Transport in ionic conducting glasses: II. Scaling relations and approximate power law behaviour

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Abstract. A recent theory of transport in ionic conducting glasses treats dielectric relaxation in a pair approximation at high frequencies, an augmented pair approximation at intermediate frequencies, and a cluster theory at low frequencies (below the α-peak in the imaginary part of the dielectric constant, $\varepsilon_2(\omega)$). The results were shown to reproduce the general features of the relaxation. Here the analysis of the results is continued, expressions for the approximate power of the high-frequency conductivity (the exponent s in $\sigma(\omega) \propto \omega^s$) are derived and the degree of the universality of the Barton–Nakajima–Namikawa relation is discussed in view of the non-universality of the power s.

1. Introduction

Recently an approach to calculating the frequency-dependent conductivity in ionic conducting glasses has been developed (Hunt 1991a) that can explain the general features of dielectric relaxation in these systems. This article develops further the mathematical treatment in the previous article, referred to as I.

In the previous article the pair approximation of Pollak and Pike (1972) for the high-frequency conductivity (which is consistent with the well-known ω^s behaviour) was shown to break down at a frequency ω_c, proportional to the DC conductivity. An enhancement of the conductivity in some range of frequencies above ω_c was proposed in the form of a multiplicative factor expressing the tendency of ions to hop in correlation with each other. Below ω_c, the manifestly non-local relaxation requires a cluster treatment. The assumed sequential correlation of critical (rate $w_{ij} \simeq \omega_c$) hops delays equilibration and makes the frequency dependence of $\sigma(\omega) - \sigma_{DC}$ on ω non-analytic in the limit of zero frequency. The sum of appropriate cluster currents in accord with cluster statistics (chosen compatibly with percolation theory) yields for $\sigma(\omega)$ a universal supralinear frequency dependence. Combined with the sublinear frequency dependence above ω_c, this generates the observed (see Jonscher (1981), Goetze (1991), among others) broad asymmetric loss peak (α-peak) with peak frequency proportional to the DC conductivity (the Barton (1966)–Nakajima (1972)–Namikawa (1975) relation).

The upward curvature (Dixon et al 1990, Ngai 1991) of the high-frequency tail of $\varepsilon_2(\omega)$ is also generated on account of the enhancement of $\sigma(\omega)$ at frequencies somewhat larger than ω_c.

Similar results have also been obtained through computer simulations by Maas et al (1991). This work also emphasized a competition between the effects of disorder

(dominant in parallel processes at high frequencies) and of Coulomb interactions (particularly important in series processes at low frequencies).

Although no comprehensive studies refer to a universal low-frequency power law, Cole–Cole plots (Kawomura *et al* 1987, Abelard and Baumand 1984, Martin and Angell 1986) seldom reveal Debye behaviour at either low or high frequencies (semicircles centred on the real axis). More commonly they yield skewed curves or semicircles with centres below the real axis. In either case the slope m of the imaginary part, ε_2, versus the real part, ε_1, of the dielectric constant in the limit of zero frequency (approaching the horizontal axis) is not infinite (as in single-mode Debye relaxation). The low-frequency power (defined here to be p) is related to m by $p = (2/\pi)|\cot^{-1}m|$.

Results for the high-frequency power s can be deduced from parameters relating to stretched exponentials; Elliott and Henn (1990) summarize the results of Boesch and Moynihan (1975) and Ngai *et al* (1984) as giving either temperature-independent values of s, or values that slowly increase towards 1 with decreasing temperature. On the other hand, Lee *et al* (1991) report that s rapidly reaches 1 as the temperature is lowered, and results of Jain and Mundy (1987) seem to indicate a minimum for s. Whether or not all these results can be consistent with the general type of approach given here is unclear, but general conditions that affect the value of s are discussed here, while more specific effects due to correlations between hopping length and hopping energies are discussed by Elliott and Henn (1990).

It should be mentioned that (ionic conducting) glasses have been classified as fragile or strong depending on the temperature dependence of their DC transport coefficients or relevant (percolation) relaxation times in the vicinity of the glass transition (Angell 1990). This classification has turned out to be somewhat arbitrary, however, as no clear boundary between the two classes can be established. It is believed here that such a continuous range of variation (from Vogel–Fulcher-type behaviour to simple activated behaviour) can easily be accounted for by differences in the distribution of barrier heights. This point will be discussed further, but no solid conclusions can be drawn. The uncertainty in the temperature dependence of the DC conductivity corresponds to the uncertainties in s mentioned above.

