New developments in the theory of the hopping conductivity of spatially random systems

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Abstract. At present the relevance of percolative transport to traditional glasses is being established. The electronic glasses represent (relatively) well defined systems in which the effects of e.g. 'interactions' and 'disorder' may be isolated, and for which the percolative aspects of transport are relatively well understood. Thus these systems (spatially random, SR, and variable-range hopping, VRH) can be useful as models for glassy conduction processes. However, some inconsistencies in the published theoretical descriptions of such systems exist, namely regarding the placement of the critical (scaling, or peak) frequency and the relationship of the frequency dependence of the AC conductivity to critical exponents from percolation theory. These questions are clarified here. Further conclusions about the nature of the scaling relationships between the AC and DC conductivities are drawn. The role of stochasticity, or randomness in the definition of the scaling frequency, is emphasized.

1. Introduction

1.1. Transport in glasses: theoretical basis

The questions of the appropriate form of glass transport equations [1–6], as well as of the best approximations to their solution [7–10] have generated enormous controversy. The term 'glass' is itself riddled with controversy [11–15]. Here the term is used in the sense of either disordered solids or liquids with continuous distributions of transition rates. The question of when a system is sufficiently disordered to be called a glass is left to other publications [16–18].

Two fundamental perspectives exist regarding transport in disordered systems. One starts from the assumed validity of 'percolative' transport [1–3]. In such a picture, space, while isotropic in the mean, is strongly inhomogeneous. Thus only certain portions of the system can be utilized for transport upon application of e.g. an electric field [2] (the description of viscous flow is somewhat more complex [18]), but temporal constancy is implied, i.e. the same transport path will be utilized in successive applications of an electric field. This is to be contrasted with diffusive transport, in which spatial homogeneity is guaranteed, but for which the exact path of transport is never repeated. Traditional glasses and/or viscous liquids obviously cannot be rigidly classified into either of these two categories. Clearly, as the temperature is dropped, the transport becomes more nearly percolative in character. There is a growing suspicion [1, 3, 19] that the cross-over occurs above the traditional glass transition, in particular at or near the mode-coupling temperature, T_c.

While the question of the character of transport in glasses generally has not been resolved, three facts about electronic glasses are clear. Electronic glasses exemplify

percolative transport [20]. The microscopic transition-rate theory is rather well developed, and the criteria for the selection of distributions of microscopic transition rates is clearly defined. Furthermore, it is possible to isolate the effects of static disorder and dynamic interactions [21–23]. Also many features of 'glassy' transport in traditional glasses are shared by electronic glasses; the general structure of $\mathrm{Re}\,\sigma(\omega)$ is the same except for the DC limit [24–26]. Although an exponential function of T in both cases, the electronic glasses are usually Arrhenius [20 or sub-Arrhenius [27] in form while 'traditional' glasses are either Arrhenius [28] or super-Arrhenius [20]. So understanding transport/relaxation in electronic glasses is relevant to interpretation of glassy relaxation. However, some inconsistencies [30, 31] in the theory of the hopping conduction of electronic glasses need to be addressed before the analogies are drawn. This is one purpose of this paper.

1.2. Experimental results: universalities

Similarities in the experimental results from various disordered systems have been noted for at least 20 years [32, 33], generating already 15 years ago the term 'universal dielectric' response [24–26]. Now it is known that the similarities run even deeper than suspected at that time. The real part of the AC conductivity in a huge number [24–25] of systems is slightly sublinear in ω and weakly temperature dependent. The DC conductivity is exponentially temperature dependent. The onset of dispersion (strong frequency dependence) occurs [34–37] at a frequency proportional to σ_{DC}. If the DC conductivity is subtracted from $\mathrm{Re}\,\sigma(\omega)$ and the result is divided by ω (i.e. yielding $\mathrm{Im}\,\epsilon(\omega)$) a peak is very often found [38–40] at a frequency ω_{p} proportional to σ_{DC}. This peak is invariably located near the onset of dispersion, i.e. the magnitude of $\mathrm{Re}\,\sigma(\omega_{\mathrm{p}})$ is not greatly different from σ_{DC}). Obviously ω_{p} cannot be located much above the onset of dispersion, or one would see the different frequency dependences below and above ω_{p} already in plots of $\mathrm{Re}\,\sigma(\omega)$ without having to subtract σ_{DC}. Furthermore, it has been demonstrated [31, 38] that results for $\sigma(\omega)$ for various temperatures and systems can be made to coincide by the choice of the scaled axes

