Hopping models and ac universality

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Some general relations for hopping models are established. We proceed to discuss the universality of the ac conductivity which arises in the extreme disorder limit of the random barrier model. It is shown that the relevant dimension entering into the diffusion cluster approximation (DCA) is the harmonic (fracton) dimension of the diffusion cluster. The temperature scaling of the dimensionless frequency entering into the DCA is discussed. Finally, some open questions about ac universality are mentioned.

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INTRODUCTION

Hopping models have been studied for many years in different contexts \[1,2,3,4\]. Our main concern here is the modeling of ac conduction in disordered solids, a field where hopping models are quite successful. There is a wealth of ac data for various disordered solids like ionic conductive glasses, amorphous semiconductors, polymers, etc. These solids behave similarly: from bulk ac data alone it is not possible to distinguish ionic and electronic conduction. The “universal” ac features \[5\] are: At low frequencies the conductivity is constant, at high frequencies it follows an approximate power law with an exponent which is less than one but slowly approaches one as frequency increases. As temperature is lowered the dc conductivity goes to zero and the frequency exponent goes to one (at any fixed frequency much below phonon frequencies). The frequency marking onset of ac conduction is proportional to the dc conductivity, while both are strongly temperature dependent (usually Arrhenius).

In this paper we first establish hopping models as part of a more general framework. We then proceed to discuss the extreme disorder limit of hopping models. In this limit the ac conductivity in properly scaled units becomes independent of the jump frequency probability distribution. Finally, new results are established for the diffusion cluster approximation, a recently proposed analytical approximation for the universal ac conductivity.

DIFFUSION AND HOPPING MODELS

First, we briefly consider diffusion in general and define the wave-number and frequency-dependent diffusion constant. Then we specialize to hopping of non-interacting particles on a cubic lattice and derive a number of relations. Many of the points made below can be found in the literature, but to our knowledge they have never been concisely written down aimed at hopping models.

If \(\rho\) is the particle density and \(\mathbf{J}\) the particle current density, the most general diffusion-type constitutive equation obeying linearity, causality and space-time homogeneity is:

\[
\mathbf{J}(\mathbf{r}, t) = - \int d\mathbf{r}' \int_0^\infty dt' \, D(\mathbf{r}', t') \nabla \rho(\mathbf{r} - \mathbf{r}', t - t') . \tag{1}
\]

It is convenient to introduce the so-called Laplace frequency \(s\) given by

\[
s = i\omega , \tag{2}
\]

where \(\omega\) is the ordinary frequency. The wave-number and frequency-dependent diffusion constant, \(D(\mathbf{k}, s)\), is by definition the Fourier-Laplace transform of \(D(\mathbf{r}', t')\):

\[
D(\mathbf{k}, s) = \int d\mathbf{r}' \, e^{-i\mathbf{k} \cdot \mathbf{r}'} \int_0^\infty dt' \, e^{-st'} D(\mathbf{r}', t') \equiv \int d\mathbf{r}' \, e^{-i\mathbf{k} \cdot \mathbf{r}'} D(\mathbf{r}', s) . \tag{3}
\]

It is possible to express \(D(\mathbf{k}, s)\) in terms of equilibrium density fluctuations. To show this we first Laplace transform the equation of continuity, \(\dot{\rho} = -\nabla \cdot \mathbf{J}\), and calculate the right hand side by means of Eq. (1). If \(\tilde{\rho}\) is the Laplace transform of \(\rho\) this leads to

\[
s \tilde{\rho}(\mathbf{r}, s) - \rho(\mathbf{r}, 0) = \int d\mathbf{r}' D(\mathbf{r}', s) \nabla^2 \tilde{\rho}(\mathbf{r} - \mathbf{r}', s) . \tag{4}
\]