All three tendencies for s have been predicted by theory. Long *et al* (1982) predict that s should pass through a minimum, whereas Elliott and Henn (1990) consider a picture that leads to $1 - s \propto T$, and Henn *et al* (1991) suggest physical conditions that lead to a nearly temperature-independent value of s. Here the fact that ω_c defines the percolation of pair processes leads to the result, $1 - s \propto -(\ln \sigma_{DC}/\sigma_0)^{-1}$ (derived here as an average s, and suggested by Hunt (1992a) to be universal) with σ_0 the prefactor of the DC conductivity, σ_{DC}. Specific modications such as those considered by Elliott and Henn (1990) or Henn *et al* (1991) may lead to results that differ in detail.

If $1 - s \propto -(\ln \sigma_{DC}/\sigma_0)^{-1}$ then different temperature dependences for σ_{DC} should imply different values for s. Determinations of s, however, are not always consistent; the value depends on whether one constructs at some specified ω a tangent to the curve of $\sigma(\omega)$, whether one takes the value near the onset of dispersion, or whether one measures an average s. These procedures should not generally be expected to lead to the same value for s. If multiplicative logarithmic factors are involved (as in the approach here), the first method above should give a temperature-independent s, the value obtained by the second method will depend critically on whether the distribution of barrier heights is monotonic in energy, and the third

method will lead to the universal relationship mentioned. The value of s determined by the second method can be contaminated by the curvature associated with the approach to DC conduction (onset of dispersion). Thus the experimental situation has not yet been resolved.

The real part of the low-frequency conductivity has been shown in I to be expressible in the form,

$$\sigma(\omega)/\sigma_{DC} = g(\omega/\omega_c) \tag{1.1}$$

where $g(x) = 1 + x^{1+d-d_f}$ (if numerical constants are suppressed). Here d is the dimension of the 'surface' in which transport is confined, and in which the clusters with fractal dimensionality d_f are formed. In the remainder of this article, d will be assumed to be three with d_f about 2.6. If the function g has the form of a power law, and if its range of validity is restricted to $0 < \omega < \omega_c$, a contribution to $\varepsilon_1(0)$, the real part of the dielectric constant at zero frequency, which has the form

$$\varepsilon_1(0) \propto \sigma_{DC}/\omega_c \tag{1.2}$$

is generated by application of Kramers–Kronig dispersion relations. Such an expression is consistent with the BNN relation

$$\sigma_{DC} = B\omega_c\varepsilon_1(0) \tag{1.3}$$

(the contribution to $\varepsilon_1(0)$ from the pair approximation regime will be discussed later in this article).

It is clear that the pair approximation yields a value of s that is intimately linked with the distribution of relaxation times in the glass, which itself is non-universal. Thus there is no reason to expect s to be universal, and in fact it is not. However, the BNN relation is often considered to be universal, in the sense that the proportionality constant B of (1.3) is considered to have a universal value. It will be demonstrated clearly in this work that a non-universal expression for s is incompatible with a universality in the BNN relation. The calculations given here give a general tendency for s to increase to 1 as T approaches zero; for unremarkable distributions of barrier heights and in the case where no correlation between barrier height and hopping length exists,

$$s = 1 - qkT/E_0 \tag{1.4}$$

where q is a number, kT the Boltzmann constant times the temperature, and E_0 the activation energy of the DC conductivity. This expression is formally identical to that of the correlated barrier hopping model of Elliott. The constant B in (1.3) will be seen to acquire some dependence on T as well as on E_0. Nevertheless, if the variation in s-values is not too great (as seems often to be the case), and if the contribution to $\varepsilon(0)$ from the pair approximation regime is not too large compared with the contribution from the low-frequency regime, the variation in B with temperature and composition may be weak. In fact, a weak temperature and composition dependence of B has been noted (Dyre 1988).

It is admitted that a rigorous treatment of these systems has not been formulated. It is useful, however, to carry out the mathematical analyses described here, in order to understand what further general conclusions can be drawn from the model, and to clarify some general relationships, about which confusion still exists.

