Universal ac conductivity of nonmetallic disordered solids at low temperatures

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It is shown that, in the low-temperature limit, the effective-medium approximation predicts a universal frequency dependence of the conductivity of nonmetallic disordered solids. The calculation is based on a macroscopic approach to ac conduction and is valid in more than one dimension. The universality prediction is confirmed by simulations in two dimensions.

For many years ac conduction has been studied in disordered solids such as amorphous semiconductors, glasses, polymers, nonstoichiometric solids, or metal–cluster compounds. All disordered solids show similar ac behavior, whether the conduction is electronic, polaronic, or ionic. The frequency-dependent conductivity follows an approximate power law with an exponent between 0.7 and 1.0. At lower frequencies there is a gradual transition to constant conductivity. The standard models for this are hopping models which deal with the random walk of noninteracting charge carriers in a random environment. While hopping models are rather successful, the importance of Coulomb interactions has recently come into focus. Unfortunately, hopping models with interactions are not amenable to simple analytic treatment. One way to include the effect of Coulomb interactions between charge carriers, instead of using hopping models, is to adopt a macroscopic point of view. This is done here where conduction in inhomogeneous media is discussed by exploring Maxwell’s equations.

Consider a disordered solid with spatially varying thermally activated conductivity \( g(E(\mathbf{r})) = g_0 e^{-\beta E(\mathbf{r})} \). Here \( \beta \) is the inverse temperature and the activation energy \( E(\mathbf{r}) \) is assumed to vary randomly in space with a finite correlation length. In some cases the activation energy probability distribution is quite narrow; however, we are concerned here with the low-temperature case where the distribution of conductivities becomes very broad. If \( \epsilon \) denotes the dielectric constant and \( \omega \) the angular frequency, the continuity equation and Gauss’ law imply for the electrostatic potential \( \phi \)

\[
\nabla \cdot ((i\omega \epsilon + g) \nabla \phi) = 0 .
\]

(1)

This equation is discretized by regarding the potential \( \phi \) as defined on the points of a simple cubic lattice and the quantity \( i\omega \epsilon + g \) as defined on nearest-neighbor links. In this way Eq. (1) becomes the Kirchhoff current conservation law for a lattice where each link is a resistor in parallel with a capacitor. If \( s \) is the lattice constant and \( D \) the dimension, the correct continuum limit is ensured if each link admittance \( y \) is given by

\[
y = a^{D-2}(i\omega \epsilon + g) .
\]

(2)

The electrical circuit is not to be interpreted literally as a physical model of the solid because the free charge currents run through the resistors only; the capacitor currents are the well-known displacement currents. However, the circuit is useful for calculating the macroscopic frequency-dependent free charge conductivity \( \sigma(\omega) \), i.e., the ratio between average free charge current and average electrical field. If \( L \) is the linear circuit dimension and \( G(\omega) \) is the admittance between opposing short-circuited faces, it is straightforward to show that, whenever \( \epsilon \) is space independent, \( \sigma(\omega) \) is given by

\[
\sigma(\omega) = \frac{G(\omega)}{L^{D-2}} - i\omega \epsilon .
\]

(3)

If the discretization length \( a \) is chosen to be the correlation length for \( E(\mathbf{r}) \) and correlations beyond \( a \) are ignored, the effective-medium approximation (EMA) may be applied to calculate \( G \). The EMA equation for the effective-link admittance, \( y_m \), is

\[
\langle (y - y_m)/(y+(D-1)y_m) \rangle_p = 0
\]

where the bracket denotes an average over the admittance probability distribution. Since \( G = N^{D-2}y_m \) where \( N = L/a \), the EMA equation and Eqs. (2) and (3) imply (where \( s = i\omega \epsilon \))

\[
\frac{1}{D(\sigma + s)} = \left( \frac{1}{g(E) + (D-1)\sigma + Ds} \right)_E.
\]

(4)

This equation has a simple solution in the limit \( \beta \to \infty \). The root \( E_g(s) \) of \( g(E) = (D-1)\sigma + Ds \) is given by

\[
E_g(s) = \ln \frac{(D-1)\sigma + Ds}{g_0} .
\]

(5)

