the B–N–N relation with any non-universal power of the frequency, whatever theory is applied.

Further research to determine whether cluster relaxation times may be always expressed as integer powers of the linear dimension of clusters is desirable. It is believed here, however, that this result will stand; since average (topologically) sideways hopping probabilities are unaffected by application of a field, and since the distribution of transition rates is very wide, assumption of 1D percolation paths should be reasonable.

Acknowledgments

Appendix

A review of the derivation of equation (2.12) is given. The idea is that clusters formed from individual bonds with $\tau \leqslant \tau_c$ are replaced by bundles of chains, each oriented more or less parallel to the applied field. The distribution of clusters is taken from Stauffer (1979). The distribution of chains on a given cluster is deduced from scaling and normalization (conservation) principles. Finally the distribution of chains in the system is obtained by a suitable integral over individual clusters.

In Stauffer (1979) a formula is given for the volume density, $n_s ds$, of clusters of s elements of unit length. The formula for systems in which the lengths scale by r_0 is modified as follows

$$n_s ds = C_1(d) s^{-\tau} f(z) r_0^{-d} ds \tag{A1}$$

where r_0 is the length of each element, f a scaling function of the variable $z = |p_c - p| s^s$, p_c the critical value of the site or bond probability p, $C_1(d)$ a dimensionally dependent constant, and τ and σ are critical exponents. As we are interested in cluster sizes right at critical percolation, we take $p = p_c$ and absorb $f(0)$ into $C_1(d)$.

A cluster of s elements has linear extent

$$r_s = m\ell = r_0 s^{\sigma\nu} C_2(d) \tag{A2}$$

where the factor r_0 gives the length of each element, m is the number of slowest elements on a linear path traversing the cluster, ℓ the separation of the slowest elements, and $1/\sigma\nu = d_f$ the fractal dimensionality.

Using

$$n_s ds = n_m dm \tag{A3}$$

for the probability density, $n_m dm$ of clusters with m elements yields

$$n_m = m^{(-d-1)} \ell^{-d}. \tag{A4}$$

The exponent $-(\tau - 1 + \sigma\nu)/\sigma\nu = -d - 1$ is given by the dimensionality dependent scaling law (Stauffer 1979). A cluster of linear extent $m\ell$ is now replaced by a bundle of chains each of length $N\ell$. The number of N-chains on a cluster for which the longest chain has m elements is assumed to obey a scaling relationship in the variable N/m, i.e.

$$n_{N,m} = m^\beta f(N/m). \tag{A5}$$

The value of β is determined by requiring that the total number of elements on all the N-chains is equal to the total number of elements on the original cluster,

$$m^{d_f} \approx m^\beta \int_0^m N f(N/m) dN = m^{\beta+2} \tag{A6}$$

so that

$$\beta = d_f - 2. \tag{A7}$$

Integration of $n_{N,m}$ over all m-clusters $(m > N)$ gives

$$n_N = \int_N^\infty dm \, C_1(d) C_2(d) (m\ell)^{-d} m^{d_f-3} f(N/m) = K(d) \ell^{-d} N^{-2-d+d_f} \tag{A8}$$

with $K(d)$ another dimensionality dependent constant. The density of chains of length $N\ell$ in a d-dimensional surface is given by equation (A8). The typical separation of such surfaces has been assumed equal to ℓ'. Thus the result for n_N referred to the three-dimensional system is

$$n_N = K(d) N^{-2-d+d_f} \ell^{-d} \ell'^{(d-3)} \tag{A9}$$

and the density of paths is proportional to the inverse cube of a length.

Equation (A9) is identical to equation (2.15). If transport is restricted to one-dimensional channels of separation ℓ', which do not interfere with each other, or cross

(as in the electron glass) then $d = d_f$ and $n_N \propto 1/N^2$. The number of chains per unit length which have length between N and $N + \Delta N$, can be obtained by integrating $n_N \mathrm{d}N$ with result N^{-1}. The length, $N\ell$, of such a chain, times the number of such chains is therefore a constant independent of N. This property can be related to 'self-similarity' (it is in agreement with Stauffer 1979) but it also holds if the distribution of chains is sharply peaked about a value of N which gradually increases with time. Thus in one dimension, the result for n_N may be unrelated to percolation theory. This is the reason why the density of clusters needs to be investigated generally.

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