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LETTER TO THE EDITOR

AC conductivity and diffusion near the percolation threshold

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Abstract. The dynamic conductivity due to charged particles performing a random walk in a percolating network near threshold is considered. It is pointed out that an approach in which the Miller-Abrahams equivalent network is used yields the same results as that based on the generalized Einstein relation. A recent equivalent network analysis of Coniglio *et al* is shown to be in error, because an inadequate equivalent network has been utilized.

The study of the dynamic conductivity in self-similar structures, in particular, percolation models near threshold, has been the subject of many investigations in the last few years [1, 2]. This matter is of equal importance for theoretical and applied research [3].

Let us recall that there are two realizations of a system exhibiting a non-trivial AC conductivity in connection with a percolation transition: (i) a network composed of resistors and capacitors, (ii) a percolating lattice in which charged particles perform a random walk. At the percolation threshold the dynamic conductivity exhibits, in both cases, a frequency dependence which can be characterized by a power law

$$\sigma(\omega) \propto (i\omega)^u. \quad (1)$$

In case (i) one has $u = t/(t+s)$, where t is the exponent due to which the DC conductivity vanishes above threshold, and s causes the dielectric constant to diverge below threshold [2, 4].

In contrast to the first case there is a controversy in the literature concerning the scaling behaviour of system (ii). Using the Einstein relation between the diffusive and conductive behaviour of charged random walkers, and averaging over the contributions of carriers situated in different clusters, Gefen *et al* [5] (referred to as GAA) showed that in this case the exponent u is given by $u = t/(t+2\nu-\beta)$, where ν and β are the exponents corresponding to the correlation length and the order parameter, respectively. In a more recent paper, Coniglio *et al* [6] (referred to as CDH) find, instead, $u = (t+\nu)/(t+2\nu-\beta)$ using an equivalent network approach. In the following we show that the analysis of CDH is incorrect. The standard equivalent network [6-10] which describes the conductivity of diffusing particles contains terms ignored by these authors. If the correct network is used, the results of GAA are recovered.

The fundamental equation of motion for non-interacting classical carriers performing a random walk in an ordered or disordered lattice is

$$\frac{d}{dt}n_i = - \sum_{j \neq i} W_{ij}n_i + \sum_{j \neq i} W_{ji}n_j \quad (2)$$

where n_i is the probability to find a carrier at site i and W_{ij} the hopping probability per unit time.

Now, there are two ways to calculate the dynamic conductivity produced by the random walk of such carriers with charge e . The first is by applying the fluctuation-dissipation theorem which takes the form of a generalized Einstein relation [11]:

$$\sigma(\omega) = \frac{1}{k_B T} n e^2 \tilde{D}(\omega) \quad (3)$$

where n is the number of carriers per volume and $\tilde{D}(\omega)$ is the Laplace transform (with frequency parameter $p = i\omega + 0$) of the velocity autocorrelation function. This function is often called frequency-dependent diffusivity, because its DC value is the diffusion coefficient. Relation (3) holds as long as linear response theory is valid, i.e. as long as the external electric field is small enough to be treated using a linear approximation. $\tilde{D}(\omega)$ is related to another quantity of interest, namely the mean-square distance walked by a particle during time τ , $\langle r^2(\tau) \rangle$, through its Laplace transform $\langle r^2(\omega) \rangle$ by [12]

$$\tilde{D}(\omega) = \frac{1}{6} (i\omega)^2 \langle r^2(\omega) \rangle. \quad (4)$$

In fractals, including percolating systems at threshold, one has anomalous diffusion [1, 13, 14]

$$\langle r^2(\tau) \rangle \propto \tau^\alpha \quad (5)$$

with $\alpha < 1$. This exponent is related to the random-walk dimension d_w which obeys the scaling relations [14]

$$d_w = \frac{2}{\alpha} = 2 + \frac{t - \beta}{\nu} = \frac{2\bar{d}}{\bar{d}} \quad (6)$$

where \bar{d} is the fractal dimension of the infinite cluster and \bar{d} its spectral (or fracton) dimension [14]. The second relation holds for any fractal.