$$y = \log\big[\sigma(\omega)/\sigma_{\mathrm{DC}}\big] \tag{1a}$$

$$x = \log\big(\omega/\omega_{\mathrm{c}}T^{p}\big) \tag{1b}$$

$$y = g(x) \tag{1c}$$

with $g(x)$ an (approximate) sublinear power of x for $\omega > \omega_{\mathrm{c}}$, and where ω_{c} is a critical frequency proportional to σ_{DC}. It has been shown [41] that a scheme for calculating a critical frequency can be developed which in variable-range-hopping (VRH) systems ($p \simeq 0.25$) and ionic glasses ($p = 0$) yields the scaling relationship (1) and also demonstrates the equality of ω_{c} and ω_{p}. This paper derives the existence of the same scaling relationship in spatially random (SR) systems (with $p = 0$), and shows that the critical frequency can be determined by the same procedure as in VRH systems. It may be significant that for $p = 0$, and with substitution of $\sigma(\omega_{\mathrm{c}})$ for σ_{DC}, (1a) yields a scaling form for $\sigma(\omega)$ observed in dipolar viscous liquids [42–44].

It is repeated here that the identification of the peak frequency in $\mathrm{Im}\,\epsilon(\omega)$ with critical percolation of pair (or renormalized-pair) processes is sufficient to make $\omega_{\mathrm{c}} \propto \sigma_{\mathrm{DC}}$ and $\sigma(\omega_{\mathrm{c}}) \simeq \sigma_{\mathrm{DC}}$. This makes a clarification of the concept and calculation of ω_{c} essential; recently incorrect expressions for ω_{c} in spatially random systems have been reported [30, 31].

· Also, it has been suggested [45, 46] that critical exponents of percolation are relevant to the frequency dependence of $\text{Re}\,\sigma(\omega)$ for $\omega > \omega_c$. An argument against this suggestion [41], was the demonstration that for VRH systems the conductivity even at ω_c was dominated by the current passing through isolated critical resistances. An aim of this article is further clarification of the role of percolation exponents in $\sigma(\omega)$; this is accomplished by addressing the frequency dependence of $\sigma(\omega)$ in the multiple-hopping regime, or MHR, just above the loss peak frequency, ω_c.

1.3. Spatial and energetical disorder

Commonly investigated electronic glassy systems include VRH systems [27, 47] and SR systems [48]. In both, electrons tunnel [49, 50] (phonon-assisted 'hopping') from localized state (at site i) to localized state (at site j). In the latter, all the sites may be taken to be at the same energy E_0 (measured from the Fermi energy, E_F), but to be distributed at random. In the former, the individual site energies also take on random values (over an energy range W with the Fermi energy usually assumed to be in the middle of the energy range). More complicated versions are possible [51], but neglected here, where we concentrate on SR systems.

It should be noted that in the more traditional glasses, 'hopping' processes are classical [4, 8, 11, 17], over a barrier. Both the energies of the states and the heights of the barriers are random variables. If the energy relief is largely due to a random distribution of charges, these random energies may be correlated. The only way to generate an exponential dependence on the 'hopping' length in traditional glasses is to write the barrier heights as an explicit function of the hopping length, as in correlated barrier hopping (CBH) [51]. So in the electronic glasses one may consider in general the cases of r percolation (SR systems) and r, E percolation (VRH systems); in the 'traditional' glasses, the case studied amounts essentially to E percolation. Nevertheless, it will be argued that the source of the randomness is not relevant to generalized 'scaling' formulations of the conductivity, only to some of the specific results. In particular, in r percolation (E percolation) the scaling frequency, ω_c, depends only on r (E), while in r, E percolation, the scaling frequency depends on a competition between r and E, just as does the DC conductivity. If either r or E (or a contribution to r and/or E) is not a random variable, then the effect of r (or E, or the non-stochastic component thereof) is felt simply as a uniform multiplicative constant in both $\sigma(\omega)$ and σ_{DC}; the ratio $\sigma(\omega)/\sigma_{DC}$ contains no contribution and neither does ω_c. Another important result is that the power p is non-zero only in the case of r, E percolation [38] (VRH [27]); otherwise p is zero.

1.4. Aims and organization

It is desired to

(A) show that critical percolation of contributing microscopic processes defines the DC conductivity *and* the loss peak frequency, ω_c,

(B) obtain a semiquantitative result for $g(\omega/\omega_c T^p) = \sigma(\omega)/\sigma_{DC}$ (corresponding to the scaled axes of (1)) in SR systems in the MHR,

(C) show [53] that the role of percolation theory in the frequency dependence of g is confined to frequencies ω such that $\omega < \omega_c$,

(D) show that, in analogy to ionic conducting glasses [54], the MHR sets in when the maximal hopping length is equal to the typical separation r_0 of contributing sites, in contrast to critical percolation, when the maximal hopping length is equal to the length of the critical, percolating hopping processes, i.e. $(2.7)^{1/3} r_0$, and

(E) show using the results from (D) that an interpretation of the departure from scaling in ionic [54, 55] and dipolar [44] glasses at frequencies some few decades above ω_c as passing from that MHR to simple pair hopping can be strengthened. The critical barrier height may exceed typical barrier heights analogously to (D); these energies may define the bounds of the MHR, possibly helping to resolve the controversy [56, 57] regarding calculation of relevant microscopic barrier heights and comparison with experiment.