We proceed by Fourier transforming this equation. If \(\rho_k\) is the Fourier transform of the density, \(\rho_k = \int d\mathbf{r} \rho(\mathbf{r}) \exp(-i\mathbf{k} \cdot \mathbf{r})\), one finds

\[
s \tilde{\rho}_k(s) - \rho_k(0) = -D(k, s) k^2 \tilde{\rho}_k(s) . \tag{5}
\]

Equation (5) implies \(\tilde{\rho}_k(s) = \rho_k(0) / [s + D(k, s)k^2]\). Multiplying this relation by \(\rho_{-k}(0)\) we find after thermally averaging

\[
\frac{\langle \tilde{\rho}_k(s) \rho_{-k}(0) \rangle}{\langle \rho_k(0) \rho_{-k}(0) \rangle} = \frac{1}{s + D(k, s)k^2} . \tag{6}
\]

We are mainly interested in the \(k \to 0\) limit. The frequency-dependent diffusion constant \(D(s)\) is defined by

\[
D(s) = \lim_{k \to 0} D(k, s) . \tag{7}
\]
We proceed to derive an equation relating $D(s)$ to the mean-square displacement as function of time, considering from now on only the case of non-interacting particles. If $d$ is space dimension and $\Delta \rho(t)$ is particle displacement in time $t$, the relevant expression is (with an implicit convergence factor $\lim_{\epsilon \to 0} \exp(-\epsilon t)$, $\epsilon > 0$):

$$D(s) = \frac{s^2}{2d} \int_0^\infty \langle \Delta \rho^2(t) \rangle e^{-st} dt. \quad (8)$$

The proof proceeds as follows. If the particle positions are denoted by $r(j)$ we have

$$\rho_k(t) = \sum_j \exp[-\imath k \cdot r(j(t))] \cdot \langle k \cdot \Delta \rho(t) \rangle \cdot \exp[-\imath k \cdot \Delta r(j(t))].$$

Consequently, it is enough to consider the motion of just one particle and

$$\langle \rho_k(t) \rho_{-k}(0) \rangle = \langle e^{-\imath k \cdot \Delta \rho(t)} \rangle. \quad (9)$$

Being only interested in the limit of small $k$, the exponential on the right hand side is expanded: $\exp(-\imath k \cdot \Delta \rho) = 1 - \imath k \cdot \Delta \rho - \frac{1}{2} (k \cdot \Delta \rho)^2 + ...$. For the thermal average we have by symmetry $\langle \Delta \rho \rangle = 0$ and thus $\exp(-\imath k \cdot \Delta \rho) = 1 - \frac{1}{2} (k \cdot \Delta \rho)^2 + ...$. Spherical symmetry implies that, if $\Delta \rho_i$ is the $i$’th coordinate of $\Delta \rho$ etc.,

$$\langle \Delta \rho_i \Delta \rho_j \rangle = \langle k_i \Delta r_i k_j \Delta r_j \rangle = k^2 \langle \Delta r^2 \rangle / d.$$

Substituting this into Eq. (8), Laplace transforming, and utilizing Eq. (3), leads to

$$\frac{1}{s + D(k, s) k^2} = \frac{1}{s} \frac{k^2}{2d} \int_0^\infty \langle \Delta r^2(t) \rangle e^{-st} dt + ... \quad (10)$$

For small $k$ the left hand side is expanded as follows:

$$s^{-1}\left[1 - s^{-1}D(k, s)k^2 + ...\right].$$

Comparing this to the right hand side and letting $k \to 0$ proves Eq. (3).