Equation (5) gives the mean-square distance walked by a single particle which started at time $\tau = 0$ on the infinite cluster. By averaging over random walks on finite clusters of different size and on the infinite cluster GAA obtained for the averaged mean-square distance

$$\langle r^2(\tau) \rangle_{av} \propto \tau^{\tilde{\alpha}} \quad (7)$$

with $\tilde{\alpha} = (2 - \beta/\nu)/d_w$. Combining (1), (3), (4), (7), and using the Tauberian theorem for the Laplace transform of power laws one readily obtains the AC conductivity exponent as

$$u = 1 - \tilde{\alpha} = t/(t + 2\nu - \beta). \quad (8)$$

For (bond or site) concentrations p larger than their critical value p_c implying a finite DC conductivity $\sigma(0) \propto (p - p_c)^t$ and a finite correlation length $\xi \propto (p - p_c)^{-\nu}$ there is a crossover to normal diffusion at a time $\tau_0 \propto \xi^{d_w}$.

The second way to calculate the dynamic conductivity of model (ii) is to construct an equivalent network which has the same electrodynamic behaviour as the random-walk system. This method has been introduced by Miller and Abrahams [7] and utilized further in various publications and textbooks [8-11]. It can be obtained by expanding n_i and W_{ij} around their equilibrium values, $n_i^{(0)}$ and $W_{ij}^{(0)}$, to linear order in the applied external field $E(t)$. The equilibrium values of the n_i can be represented in terms of local energies ϵ_i as $n_i^{(0)} = \exp\{-\epsilon_i\} / \sum_i \exp\{-\epsilon_i\}$ [15], and one has the fundamental detailed-balance relation

$$W_{ij} = W_{ji} \exp\{(\epsilon_i - \epsilon_j - e[U_i - U_j])/k_B T\} \quad (9)$$

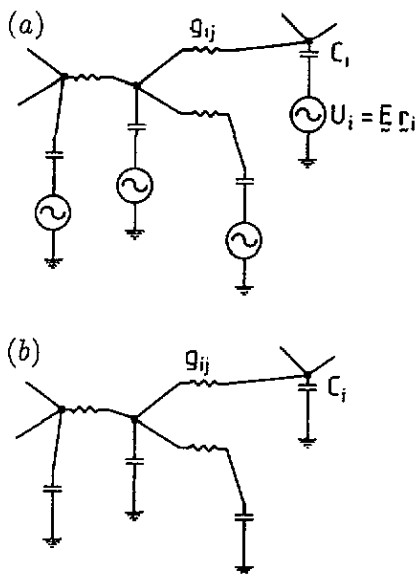


Figure 1. (a) Miller-Abrahams equivalent network corresponding to (10). (b) CDM network, where the sources U_i are missing.

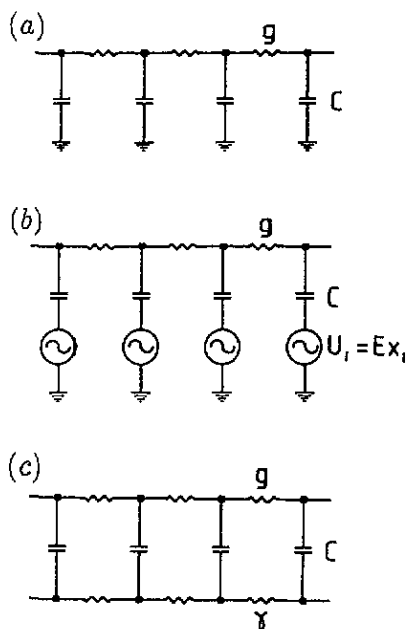


Figure 2. (a) One-dimensional version of an ordered CDM network. (b) One-dimensional version of an ordered Miller-Abrahams network. (c) Miller-Abrahams Network with sources replaced by a potentiometer array.

where $U_i = E \cdot r_i$. Representing the n_i as $n_i = n_i^{(0)} \exp \mu_i / k_B T$ and defining local electrochemical potentials as $V_i = \mu_i / e - U_i$, effective capacitances as $C_i = e^2 n_i^{(0)} / k_B T$ and effective conductances as $g_{ij} = e^2 n_i^{(0)} W_{ij}^{(0)} / k_B T$ one arrives, to linear order in the V_i and U_i at

$$C_i \frac{d}{dt} (V_i + U_i) = \sum_j g_{ij} (V_j - V_i). \tag{10}$$

This set of equations [7-11] can be interpreted as Kirchhoff's equations for a network composed of conductances g_{ij} , where at each vertex there is a local AC voltage source U_i , coupled capacitively via the C_i . This network is depicted in figure 1(a).

To proceed further one can rederive the generalized Einstein relation (3) using the Miller-Abrahams network, as done, for example, in [10, 11]. Alternatively, one can consider directly the scaling properties of the specific admittance of the equivalent network.