2. The BNN relation and the power *s*

It was mentioned above that the low-frequency conductivity can be written in the form

$$\sigma(\omega) = \sigma_{DC}[1 + K(d)(\omega/\omega_c)^{1+d-d_t}]. \tag{2.1}$$

This expression was derived in I. At $\omega = \omega_c \equiv \nu_{ph}\exp(-E_0/kT)$ one has

$$\sigma(\omega_c) = \sigma_{DC}[1 + K(d)]. \tag{2.2}$$

In the above, ν_{ph} is a phonon frequency, about 10^{12} Hz, and E_0 is the activation energy of the DC conductivity. It was also argued that

$$\sigma_{DC} = \omega_c e^2 r_0/kTl^2 \tag{2.3}$$

where r_0 is a typical hopping distance of the order of the ion separation (at high ionic concentrations) and l is the typical separation of pairs with barrier heights within kT of E_0, i.e. critical relaxation times $\tau_c = \omega_c^{-1}$. r_0 can be taken as an average value since τ is assumed to be a function of E only; i.e. whatever variation r_0 may have is assumed to be independent of E, allowing r_0 to be averaged separately from the integration. (The correlated barrier hopping (CBH) model of Elliott relaxes this approximation making E an explicit function of the hopping length.) The pair approximation yields

$$\sigma(\omega) = \sigma_{DC} + (\omega e^2 r_0^2/kT)\int_{kT[\ln(\nu_{ph}/\omega)-1]}^{kT[\ln(\nu_{ph}/\omega)+1]} dE\, n(E) \tag{2.4}$$

where $n(E)$ is the concentration of pairs with separation r_0 and barrier height E. The range of the integration is defined by the condition $\tau \simeq 1/\omega$ which serves to maximize the real part of the pair response. The particular choice of a range of energies equal to $2kT$ (rather than say kT, or $4kT$) is of course arbitrary. Near ω_c faster processes may be blocked through Coulomb repulsion by slower (critical) transitions (with $w_{ij} \simeq \omega_c$) on the same 'percolation' path, with the result that their contribution to the polarization current is delayed so as to be in phase with the external field. The enhancement related to multiple hopping (Pollak 1974) is represented by a multiplicative factor giving the number of ions freed by the breaking of the log-jam, i.e. the ratio of the number of faster transitions to critical transitions located on the one-dimensional conducting paths. This number is approximately l/r_0 (near ω_c), so in the multiple-hopping regime

$$\sigma(\omega) = \sigma_{DC} + (\omega e^2 r_0 l/kT)\int_{kT[\ln(\nu_{ph}/\omega)-1]}^{kT[\ln(\nu_{ph}/\omega)+1]} n(E)\,dE. \tag{2.5}$$

Evaluated at $\omega = \omega_c$ this yields

$$\sigma(\omega_c) = \sigma_{DC} + (\omega e^2 r_0 l/kT)\int_{E_0-kT}^{E_0+kT} n(E)\,dE = \sigma_{DC}(1+1) \tag{2.6}$$

in view of the definition of l

$$l^{-3} \equiv \int_{E_0 - kT}^{E_0 + kT} n(E)\, \mathrm{d}E \tag{2.7}$$

and (2.3) for the DC conductivity. The latter equality of equation (2.6) can also be arrived at (as in Almond *et al* 1982) by a strictly geometrical procedure relating the frequency at the onset of dispersion to the DC conductivity (when the frequency-dependent additive term is nearly linear in ω). Numerical constants in the frequency-dependent portion of the conductivity as well as in the DC conductivity have been suppressed because of the lack of knowledge of the distribution of relaxation times, and because numerical constants derived from cluster statistics of percolation theory are not known. Moreover the discussion of the lengths that appear in the expressions for the conductivity is only qualitative. Equations (2.6) and (2.5) were given in I; subsequent quantitative analysis is new, but is based on the results of I.

As a consequence of (2.6), it must also be possible to express the conductivity for $\omega > \omega_c$ in the form

$$\sigma(\omega) = \sigma_{DC} h(\omega/\omega_c) \tag{2.8}$$

with h some scaling function. The experimental proportionality of $\sigma(\omega)$ to a power less than one implies therefore that

$$\sigma(\omega) = \sigma_{DC}[1 + A(\omega/\omega_c)^s] \tag{2.9}$$

with A an unknown constant. In the type of approach described here, the power law formulation can only be approximate; methods of determining s consistent with any theory based on a pair approximation will be discussed later in this article. We now have