2. Model

Spatially random electronic 'hopping' systems consist of N sites per unit volume, distributed randomly (with uniform spatial probability density). All sites have energies E_0 (measured from the Fermi energy). Such a model can represent impurity conduction systems [58] if the width of the distribution of site energies is small compared with the distance E_0 from the centre of the distribution to the Fermi energy, and if kT is large compared with the energy of interaction of electrons on neighbouring sites. Mapping the rate equation for transport

$$\mathrm{d}f_i/\mathrm{d}t = \sum_{j \neq i} f_j(1 - f_i)w_{ji} - f_i(1 - f_j)w_{ij} \qquad (2)$$

onto a random impedance network [49, 59] yields

$$R_{ij}^{-1} = \left(e^2 \nu_{\mathrm{ph}}/kT\right)\exp\left(-E_0/kT - 2r_{ij}/a\right) \qquad (3a)$$

$$C_i = \left(e^2/kT\right)\exp\left(-E_0/kT\right) \qquad (3b)$$

for the impedance values. R_{ij} connects sites i and j, and C_i connects site i through a potential generator to ground. The meanings of the symbols are as follows: w_{ij}, the quantum-mechanical transition rate from i to j; f_i, the occupation probability of site i (according to Fermi–Dirac statistics); e^2, square of the electronic charge; kT, the Boltzmann constant multiplied by the temperature; ν_{ph}, a fundamental rate constant roughly 10^{12} Hz; a, the localization radius; and r_{ij} the site separation i, j. Physically, R_{ij} represents the difficulty of transferring a unit charge from i to j, while C_i describes the amount of charge generated at a site i by a unit change in the external potential. The product of R and C has the usual interpretation of a relaxation time [31, 59].

One can also write

$$R_{ij} = R_0 \exp\left(E_0/kT + 2r_{ij}/a\right) \equiv R_0' \exp\left(2r_{ij}/a\right) \equiv R_0' \exp \xi_{ij} \qquad (4)$$

since $\exp E_0/kT$ is common to all R values. Note that any simple combination of R and C values representing a pair (or augmented-pair) relaxation time will have a form similar to

$$R_{ij}C_iC_j/(C_i + C_j) = R_{ij}C_0/2 = \tfrac{1}{2}\nu_{\mathrm{ph}}^{-1} \exp\left(2r_{ij}/a\right) \qquad (5)$$

because all the capacitances are equal, and the energy exponential will always cancel.

3. Calculations

3.1. DC conductivity

The DC conductivity is now calculated. Several related expressions [58, 60, 61] have been proposed for σ_{DC}; we choose a procedure introduced in [60]. σ_{DC} is closely related to the critical resistance, R_c, defined such that the subnetwork consisting of all R with $R \leqslant R_c$ just percolates. Of course, for $R = R_c$, the correlation length χ, which gives the separation of 'conducting' paths, diverges [20, 62], so the calculation of σ_{DC} must involve paths with largest R values somewhat greater than R_c. The method used here to approximate σ_{DC} is to consider the network formed by including all R with $R \leqslant R_{opt} > R_c$, and calculate both the typical resistance of the paths generated and the density of such paths in terms of R_{opt}. R_{opt} is then used as an optimization parameter. The result yields the highest conductivity one can associate with such a parametrization of the network. Of course physically adding further resistances to the network consistent with the actual distribution could not really decrease the conductivity; the assumption is that the optimization yields an R_{opt} for which the additional contributions to σ_{DC} from including even larger resistances is negligible (due to the exponential dependence on the random variables).

First define r_0 as the typical separation of sites, i.e. $\frac{4}{3}\pi r_0^3 N = 1$. Then the typical number, α, of resistors connected to an arbitrary site with $R < R_0' \exp(2r.a)$ is

$$\alpha = \int_0^r 4\pi r_2' N \, \mathrm{d}r'. \tag{6}$$

Percolation is assured [20, 63] when $\alpha = \alpha_C \simeq 2.7$, i.e.