The case of “ordinary” diffusion is characterized by $\langle \Delta r^2(t) \rangle = 2 d t$ where $D$ is the ordinary diffusion constant. Substituting this into Eq. (8) gives $D(s) = D$ at all frequencies. Thus the definition of $D(s)$ is a consistent generalization of the ordinary diffusion constant. Finally, we note that Eq. (8) may be rewritten by performing two partial integrations:

$$D(s) = \frac{1}{d} \int_0^\infty \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle e^{-st} dt. \quad (11)$$

Henceforth we specialize to the case of non-interacting particles hopping on a finite cubic lattice in $d$ dimensions. Hopping models have been discussed for several years in the literature. Some reviews of hopping are listed in Refs. [1, 2, 3, 4]. As mentioned already, it is only necessary to consider the motion of one particle. A hopping model is defined as follows. Adopting the bra-ket notation of quantum mechanics the lattice sites are denoted by $|j\rangle$. Any state of the system $|P\rangle$ is given by an expression of the form $|P\rangle = \sum_m P_m |m\rangle$, where $P_m$ is the probability to find the particle at site $m$. The state space is a real Hilbert space when equipped with ordinary inner product but, of course, only states with positive probabilities summing to 1 are physical. Time development is described by a master equation which is conveniently written in terms of a “Hamiltonian” as follows:

$$\frac{d}{dt} |P\rangle = H |P\rangle. \quad (12)$$

Here, $H$ is the well-known master equation time-development matrix constructed from the transition probabilities. $H$ has the following properties [10]. All diagonal elements of $H$ are non-negative (giving the decay rate from a state), all off-diagonal elements are non-negative (giving the transition rate from one state to another). The condition $\sum_j H_{jm} = 0$ ensures probability conservation. If $P_m(0)$ is the canonical probability to find a particle at site $m$ in thermal equilibrium, for any states $|j\rangle$ and $|m\rangle$ the principle of detailed balance demands that $H_{jm} P_m(0) = H_{mj} P_j(0)$.

Since the solution of Eq. (12) is $|P(t)\rangle = \exp(Ht)|P(0)\rangle$ the mean-square displacement in thermal equilibrium is given by

$$\langle \Delta r^2(t) \rangle = \sum_{jm} (r_j - r_m)^2 \langle j| e^{Ht} |m\rangle P_m(0). \quad (13)$$

As always when dealing with a master equation it is convenient to switch to the “symmetric” representation [14]: First we define the operator $T$ by $T|m\rangle = \sqrt{P_m(0)|m\rangle = |\psi_m\rangle}$. It is easy to show that the principle of detailed balance implies that the operator $\hat{H} \equiv T^{-1}H T$ is Hermetian (real and symmetric). Furthermore, $\langle j| \exp(Ht)|m\rangle = \langle j| \exp(THT^{-1}t)|m\rangle = \langle j| T \exp(HT)T^{-1}|m\rangle = \langle \psi_j| \exp(HT)|\psi_m\rangle P_m(0)$. Substituting this into Eq. (13) leads to

$$\langle \Delta r^2(t) \rangle = \sum_{jm} (r_j - r_m)^2 \langle \psi_j| e^{HT} |\psi_m\rangle. \quad (14)$$

From this important conclusions are arrived at. First, note that if any state may be reached from any other, ergodicity, $\hat{H}$ has a unique “ground state” with eigenvalue 0 [10]. This state, $|0\rangle$, is the symmetric representation of the state of thermal equilibrium. It
is straightforward to show that this normalized eigenstate is given by $|0\rangle = \sum_m \psi_m$. All other eigenvalues of $\hat{H}$, denoted by $-\gamma_n$, are strictly negative (i.e., $\gamma_n > 0$). If the corresponding eigenstates of $\hat{H}$ are denoted $|n\rangle$, the usual trick of “sandwiching in” the orthonormal set of eigenstates leads to $\langle \psi_j | \exp(\hat{H}t) | \psi_m \rangle = \sum_n \langle \psi_j | n \rangle \langle n | \psi_m \rangle \exp(-\gamma_n t)$. Substituting this into Eq. (14) leads to

$$\langle \Delta \mathbf{r}^2(t) \rangle = \sum_{jm} (r_j - r_m)^2 p_j(0) p_m(0) - \sum_n \mu_n e^{-\gamma_n t},$$

where $\mu_n = -\sum_{jm} (r_j - r_m)^2 \langle \psi_j | n \rangle \langle n | \psi_m \rangle$. Since $\langle \Delta \mathbf{r}^2(t) \rangle = 0$ for $t = 0$, Eq. (15) may be rewritten as

$$\langle \Delta \mathbf{r}^2(t) \rangle = \sum_n \mu_n \left(1 - e^{-\gamma_n t} \right).$$