$$\sigma(\omega) = \begin{cases} \sigma_{DC}[1 + K(d)(\omega/\omega_c)^p] & \omega < \omega_c \\ \sigma_{DC}[1 + A(\omega/\omega_c)^s] & \omega > \omega_c \end{cases} \tag{2.10}$$

with $p > 1$ and $s < 1$ generating the broad asymmetric loss peak. While experimental results are not generally presented in this form, the non-analytic behaviour resulting from $p < 2$ is consistent with the observed behaviour of typical Cole–Cole plots mentioned in the introduction. The lack of knowledge of A and $K(d)$ will hamper the subsequent analysis, but cannot be avoided at this time. In any case $K(d)$ is expected to be a universal constant (from I) while A can vary from system to system. Still, it is expected that A should not be too different from K (otherwise the assumption that ω_c is also the loss peak frequency would be inconsistent; also significant differences in scaling relationships in different systems could result). On the other hand, if A is not smaller than $K(d)$, a significant non-universality in B can result if s approaches 1 too nearly. It should be emphasized that these uncertainties are not specific to this theory as they are in fact a consequence of internally inconsistent summaries of experimental results.

A further complication is that at large frequencies the frequency-dependent term in $\sigma(\omega)$ must be reduced by the factor r_0/l, consistent with a 'bare' pair approximation.

Application of the Kramers–Kronig dispersion relations to a conductivity of the form of (2.10) yields

$$\varepsilon(0) = \int_0^\infty \sigma(\omega)\,d\omega/\omega^2 = (\sigma_{DC}/\omega_c)[K(d)/(p-1) + A/(1-s)] \qquad (2.11)$$

ignoring a numerical factor of order unity. This relationship may be written as

$$\sigma_{DC} \simeq \omega_c \varepsilon(0)[K(d)/(p-1) + A/(1-s)]^{-1}. \qquad (2.12)$$

As pointed out, if s has a temperature dependence, the BNN relation

$$\sigma_{DC} = B\omega_c\varepsilon(0) \qquad (2.13)$$

cannot have a universal value for B. In fact, A probably has a factor $1/3$ arising from directional averaging of pairs that is not present in $K(d)$ (since clusters are on the average isotropic), so an approximate universality may be possible; but since other unknown numerical factors enter into these constants, further speculation on this point is not useful.

In I it was assumed that

$$\int_0^{E_0} n(E)\,dE = \alpha/r_0^3 \qquad (2.14)$$

defines the activation energy E_0 of the DC conductivity, where α is a critical value of the bond 'percolation' probability. Comparing this *ansatz* with (2.7) gives

$$l^{-3} = C_1 r_0^3 E_0/kT \qquad (2.15)$$

with C_1 an unknown constant. As can be seen from the substitution $x \equiv E/E_0$, equation (2.14) implies that $n(E)$ have the following form:

$$n(E) = (C_2/E_0 r_0^3)f(E/E_0). \qquad (2.16)$$

A specific example might be a Gaussian:

$$n(E) = (C_2/E_0 r_0^3)\exp[-(E - E')^2/2\beta E_0^2] \qquad (2.17)$$

with E' a typical barrier height and the factor β introduced to allow consistency with the percolation condition (2.14). Such a density of relaxation times has been treated in a random walk approach by Bässler (1987) and by Richert and Baessler (1990) who argued that a DC viscosity η ($\propto \exp(T_0/T)^2$) would result (steeper than Arrhenius). In any case it was then shown that an expression for the glass transition temperature, $T_g \propto E_0$, could be derived by setting the relevant relaxation time determining η equal to the experimental time (inversely proportional to the cooling rate, dT/dt). The results for the viscosity and for T_g were found to agree with experiment in a large number of systems. It is interesting that the same proportionality to E_0 (and a similar dependence on dT/dt) develops if the theory of Hunt (1989, 1991b) is applied (to be strictly comparable, it would be necessary to have $\sigma_{DC} \propto \eta^{-1}$, which is only true if effective-medium theories apply). In this case the proportionality of T_g to the width of the Gaussian is clearly a consequence of the percolation of pair processes at an energy

E_0; the increase in steepness of η compared to a simple Arrhenius behaviour could be interpreted as a crossover from an effective-medium theory dominated by a typical relaxation time (proportional to $\exp E'/kT$) to a percolation theory dominated by an optimal relaxation time (proportional to $\exp E_0/kT$). Since the glass transition occurs in a temperature range not too far from this crossover, both approaches seem to work roughly equally well.