$$R_c = R_0' \exp 2r_c/a \equiv R_0' \exp \xi_c \tag{7a}$$

$$\alpha_c = \int_0^{r_c} 4\pi r_2' N \, \mathrm{d}r'. \tag{7b}$$

Next, the correlation length (size of the largest clusters for $\alpha < \alpha_c$, separation of current carrying paths for $\alpha > \alpha_c$) is calculated from [62] (with the normalized bond probability, p, assumed to be proportional to the average number of bonds, α, and the condition that $\chi(\alpha = 1) = r_0$, explained following the equation)

$$\chi = \chi_0 |(p - p_c)/p_c|^{-\nu} = r_0 |(\alpha_c - 1/\alpha_c - \alpha)|^{\nu} \tag{8}$$

with $\nu \simeq 0.88$ the critical exponent of the correlation length, and where χ_0 is the typical bond (resistance) length. To make sure that χ takes on reasonable values in the MHR, χ_0 is chosen to be the typical size of a 'cluster' with one (maximally valued) resistor ($R = R_0' \exp(2r_0/a)$) at the onset of the MHR, and to be approximately the size of the largest resistor on the 'cluster' when the cluster contains more than one resistor.

Choosing $\alpha = 1$ as the onset of significant cluster formation is natural; for larger values of α one may expect typical 'clusters' to have more than a single resistor, and the characteristic

number of resistances in a cluster will grow rapidly with $\alpha > 1$. In fact, the typical number s of sites on a cluster will be

$$s = (\chi/r_0)^{1/\sigma\nu} = |(\alpha_a - 1)/(\alpha_c - \alpha)|^{1/\sigma} \tag{9}$$

where the combination, $1/\sigma\nu$, of critical exponents is known as the fractal dimensionality [62]. Using (7b) yields

$$r_c = \alpha_c^{1/3} r_0 \tag{10}$$

and

$$\chi = r_0 |(\alpha_c - 1)/\{\alpha_c - [(a/2r_0)\ln(R/R_0')]^3\}|^\nu$$
$$\simeq r_0 [(\alpha_c - 1)/3\alpha_c]^\nu |\ln(R_c/R_0')/[\ln(R_c/R_0') - \ln(R/R_0')]|^\nu \tag{11}$$

where the approximate equality follows using $\alpha - \alpha_c \simeq 3\alpha_c|1 - r/r_c|$, i.e. assuming r near r_c. The optimization (16) yields $r = r_c(1 + av/r_c)$, justifying the approximation. (Note, however, that it will not be sufficient to make this approximation for calculations of $\sigma(\omega)$ in the MHR because α may be as small as unity, and unity is *not* close to $\alpha_c \simeq 2.7$.) The typical separation, r_{av}, of all resistors with $R \leqslant R_c$ is

$$r_{av} = r_0/\alpha_c^{1/3}. \tag{12}$$

If one groups the resistors in orders of $e = 2.718\ldots$, then the ratio, f_0, of resistances with $R \simeq R_c$ to the total number of resistors with $R \leqslant R_c$ is

$$f_0 = 3a/2\alpha_c^{1/3} r_0. \tag{13}$$

As a consequence, one may calculate the typical separation, l, of R values with $R \simeq R_c$ as

$$l = f_0^{-1/3} r_{av} = r_0 (2r_0/3a\alpha_c^{2/3})^{1/3}. \tag{14}$$

From [60] and [61], one expresses the DC conductivity, σ_{DC}, in terms of separation l' of R_{opt} values on the percolation path and the separation, $\chi(R_{opt})$, of such paths as

$$\sigma_{DC} = l'(R_{opt})/R_{opt}\chi^2(R_{opt}) \simeq l(R_c)/R_{opt}\chi^2(R_{opt}). \tag{15}$$

Two approximations must be explained. l is a function of $\ln R$ (slowly varying, compared with χ, which diverges at R_c, and with R). l' has been replaced with l, since it

has been shown [48] that l' is a slightly different power of f_0 from l' (the power is $-(1 + \sigma \nu)/(1 + d) \simeq -0.35$ rather than -0.33). This difference will never be detected.

Optimization of (15) yields

$$R_{\text{opt}} = R_c \exp(2\nu) \tag{16a}$$

$$L \equiv \chi(R_{\text{opt}}) = r_0 \big[(\alpha_c - 1) r_0 / 3 \alpha_c^{2/3} \nu a \big]^{\nu}. \tag{16b}$$

Using (14) and (16b) in (15) yields

$$\sigma_{\text{DC}} = (1/r_0) \big[3 \alpha_c^{2/3} \nu a / (\alpha_c - 1) r_0 \big]^{2\nu} (2 r_0 / 3 \alpha_c^{2/3} a)^{1/3} (e^2 \nu_{\text{ph}} / kT)$$
$$\times \exp(-2\nu - 2 \alpha_c^{1/3} r_0 / a - E_0 / kT). \tag{17}$$