We proceed to prove that $\mu_n \geq 0$. Suppose that $\lambda_j$ are real numbers summing to zero. Then $\sum_{jm} (r_j - r_m)^2 \lambda_j \lambda_m \leq 0$, because the sum may be rewritten as $(\sum_j \lambda_j r_j^2) (\sum_m \lambda_m) + (\sum_j \lambda_j r_j^2 - 2 (\sum_j \lambda_j r_j)^2$ and the first two terms vanish. It follows that $\mu_n \geq 0$ because for any $|n\rangle$ one has $\sum_j \langle \psi_j | n \rangle = \langle 0 | n \rangle = 0$.

We are now able to prove a result for the mathematical structure of the mean-square displacement in hopping models: By repeated differentiations Eq. (16) implies

$$\frac{d}{dt} \langle \Delta \mathbf{r}^2(t) \rangle \geq 0$$

$$\frac{d^2}{dt^2} \langle \Delta \mathbf{r}^2(t) \rangle \leq 0$$

We now specialize to hopping models with only nearest-neighbor jumps, and focus on the simplest model of this kind, the random barrier model (also called the symmetric hopping model). For this model all sites on the cubic lattice have equal energy. Thus, detailed balance implies for the jump rates $\Gamma_{jm} = \Gamma_{mj}$. Because we want to model a disordered solid the jump rates are taken to vary randomly and uncorrelated from link to link. Moreover, we shall assume that the jump rates are given by a free energy barrier $E$: $\Gamma = \Gamma_0 \exp(-\beta E)$. Here $\beta$ is the inverse temperature if classical barrier hopping is considered and inverse wave function size if quantum mechanical tunneling is considered. The model is completely defined in terms of the free energy barrier probability distribution, $p(E)$.

At large values of $\beta$ the jump rates vary many orders of magnitude. The limit $\beta \to \infty$ is termed the extreme disorder limit. In this limit, although all jump frequencies
conductivity $\sigma$ go to zero and consequently $\sigma \rightarrow 0$, one may ask how the conductivity relative to the dc level, $\tilde{\sigma} \equiv \sigma / \sigma(0)$, behaves as a function of frequency $\tilde{\omega}$ or Laplace frequency $\tilde{s}$, as $\beta \rightarrow \infty$ the conductivity $\tilde{\sigma}(\tilde{s})$ converges to some value which is independent of $p(E)$. In computer simulations we find that the larger $\tilde{s}$ is, the larger $\beta$ must be before there is convergence. Since $\tilde{s} \sim 1$ defines the region below which the conductivity is virtually frequency independent, this means that the convergence to universality is fastest around the onset of ac conduction.

Although no mathematically rigorous proof of ac universality exists, there is convincing evidence for ac universality from several sources. First of all, ac universality is clearly seen in computer simulations, where several quite different $p(E)$’s lead to the same $\tilde{\sigma}(\tilde{s})$ in the extreme disorder limit. Secondly, the effective medium approximation (EMA) implies ac universality in the extreme disorder limit with the following prediction:

$$\tilde{\sigma} \ln \tilde{\sigma} = \tilde{s}. \quad (22)$$

This equation was first derived by Bryksin as the EMA solution of the hopping model describing electrons tunneling between random positions in space. Finally, it is possible to physically understand the origin of universality; basically it stems from the fact that percolation dominates conduction in the extreme disorder limit.