We return to the suggestion (Hunt 1992a) that s can be related generally to DC transport coefficients. If, e.g., $\sigma_{DC} \propto \exp(-\xi_c(T))$, then s should obey $1 - s \propto \xi_c(T)^{-1}$. If such an expression for s (essentially a geometric argument) is valid also at higher temperatures where $\sigma_{DC} \propto \eta^{-1}$ a temperature dependence of $\xi_c(T)$ such as that derived by Richert and Baessler would be consistent with $1 - s \propto T^2$. This is a much more rapid approach to 1 with a reduction of T of the exponent s—somewhat similar to the behaviour observed recently by Lee *et al* (1991). Although these topics are not exactly the subject of this paper, they serve to illustrate the connections between thermal, mechanical and dielectric relaxation, and the relevance of the particular distribution of relaxation times; they may also contribute to a more general scheme for interpreting experiment.

Substituting (2.16) into (2.5) yields, after some manipulation

$$\sigma(\omega) = \sigma_{DC} \left\{ 1 + (\omega/\omega_c) f[kT \ln(\nu_{ph}/\omega)/E_0]/f(1) \right\}$$
$$= \sigma_{DC} \left\{ 1 + (\omega/\omega_c) f[1 - kT \ln(\omega/\omega_c)/E_0]/f(1) \right\} \qquad (2.18)$$

if $\ln(\nu_{ph}/\omega)$ is replaced everywhere by $\ln(\nu_{ph}/\omega_c) - \ln(\omega/\omega_c) = E_0/kT - \ln(\omega/\omega_c)$. Moreover, the assumption has been made that $kT/E_0 \ll 1$ allowing the neglect of terms with a higher order of kT/E_0 and thereby the simple representation above. It is possible to show that if $kT/E_0 < 1/10$ (required for the superiority of percolation theory compared with effective-medium theories) the magnitude of the first neglected term is less than 1/500 of the term retained as long as f is not too strongly varying. Such a condition can be quantified by demanding that the second derivative of f evaluated at $f = 1$ be less than or equal to $f(1)$.

Defining $\omega/\omega_c \equiv \omega'$ and $\sigma(\omega)/\sigma_{DC} \equiv \sigma'(\omega)$, and using the fact that $E_0/kT = -\ln(\sigma_{DC}/\sigma_0) \equiv -\ln \sigma'_{DC}$ permits rewriting (2.18) in the following form:

$$\sigma'(\omega') = 1 + \omega' f[1 + \log \sigma'_{DC}\omega']/f(1). \qquad (2.19)$$

An exact result for the function f (in the range $E < E_0$) could be extracted from the conductivity data like this:

$$f[1 + \log \sigma'_{DC}\omega'] = f(1)(\sigma'(\omega') - 1)/\omega' \qquad (2.20)$$

(essentially a scaled form of $\text{Im}\varepsilon(\omega)$) if the measurements could be made in the limit of zero temperature. Of course, even at very low temperatures the relaxation is so slow that measurements are possible only at very high frequencies. Use of such a relation at higher temperatures involves the risk of missing significant structure, as all features of $f(E/E_0)$ on a scale smaller than kT will not be even approximately reproduced. If the magnitude of such a rapid variation of f is small, it will not be observed at all.

It must also be noted that the ideal scaling form of (2.19) breaks down at high frequencies where the enhancement factor l/r_0 gradually disappears. This causes

an upward curvature of the relaxation spectrum, $\epsilon_2(\omega)$, as the (negative) slope is reduced. From experimental results on ionic conducting glasses (Ngai 1991) and also on dipole glasses (Dixon *et al* 1990) such results have been reported; the failure of scaling pictures due to such an upward curvature at high frequencies has been attributed to the importance of pair relaxation (Ngai 1991).

Equation (2.18) is probably more useful in that it demonstrates that at the onset of dispersion the power s must be expressible as

$$s = 1 - qkT/E_0 \tag{2.21}$$

where

$$q = (1/f(1))\,df/dx|_{x=1} \tag{2.22}$$

at least for a frequency range that does not depart too radically from the onset of dispersion at ω_c (so that the argument of f does not differ greatly from 1). Equation (2.21) is formally identical to one derived for the CBH model by Giuntini *et al* (1988). A specific result that can be proven is

$$s = 1 - pkT/E_0 \tag{2.23}$$

if

$$n(E) \propto E^p. \tag{2.24}$$

It is also evident that

$$s = 1 \tag{2.25}$$

if $n(E) = $ constant obtains as a special case of (2.23).