3.2. AC conductivity

A published result [64] for the AC conductivity in the pair-approximation regime is

$$\text{Re} \, \sigma(\omega) = \sigma_{\text{DC}} + (\pi/16)(e^2/kT) \exp(-E_0/kT) N^2 a^5 \omega \big[\ln(\nu_{\text{ph}}/\omega) \big]^4. \tag{18}$$

(18) is derived from the known formula for the pair current [64, 65],

$$\text{Re} \, I_{\text{pair}}(\omega) = (x^2/R) \omega^2 t^2 / (1 + \omega^2 \tau^2) \tag{19}$$

(with x the pair separation and $\tau = RC/2$) and the volume concentration of contributing pairs (with $\tau \simeq 1/\omega$). The justification for adding the DC conductivity as a parallel contribution is given in dielectric treatments [54, 66, 67] of the relevant inhomogeneities (pairs) in a medium with a background dielectric constant.

In (18) the factor ω arises from setting $\tau = 1/\omega$ in (19), two factors $(a/2) \ln(\nu_{\text{ph}}/\omega)$ originate from the factor x^2 in (19), and the remaining two factors of $(a/2) \ln(\nu_{\text{ph}}/\omega)$ and N^2 originate from the random statistics, i.e. the probability of locating a second site a distance x (the length of the hopping transition) from the first. The condition $\tau = 1/\omega$ sets the condition on R, and thus on x, (traditionally denoted by r_ω in the pair hopping regime). The fifth factor $a/2$ results from the specification of the value of the resistance to within a factor $e = 2.718\dots$ The factor $(e^2/kT) \exp(-E_0/kT) \equiv C_0$ is the uniform single-site capacitance, and results from the division by R. The numerical factors result [59] from the appropriate averaging (e.g. over pair orientation).

The condition setting $\omega \tau = 1$ leads to

$$x = r_\omega = (a/2) \ln(\nu_{\text{ph}}/\omega). \tag{20}$$

Imagine that the frequency is lowered continuously. At $\omega = \nu_{\text{ph}} \exp(-2r_0/a) \equiv \omega_0$ all pairs with $R \leqslant R_0' \exp(2r/a)$ have $\tau \leqslant 1/\omega$. For those pairs with $\tau < 1/\omega$, the current

is out of phase with the field, and as long as they do not coincidentally connect with pairs for which $\tau \simeq 1/\omega$, they have only a minimal influence on the real part of the conductivity and may be treated as shorts (influencing only the imaginary part of the conductivity). If the frequency is reduced to below ω_0, however, typical clusters will have more than one resistance [59]. It is still appropriate to treat the smaller resistances as shorts [59], but they may no longer be ignored, as the charge generated by their associated capacitors also flows through the largest resistance in the cluster. The regime where such clusters (with one maximally valued resistor and some number of connected shorts) are relevant to $\sigma(\omega)$ has been termed the multiple-hopping regime (MHR) [50, 59].

In the MHR one must now formulate (1) the condition defining the appropriate clusters, i.e. those *independent* portions of the network which generate the dominant contribution to Re$\sigma(\omega)$, (2) the description of the currents in these clusters, (3) a condition for the statistics of these clusters, and (4) a condition defining the *lowest* frequency for which multiple hopping is the dominant transport mechanism, i.e. when relevant clusters are required to contain more than one maximally valued resistor. For lower frequencies relaxation is manifestly a non-local process. To a very good approximation (as will be seen) the cross-over occurs at the loss peak frequency [41, ,54 61] (provided, of course, that Re$\sigma(\omega)$ for $\omega < \omega_c$ is a superlinear function of ω).

The method to choose relevant clusters is proposed to be that at any ω (not just in the pair-approximation regime) the dominant contribution to Re$\sigma(\omega)$ will originate from those pairs for which the maximum τ_{cluster} is

$$\tau_{\text{cluster}} \simeq 1/\omega. \tag{21}$$

For clusters with a single maximal R, it has been shown in one dimension generally [68], and argued also in three-dimensional VRH systems, that smaller resistances in the contributing clusters may be replaced with shorts [41, 59], allowing combination of their capacitances (configured in parallel) into two capacitors, one on each side of R. In the most likely situation, when the numbers on each side are identical, one can find the total capacitance of the cluster

$$C = sC_0/2 = (s/2)(e^2/kT) \exp[-E_0/kT]. \tag{22}$$

The actual structure [62] of the cluster is irrelevant (in this approximation) to finding τ, since charge transport through the shorted resistors R is instantaneous. Using (9) for the number of sites

$$\tau_{cluster} = \nu_{\text{ph}}^{-1} \exp(2r_\omega/a)\left[(\alpha_c - 1)/\alpha_c\right]^{1/\sigma} \left\{1/\left[1 - (1/\alpha_c)(r_\omega/r_0)^3\right]\right\}^{1/\sigma} = 1/\omega \tag{23}$$

where the maximal R is simply $R_{\max} = R_0' \exp(2r_\omega/a)$; i.e., in the MHR, one must distinguish the length r_ω, from the size of the cluster, x. (For self-consistency, subsequent calculations must use for x the correlation length, χ, as a function of $R_{\max}$.) This transcendental equation for r_ω cannot be solved exactly; in fact a meaningful approximation is rather difficult, and is postponed until later.