The EMA universality equation (22) has the correct qualitative features of the universal ac conductivity: a constant low frequency conductivity and an ac conductivity which at high frequencies follows an approximate power law; the exponent is below one but converges logarithmically to one as frequency diverges. Quantitatively, however, Eq. (22) is not accurate in three dimensions, and even less accurate in two dimensions. In both cases the onset of ac conduction is less dramatic than predicted by Eq. (22). One may speculate, however, that Eq. (22) becomes exact in and above 6 dimensions, because here mean-field theory for percolation is exact (when regarded as a critical phenomenon), and EMA is a sort of mean-field theory. We have preliminary simulation data for 4 dimensions indicating that Eq. (22) indeed works better as dimension is increased.

Before proceeding to a discuss a more accurate analytical approximation to the universal ac conductivity, let us briefly sketch how Eq. (22) is derived because this is relevant for the following. The units used are “rationalized units” where conductivity, diffusion constant and jump rate are all identical in the ordered (homogeneous) case. The general EMA equation for finite disorder is a rather complicated self-consistency equation for $\sigma(s)$ [3]. This equation involves the diagonal element of the Green’s function for a “homogeneous” random walk with uniform jump frequency $\Gamma$, $\tilde{G}_0 \equiv \langle \chi(x) \chi(y) \rangle$, where $G_0 = 1/(s - H_0)$ is the resolvent operator for the uniform-case “Hamiltonian” $H_0$. $\tilde{G}_0$ is a function of $\Gamma(= \sigma)$, besides of course also a function of $s$. In the extreme disorder limit the EMA self-consistency equation reduces [4] to

$$\ln \tilde{\sigma} \propto \beta \, s \tilde{G}_0. \quad (23)$$

It is straightforward to show that $s \tilde{G}_0 \propto s / \sigma$ for small $s$ in two and more dimensions [4]. When this is substituted into Eq. (23) one arrives at Eq. (22) after a suitable rescaling of $s$ to define the dimensionless quantity $\tilde{s}$:

$$\tilde{s} = f(\beta) \frac{s}{\sigma(0)}, \quad (24)$$

where $f(\beta) \propto \beta$.

As mentioned already Eq. (22) does not give an accurate representation of the universal ac conductivity in three dimensions. A better fit to data is provided by what we term the “diffusion cluster approximation” (DCA), which leads [4] to

$$\ln \tilde{\sigma} \propto \left(\frac{s}{\tilde{s}}\right)^{d_0/2}. \quad (25)$$

Our simulations in 3-d are well fitted by $d_0 = 1.35$. An equation similar to Eq. (25) was derived by Zvyagin in 1980 [17] by reference to cluster size statistics at percolation. Zvyagin’s equation, however, is real: He has $\omega$ where we have $i\omega$ and $\text{Re}(\tilde{\sigma})$ where we have $\tilde{\sigma}$.

In the original derivation of Eq. (23) $d_0$ was identified with the dimension of the “diffusion cluster” [16]. This set is defined as follows. We first recall that at extreme disorder conduction takes place on the percolation cluster [18, 19, 20]. More precisely, links with jump rates much smaller than the “percolation jump rate” can be removed without affecting the overall (dc) conductivity of the lattice; for any finite $\beta$ this leaves us with the “fat” percolation cluster [4] (which becomes the true percolation cluster as $\beta \rightarrow \infty$). However, more links may be removed. First of all, those on dead ends of the percolation cluster may be removed, leaving the so-called backbone. Moreover, if there are two different paths between any two points below the correlation length, because of the extreme disorder one of them is much more favorable than the other which may be removed. After this diluting of the percolation cluster the remainder is by definition the diffusion cluster.

- **In the extreme disorder limit not only dc but also ac conduction takes place mainly on the diffusion cluster.**

This assumption runs contrary to the traditional use of percolation theory to calculate $\sigma(s)$. The assumption should be checked by computer simulations, but we
have not yet done so. Please note that, at any finite $\beta$ the assumption applies only at not too high frequencies; there are always isolated islands of well-conducting regions which are important at sufficiently high frequencies. Our conjecture, however, is that the scaled frequency below which the conjecture applies diverges as $\beta \to \infty$.