An alternative method for calculating s is now given that relates the value obtained to an average slope over the entire frequency range $\omega_c < \omega < \nu_{ph}$. Take

$$\int_{\omega_c}^{\nu_{ph}} \sigma(\omega)\,d\omega/\omega^2 = (\sigma_{DC}l^3/\omega_c)\int_0^{E_0} dE\,n(E)\int_{\omega_c}^{\nu_{ph}} \tau\,d\omega/(1 + \omega^2\tau^2)$$

$$= (\sigma_{DC}l^3/\omega_c)\int_0^{E_0} n(E)\,dE\,[\tan^{-1}\exp(E/kT)$$

$$- \tan^{-1}(\exp(E - E_0)/kT)]$$

$$= \sigma_{DC}l^3/\omega_c)\int_0^{E_0} dE\,n(E)$$

$$= \sigma_{DC}(l^3\pi\alpha/2\omega_c r_0^3)$$

$$= (\sigma_{DC}/\omega_c)\{1 - \exp[-(1-s)E_0/kT]\}/(1-s) \tag{2.26}$$

since the difference between the two arctangent functions can be approximated as $\pi/2$ over nearly the entire energy range $0 < E < E_0$. Here (2.9) has been substituted for $\sigma(\omega)$ on the left-hand side of the equation. As a consequence one has

$$s = 1 - (2/\pi\alpha)(r_0/l)^3\{1 - \exp[-(1-s)E_0/kT]\} \approx 1 - C'kT/E_0 \tag{2.27}$$

where (to a first approximation) $C' = 2C_1/\pi\alpha$. If one neglects the exponential factor (permissible if s not too near 1) one obtains

$$C' = p + 1 \qquad s = 1 - (1 + p)kT/E_0 \tag{2.28}$$

for an average power. In the limit $p \to 0$, however, s becomes very nearly 1 and the exponential factor must be included in the analysis. In this case, use of l'Hôpital's rule in (2.26) yields $C' = p$, and $s = 1 - pkT/E_0$. Thus, a constant density of barrier heights, $p = 0$, yields $s = 1$ throughout the frequency range.

Another relationship, which may have some use, is obtained by integrating the frequency-dependent conductivity from ω_c to ν_{ph}, i.e.

$$\int_{\omega_c}^{\nu_{ph}} \sigma(\omega)\,d\omega = (\sigma_{DC}l^3/\omega_c) \int_0^{E_0} \tau^{-1}\,dE\,n(E) \int_{\omega_c}^{\nu_{ph}} \omega^2\tau^2\,d\omega/(1 + \omega^2\tau^2)$$

$$= (\sigma_{DC}l^3/\omega_c) \int_0^{E_0} \tau^{-1} n(E)\,dE\,[(\nu_{ph} - \omega_c)$$

$$+ \tau^{-1}(\tan^{-1}\omega_c\tau - \tan^{-1}\nu_{ph}\tau)]$$

$$= \sigma_{DC}\nu_{ph}l^3 \exp(E_0/kT)[1 - \exp(-E_0/kT)N(1/kT)$$

$$- (\pi/2)N(2/kT)] \tag{2.29}$$

where $N(1/kT)$ is the Laplace transformation of $n(E)\theta(E_0 - E)$, and with $z = 1/kT$ and $\theta(x)$ the Heaviside step function of x. This calculation uses again the approximation (valid when $E_0/kT \gg 1$) that the difference of the inverse tangent functions in the range $0 < E < E_0$ is $\pi/2$, and the fact that pairs with $E > E_0$ are irrelevant to transport. These approximations are consistent with the application of percolation theory. Although inversion of this formula would yield an approximate value of $n(E)$, it is not likely that this will be very useful. Apart from the difficulty of the cut-off at E_0, and the fact that both $N(1/kT)$ and $N(2/kT)$ appear in the same expression, one would need N for all temperatures; but at high temperatures the assumption of the validity of percolation theory is incorrect.