(23) is the important result of this paper. It synthesizes the physics of the low- and high-frequency regimes. Because it is based on a typical cluster size, with a single maximally

valued resistor, it has characteristics in common with the pair-hopping regime, i.e. the number of clusters per unit volume is given by the statistics of the resistors themselves (discussed below). As a logical continuation of this regime it provides for a smooth variation of the conductivity, and allows one to continue to isolate the chief contribution to $\text{Re}\sigma(\omega)$ by choosing relaxation times equal to the inverse of the frequency. Because it contains the appropriate size of such clusters, as the frequency is reduced (in the vicinity of the loss peak) it allows a natural transition to the cluster-current regime at and below the loss peak. This type of procedure may now be applied to any system with a random distribution of elementary transition rates, and for which percolation theory is appropriate.

Assuming that one has a solution to (23) for r (and hence R), how does one proceed to calculate $\text{Re}\sigma(\omega)$? It is assumed here that the pair statistics used are relevant for typical resistors R in the MHR since we took the maximally valued R of the cluster to be $R'_0 \exp(2r_0/a)$ at the onset of the MHR and used *typical* cluster sizes for every $R > R'_0 \exp(2r_0/a)$ (when ω is reduced). Thus the occurrence of the clusters is equal to that of the resistors R themselves. This is a critical point. It means that the structure of $\sigma(\omega)$ is not changed by the necessity of choosing a different statistical representation on passing to the MHR.

As shown in [53], and is easy to understand, combining the capacitors on both sides of the single $R_{\max}$ individually allows one to use (19) for the current in a single pair, where now $C/2 = C_0/2$ must be replaced by $C_0s/2$, and x must reflect the actual RMS value of the site separations on opposite sides of $R_{\max}$. Thus the cluster current is a generalized pair current, and the appropriate result for $\sigma(\omega)$ in the MHR is the same as (18) for the pair regime, but with multiplicative factors describing the enhancement of C, τ, and x [41, 68]. The number of pairs is not enhanced, so only two factors of x are changed to the cluster dimension χ. The result for $\sigma(\omega)$ is now

$$\sigma(\omega) = \sigma_{\text{DC}} + (\pi/2)n^2\left(e^2/kT\right)a\omega s r_\omega^2 \chi^2 \exp\left(-E_0/kT\right) \tag{24}$$

with r_ω given in (23) and χ appropriate for the particular r_ω. Note that at the onset of the MHR, $s = 1$, $r = \chi = r_0$, in agreement with (18). In the MHR it will gradually become unnecessary to average over orientations [64] because the clusters are isotropic in the mean, and the charge transport will not be restricted to the maximally valued resistor (which has an orientation). Ignoring this numerical change tends to underestimate $\sigma(\omega) - \sigma_{\text{DC}}$ by a factor of two. On the other hand, substituting χ^2 for $\langle x^2 \rangle$ may tend to overestimate the RMS value, and assuming that all relevant resistors form typical clusters may tend to overestimate the number of clusters. These (presumably) numerical adjustments will tend to cancel, and are neglected (providing for the continuity of $\sigma(\omega)$ as well).

If one writes for the enhancement of the capacitance $f^{-1}(\omega)$ one can express (23) as

$$\omega R C f^{-1}(\omega) = 1. \tag{25}$$

As long as $1 \leqslant f^{-1}(\omega) \leqslant f_0^{-1}$ the resulting transcendental equation is appropriate. At a frequency ω^*, very near, but not quite at critical percolation, such that $f^{-1}(\omega) = f_0^{-1}$, continued application of this formula apparently implies that typical clusters with more than one maximal R become relevant. But then one would be required to use cluster statistics, since one would not be describing relaxation in single-maximal resistors. The question may legitimately be asked: 'is ω^* the loss peak frequency?' We do not think so.

It is possible to consider *independent* clusters with one maximal R and f_0^{-1} shorts (with associated capacitors) in the range $\omega_c < \omega < \omega^*$. In this case R continues to grow with decreasing frequency until it reaches the critical value, R_c. When a path of resistors R with all values less than or equal to the critical value spreads from one electrode to the other, however, it is no longer possible to lower ω and still increase R and consider the relaxation in the various resistors as independent [48]. The largest resistors R on the path are already R_c. The relaxation can not be further slowed by choosing a larger capacitance either because to do so automatically brings in more resistors R_c into any given cluster.