The approach of CDH is an attempt at this second possibility. However, in the equivalent network they considered the 'generators' U_i are missing. As can be verified from the above analysis (see, for example, [11]) these terms arise from the fact that in systems with mobile charges the driving forces for local currents are local voltage drops and local chemical potential gradients. Ignoring them amounts to either violating particle conservation or the detailed-balance relation (9).

Ignoring the U_i terms CDH dealt with a hypothetical network in which each node is grounded capacitively (see figure 1(b)). As demonstrated by these authors the impedance of their hypothetical network exhibits an unusual length dependence. The impedance of an ordered linear infinite chain of this type (figure 2(a)) becomes independent of the number of

beads if the number becomes large. Therefore a three-dimensional capacitatively grounded network (figure 1(b)) has, at finite frequencies, a conductivity which is proportional to the linear dimension of the sample. From this strange scaling behaviour (which is never observed in the AC conductivity of real materials) they find their scaling relation for u quoted above.

A regular chain of the Miller–Abrahams type (i.e. $g_{ij} = g$, $C_i = C$, see figure 2(b)) can be converted by a potentiometer array with beads $\gamma_{ij} = \gamma$ to the chain depicted in figure 2(c). This chain obviously has an impedance which increases linearly with its length. Therefore the conductivity of a three-dimensional (and two-dimensional) ordered version of the Miller–Abrahams equivalent circuit has a well behaved length-independent dynamic conductivity. This behaviour holds also for a percolating lattice at finite frequency, because in this case one can convert the equivalent network with percolating conductances as in figure 2(c) into an effective lattice network in which all connecting admittances are finite. The specific admittance of this network does not depend on the linear dimension of the sample.

Keeping these findings in mind we now perform a scaling analysis of the percolating network. For our purposes it is sufficient to consider only the case $p > p_c$. Near the percolation threshold p_c the conductivity is expected to exhibit scaling behaviour according to

$$\sigma(\omega) = \sigma_0 \xi^{-t/\nu} f[(i\omega)\phi\xi] \quad (11)$$

The length–frequency scaling exponent ϕ for a fractal with dynamics governed by equations of motion (2) or (10) is given by [13, 14, 16] $\phi = \alpha/2 = 1/d_w = \bar{d}/2\bar{d}$. For $x = \omega\phi\xi \ll 1$ the static behaviour $\sigma \propto \xi^{-t/\nu}$ must be recovered, so that in this limit $f(x) = f(0) = \text{constant}$. According to the above argument, for high frequency $x \gg 1$, the conductivity should be independent of the characteristic length scale ξ so that in this limit we must have $f(x) \propto x^{t/\nu}$. From (6) this yields an AC conductivity of the form (1) with $u = \phi t/\nu = t/(t + 2\nu - \beta)$. The DC–AC crossover frequency ω_c defined by $\omega_c^\phi \xi \sim 1$ is, as expected, equal to the inverse of the characteristic time $\tau_0 \propto \xi^{d_w}$ which determines the crossover from anomalous to normal diffusion.

The present argumentation is in accord with a remark of CDH in which they state that, if the AC conductivity is length-independent, their scaling analysis yields the results of GAA.

Let us now consider the numerical values of u predicted by the GAA relation (8). In [14] results of various types of calculations of critical exponents for the percolation problem have been compiled. In two dimensions β and ν are known exactly: $\beta = \frac{5}{36}$, $\nu = \frac{4}{3}$. Numerical calculations of t † vary between 1.26 and 1.31 with error bars of 0.5% to 1%. This yields a value of $u = 0.336 \pm 0.004$. In a similar way we obtain in three dimensions $u = 0.61 \pm 0.03$. Using the CDH relation $u = (t + \nu)/(t + 2\nu - \beta)$ instead, one would obtain $u \approx 0.7$ in $d = 2$ and $u \approx 0.9$ in $d = 3$.

Finally I would like to add a word of caution concerning the comparison of percolation exponents with AC conductivity data in composite materials. First of all, most disordered and composite materials exhibit a frequency dependence of type (1) not as a consequence of fractal scaling but of the presence of disorder [17] or correlation effects [18, 19]. If such materials (for example porous Si [3]) exhibit fractal properties, which can be proved by small-angle x-ray [20, 21] or neutron [22] scattering, this does not mean that a percolating lattice is an adequate model for such a material. For example, in the material under consideration ‘finite clusters’ might be absent so that the exponent u becomes [3] $u = 1 - \alpha = 1 - 2/d_w = 1 - \bar{d}/\bar{d}$. In such a case u can be predicted if \bar{d} is known from small angle scattering data and \bar{d} from the specific heat or the phonon density of state.

† The conductivity exponent is called μ in [5, 14].

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