The results given here demonstrate that the frequently (but not universally) observed tendency of s to approach 1 with a reduction of temperature follows naturally from this approach. The absence of the factor (l/r_0) at higher frequencies complicates the analysis, but it can also be shown (Hunt 1991c) (by a Kramers–Kronig-type analysis as in (2.26) and (2.27)) that in each regime separately a relationship of the form of (2.27) must hold (with a small difference in the numerical coefficients) meaning that an average s will also be of this general form. According to the arguments here, as the temperature is lowered the ratio l/r_0 increases, leading to a more pronounced upward curvature in $\varepsilon_2(\omega)$ for $\omega > \omega_c$. The ranges of applicability of the 'bare' pair and 'augmented' pair regimes change as well. The combined effect might be to produce a minimum (reported in some cases; see Elliott 1988) in the value of s, depending on the techniques employed for its determination. In fact, however, this question is unresolved, and such a minimum may have more to do with the particular form of $n(E)$. Beyond this, if the minimum is broad, s may be effectively a constant over relatively small ranges of temperature. Also, a non-monotonic variation of $n(E)$ with E can lead in this treatment to s-values less than unity but that remain nearly constant over a fairly wide temperature range. Moreover, the possible effects of correlated barrier hopping have been neglected in this treatment. The combined effects of correlated barrier hopping and sequential correlations within the context of percolation theory cannot be judged at this time.

3. Conclusions

It has been demonstrated that it is possible to reproduce the general features of relaxation in ionic conducting glasses by an application of a 'bare' pair approximation at high frequencies, a renormalized, or 'augmented' pair approximation at intermediate frequencies, $\omega > \omega_c$, and a percolation or cluster treatment for $\omega < \omega_c$.

The existence of a BNN relationship follows whenever it is possible to represent the frequency-dependent conductivity in a scaled form, i.e.

$$\sigma(\omega)/\sigma_{DC} = \begin{cases} 1 + K(d)(\omega/\omega_c)^p & \omega < \omega_c \\ 1 + A(\omega/\omega_c)^s & \omega > \omega_c. \end{cases} \tag{3.1}$$

Such a scaling form follows naturally from the theory described here and in I. The value of p is universal, as is $K(d)$. The constant B in the BNN relation has contributions from both frequency ranges and is not, strictly speaking, universal. Nevertheless, when the contribution from $\omega < \omega_c$ dominates, a quasi-universal expression for B results, with the variation in distinct systems at distinct temperatures minimal. It might seem reasonable to assume that the contribution from the pair approximation regime should also be universal because the limits of applicability of the pair approximation are defined by the phonon frequency and a critical percolation frequency. This is not, however, confirmed. The existence of such a scaling relationship allows suitably scaled plots of $\log \sigma(\omega)$ versus $\log \omega$ for different temperatures and different systems to coincide.

A general tendency for s to approach 1 as the temperature is lowered is predicted; the precise results depend on the distribution of barrier heights and on other factors such as correlations between barrier heights and hopping distances.

In addition it has recently been demonstrated (Hunt 1992a) that (3.1) without the additive terms σ_{DC} and with the factor σ_{DC} replaced by $\sigma_0 \equiv \sigma(\omega_c)$ is generated in dipole glasses; such a scaling law is sufficient to explain the scaling observed in salol and glycerol by Dixon *et al* for $\log \varepsilon_2(\omega)$ versus $\log \omega$. The value $p = 2$ is associated with a maximum relaxation time $\tau = \omega_c^{-1}$; relaxation in dipole glasses is (as expected) local at all frequencies. This fact bears on the discussion of the results of Richert and Baessler for viscosities of melts, the glass transition temperature and the power s.

It has recently been shown (Hunt 1991b) that it is possible to calculate a glass transition temperature and jump in the dynamic heat capacity from considering a time-dependent accessible entropy with a point of inflection at a critical 'percolation' time $\tau_c = \omega_c^{-1}$. In that article it was implied, although not stated explicitly, that the enhancement of relaxation times of compound, or many-body relaxation process on timescales longer than the time required for percolation of individual pair processes was relevant to the jump in the dynamic heat capacity. However, this condition may not be necessary; Debye relaxation at low frequencies (below a percolation cut-off) also leads to an inflection point in a time-dependent accessible entropy, and may also be consistent with a (smaller) jump in the dynamic heat capacity. This remains an open question.

Thus, although a certain unity has been attained in the treatment of conducting glasses, and while evidence exists to suggest that the general physical approach may also have application to non-conducting glasses and supercooled liquids, substantial questions remain even for ionic conducting glasses.

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