Although this condition does not rigorously define $\omega_c[R_c f_0^{-1} C_0]^{-1}$ as the lower limit of the MHR, it clearly shows that the lower bound cannot be lower than ω_c. It is important that using cluster statistics and cluster-relaxation processes leads to a superlinear frequency dependence as long as the dominant clusters have more than one critical resistor; since the larger response (consistent with Maxwell's equations, i.e. provided that the relevant portions of the network considered are indeed independent) is the sublinear (pair-structure) function of the frequency, it is preferred.

In the approximation scheme chosen it is possible to solve analytically for $\sigma(\omega)$ in the frequency range, $\omega_c < \omega < \omega^*$. (23) reduces to

$$\omega R C_0 f_0^{-1} = 1 \qquad R = f_0/\omega C_0 \qquad r = (a/2)\ln(f_0 \nu_{\text{ph}}/\omega) \qquad \left(\text{not } (a/2)\ln(\nu_{\text{ph}}/\omega)\right). \tag{26}$$

When $\omega = f_0 \nu_{\text{ph}} \exp(-2r_c/a) \equiv \omega_c$, $r = r_c$, and critical percolation is reached. Note that the length of the relevant resistances is then r_c as demanded, and the separation of all resistances $R \leqslant R_c$ is also r_c, but the separation of maximally valued resistances R_c is given in (14), and may be much greater than r_c. Note that the enhancement of cluster capacitances (in contrast to VRH systems [41]) has led to a significant diminution of the critical frequency. At $\omega = \omega_c$, $\chi = l$, the separation of critical resistors, since connection of infinite clusters of resistors R with $R \leqslant R_c$ *and a typical number, f_0^{-1}, of smaller resistors R per R_c demands that the size of the considered clusters not exceed the separation of critical resistances.*

Evaluation of $\sigma(\omega_c)$ using $\chi = l$ and $C = f_0^{-1} C_0$ yields

$$\sigma(\omega_c) = \sigma_{\text{DC}}\left[1 + \tfrac{3}{8}\exp 2\nu(L^2/l^2)\right]. \tag{27}$$

Representation of $\sigma(\omega)$ as an (approximate) power law [1, 68] (i.e. $\sigma(\omega) \propto \omega^s$) for $\omega > \omega_c$ yields

$$\sigma(\omega) = \sigma_{\text{DC}}\left[1 + \tfrac{3}{8}\exp 2\nu(L^2/l^2)(\omega/\omega_c)^s\right] \propto (\omega/\omega_c)^s L^2/l^2 \tag{28}$$

and, by comparing with (1c), the form of g may be determined, if the approximate power s (discussed below (30)) can be found. This is easy for $\omega_c < \omega < \omega^*$, but for $\omega^* < \omega < \omega_0$ it is difficult.

The approximate result for $\sigma(\omega)$ for $\omega_c < \omega < \omega^*$ is

$$\sigma(\omega) = \sigma_{\text{DC}} + (\pi/16)(e^2/kT)N^2 a^5 \omega\left[\ln(f_0 \nu_{\text{ph}}/\omega)\right]^2(l^1/r_c^2 f_0)\exp(-E_0/kT). \tag{29}$$

For $\omega^* < \omega < \omega_0$, a reasonable approximation (exact in the limit $\omega \to \omega_0$, but not very accurate in the limit $\omega \to \omega^*$) is

$$r = (a/2)[\ln(\nu_{ph}/\omega) - 3\alpha_c/\sigma(\alpha_c - 1)]/[1 - 3\alpha_c a/2\sigma(\alpha_c - 1)r_0]$$

$$R = R'_0 \exp(2r/a)$$

(30)

and all other quantities follow.

The value of s can be calculated in both of these frequency ranges. For $\omega_c < \omega < \omega^*$ one obtains $s = 1 - 2/\ln(f_0\nu_{ph}/\omega)$, but for $\omega^* < \omega < \omega_0$ the calculation is complicated, and not particularly enlightening. Certainly $1 - s$ is again proportional to some function of the ratio of the phonon frequency to the angular frequency, ω, but in this case an extra factor $f(\omega)$ multiplies the phonon frequency. The renormalization of the capacitance effectively renormalizes the phonon frequency. Although this result may be quite general, in VRH systems it seems not to apply because, even though the number of capacitors per critical resistance grows noticeably with decreasing temperature, the typical capacitance of the relevant capacitors shrinks in inverse proportion to the number of capacitors C and the product remains relatively constant e^2/kT.

In any case, no relationship to the fractal dimensionality is seen in the power s.