What is the structure of the diffusion cluster? Let us first recall the “nodes-links-blobs” model of the backbone. According to this model [21] the backbone comprises links (i.e., quasi one-dimensional strings) and nodes at the intersection of links. The “blobs” refer to the fact that for $0 \leq 1$ percolation there are occasional “strongly bonded” regions along any link. However, as argued above, blobs are unimportant in the extreme disorder limit of a continuum distribution of jump rates because, of any two different paths between two points one will strongly dominate.

Our picture is now the following: At any finite $\beta$, the time scale on which the particle moves more than the node-node distance corresponds to frequencies where the conductivity is frequency independent; here we agree with the standard use of percolation theory to ac phenomena. On a smaller distance scale the diffusion cluster is fractal. In our original derivation of Eq. (25) we used the EMA equation Eq. (23) for hopping on the diffusion cluster and identified $d_0$ with the dimension of the diffusion cluster, having in mind the fractal dimension $d_f$. More correctly, $d_0$ should be identified with the so-called harmonic or fracton dimension $d_{\text{h}}$, which for homogeneous (uniform jump rate) random walks on the diffusion cluster gives the probability $P(t)$ to be at the same place as at $t = 0$: By definition $P(t) \propto t^{-\frac{d_f}{2}}$ and $G_0$ is basically the Laplace transform of $P(t)$, which implies $sG_0 \propto (s/\sigma)^{d_f/2}$. The connection between $d_f$ and $d_{\text{h}}$ [21, 22] is

$$d_{\text{h}} = \frac{\delta d_f}{2 + \delta},$$

where the exponent $\delta$ is given by $\langle \Delta r^2(t) \rangle \propto t^{2/(2+\delta)}$ for a homogeneous random walk on the diffusion cluster.

Is it possible that $d_{\text{h}} = d_f$, corresponding to $\delta = 0$? In our opinion the answer is yes, because $\delta = 0$ for any fractal without dead ends and without loops, e.g., a self-similar curve like the Koch curve [21, 22]. If the links of the nodes-links model for the diffusion cluster are of this kind one has $d_{\text{h}} = d_f$. Indeed, we argued above that the diffusion cluster has no dead ends or loops.

We finally briefly discuss the temperature scaling of the dimensionless frequency in the DCA. As mentioned above, for homogeneous random walks on the diffusion cluster $sG_0 \propto (s/\sigma)^{d_0/2}$ where $d_0 = \bar{d}$. When this is substituted into Eq. (23) we find that the function $f(\beta)$ in Eq. (24) is given by $f(\beta) \propto \beta^{2/d_0}$. For $d_0 = 1.35$ one gets $f \propto \beta^{1.48}$. In our simulations we find a similar power law for $f(\beta)$, albeit with exponent $1.37 \pm 0.03$. Roling finds an exponent equal to $1.3 \pm 0.2$.

### OPEN QUESTIONS

Many questions about ac universality in the extreme disorder limit remain unanswered:

- For the random barrier model: How does the universal ac conductivity depend on dimensionality? In particular: Is Eq. (22) exact in $6$ dimensions and above?
- For the more general asymmetric hopping model, i.e., with lattice sites of differing energies: Does this model also have ac universality in the extreme disorder limit? If yes: Does the universal ac conductivity depend on the choice of transition rates? How does it depend on dimensionality?
- More realistically one should consider hopping with only room for one particle at each site. For “Fermi hopping” Is there ac universality in the extreme disorder limit? If yes: Is this the same as the ac universality for the random barrier model, which is the mean-field (Hartree) limit of the Fermi model [2][3]?

In our opinion much remains to be done in this challenging field of research. Compared to the 1970’s and 1980’s one now has the possibility of extensive computer simulations at hand. This is likely to bring further progress in the field.
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