3.3. Low-frequency $\sigma(\omega)$

In this range, calculations have shown for both VRH [41] and SR [53] systems that the ratio of AC to DC conductivities can be written as

$$\sigma(\omega)/\sigma_{DC} = h[\omega L^2/\omega_c l^2]$$

(31)

(not a power of (ω/ω_c) times L^2/l^2, as for $\omega > \omega_c$). The result for the scaling function, h, has not yet been clearly established. But the scaling of the axes (defined in (1)) is clear. If the conductivity for $\omega > \omega_c$ is almost linear in the frequency ($s \to 1$), then the arguments of g and h are nearly identical; in VRH systems this means that the power p is usually slightly different for $\omega > \omega_c$ than for $\omega < \omega_c$. In SR systems, $p = 0$ on both sides because L and l are independent of T.

If (as for SR systems in [53]) only clusters formed from maximal resistances $R = R_c$ are considered, the functional form of $\sigma(\omega)$ for $\omega < \omega_c$ is linear. If (as for VRH systems in [41]) one includes also clusters with arbitrary maximal R values, a superlinear frequency-dependent term is also generated. Thus for VRH systems, $\sigma(\omega)$ has been written as a sum of two terms, one linear in ω, and one superlinear. This is partly a consequence of evaluating a finite series of terms (corresponding to the discretized distribution of resistances) using an integral approximation. A similar decomposition could be tried in SR systems as well, although it was not attempted in [53]. While a superlinear frequency dependence it observed [38] in VRH systems, the prefactor [41] on such a superlinear term would be much smaller in SR systems. And if very low frequencies were to be investigated, then it is hard to imagine that $\sigma(\omega)$ could drop below the (linear in ω) contribution from clusters with maximal $R = R_c$.

In the original work [53] on SR systems it was claimed that the frequency dependence of $\sigma(\omega)$ should be the same as in VRH systems. This may be true, but the form suggested in [53] lacks the superlinear term; it is also difficult to tell whether both frequency-dependent terms will be observable in SR systems, even if the frequency dependence is the same, because of the much smaller magnitude of the prefactor.

4. Conclusions

A treatment of the AC conductivity in the MHR of spatially random electronic hopping conduction systems has been attempted. The frequency dependence of $\sigma(\omega)$ is slightly sublinear. The result $\sigma(\omega)/\sigma_{DC}$ is found to scale as a function of the ratio ω/ω_c multiplied by the factor (L^2/l^2), a clearly general result from application of percolation theories, where ω_c is proportional to $\exp(-\xi_c)$, the critical value of the stochastic part of the elementary microscopic rates, and (L^2/l^2) is the ratio of the density of 'paths' relevant to DC and AC conduction respectively. The activation energy arising from a uniform contribution to all microscopic rates appears in both the AC and DC conductivities, and divides out of the quotient $\sigma(\omega)/\sigma_{DC}$, and also out of the product R_c and $C_c = C_0 f_0^{-1}$, where C_c is the equivalent parallel capacitance per critical resistance, R_c, and f_0 is the fraction of critical resistances in the subnetwork defined by connecting all $R \leqslant R_c$. The temperature independence of both the separation of critical resistances and the DC correlation length means that the scaling function $g(\omega/\omega_c) = \sigma(\omega)/\sigma_{DC}$ has no explicit temperature dependence, in contrast to VRH systems. The generalization is clear; without a competition between distance and energy random variables, the ratio of the AC and DC conductivities in glasses will scale as a function of $\omega R_c C_c \equiv \omega/\omega_c$, with no explicit temperature dependence and in (1*b*) $p = 0$, except for VRH systems.

The onset of the MHR occurs when the separation of sites is equal to the average length of processes with $\tau \leqslant 1/\omega$. Critical percolation occurs at a lower frequency, when the ratio of lengths to separations is approximately $\alpha_c^{1/3}$, or about 40% larger than at the onset of the MHR. It is suggested that this is relevant to the problem of ionic conducting glasses, and that the regime of the MHR is that in which frequency-dependent scaling is closely obeyed, and in which the conductivity is significantly sublinear. The cross-over to nearly linear conductivity discussed recently [39, 57] is then a cross-over to pair hopping. It has already been pointed out [54] that there is a relationship between the powers of ω in these two regimes; it is suggested that this may help explain why the data of Dixon *et al* [44] for dipolar glasses (which are known to closely obey the same sort of scaling relationship near the critical frequency) also obeys related scaling at frequencies further removed from the critical frequency (if the analogue to the onset of the MHR involves the onset of correlations, as in ionic glasses, and similarly to a theory for dipole glasses [69]). Moreover this analysis shows how the controversy regarding activation energies in ionic conducting glasses might be resolved. The DC activation energy is likely to be larger than the typical barrier heights if the distribution of barrier heights is strongly asymmetric; such a typical barrier height may be related to the onset of the MHR.

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