If \( p(E) \) is the activation-energy probability distribution, Eq. (4) at low temperatures becomes
\[
\frac{1}{D(\sigma + s)} = \frac{1}{(D-1)\sigma + Ds} \int_{E_{\xi}(1)}^{E_{\xi}(0)} p(E) dE
\]  \hspace{1cm} (6)

or

\[
\frac{D-1}{D} + \frac{s}{D(\sigma + s)} = \int_{E_{\xi}(0)}^{E_{\xi}(1)} p(E) dE .
\]  \hspace{1cm} (7)

For large \(\beta\) subtracting the \(s=0\) case of Eq. (7) from Eq. (7) itself leads to

\[
\frac{s}{D(\sigma + s)} = \int_{E_{\xi}(0)}^{E_{\xi}(1)} p(E) dE
\]

\[
= p(E_{\xi}(0)) \frac{1}{\beta} \ln \left( \frac{\sigma}{\sigma(0)} + \frac{D}{D-1} \frac{s}{\sigma(0)} \right) .
\]  \hspace{1cm} (8)

Introducing the dimensionless variables

\[
\bar{\sigma} = \frac{\sigma}{\sigma(0)} , \quad \bar{\xi} = \frac{\beta}{Dp(E_{\xi}(0))\sigma(0)} s ,
\]  \hspace{1cm} (9)

Eq. (8) for \(\beta \to \infty\) reduces to

\[
\bar{\sigma} \ln(\bar{\sigma}) = \bar{\xi} .
\]  \hspace{1cm} (10)

Equation (10) was derived by Fishchuk for the uniform energy barrier distribution with cutoffs where the average in Eq. (4) can be calculated explicitly.\(^{20}\) Here it has been shown that, in the low-temperature limit, the EMA predicts a universal frequency dependence of the conductivity (in any dimension \(D > 1\)). There is, however, some doubt whether the EMA is reliable for systems with extremely broad distributions of admittances.\(^{25,26}\) Therefore, computer simulations were carried out to test Eq. (10). At low temperatures large lattices are needed to obtain reasonable statistics, and the simulations are quite demanding. Only the two-dimensional case was studied where the highly efficient Frank-Lobb algorithm is available.\(^{27}\) For simplicity the simulations were carried out for real \(\bar{\xi}\); by analytic continuation this is possible when the purpose is to compare the simulation results to an analytic function. Bonds were defined via Eq. (2) where \(g\) is given by a randomly chosen activation energy. Several different activation-energy distributions were used. The conductivity was evaluated from Eq. (3). Averages of 20 simulations of a \(100 \times 100\) square lattice are shown in Fig. 1. The results confirm the EMA prediction of universality as the temperature is lowered. The universality represents a new type of regularity, appearing gradually as the "relaxation time distribution" becomes extremely broad. The universality is not a consequence of a diverging correlation length, as for a second-order phase transition, and there are no critical exponents. While Eq. (10) and the simulations are concerned with the free charge contribution to the conductivity only, it is easy to show\(^{23}\) that the dipolar contribution to the total conductivity is insignificant at low temperatures in the frequency range of interest. Thus, both prediction and simulations may be thought of as concerned with the total conductivity.

The observed universality reflects the fact that for \(T \to 0\) all energy distributions effectively tend to the uniform distribution so the conductance distribution be-
comes $P(g) \sim 1/g$. However, it is noteworthy that even at low temperatures there is a sharp cutoff in the “relaxation
time distribution.” This is due to the existence of a
percolation threshold.

The asymptotic behavior $\sigma \sim z$ found for $z \to \infty$ is a
subtle effect which is not directly due to the capacitors
[since the capacitor currents do not contribute to the
conductivity in Eq. (3)]. Indirectly, however, the capacitors
do give rise to the observed frequency dispersion via
their influence on the node potentials that in turn determine
the resistor currents.

The EMA equation (10) was first derived by Bryskin
for a model of noninteracting electrons tunneling between
positionally disordered sites; it has also been shown to
apply for a hopping model with a box-type distribution
of energy barriers. Hopping models are neither physically
nor mathematically equivalent to the macroscopic
approach taken here. But both types of models lead to
large sparse matrix equations expressing local current
conservation. In view of the present findings it seems
likely that, in the limit of severe disorder, the EMA for
any problem of this type leads to Eq. (10) for the
frequency-dependent conductivity (or diffusion constant).

An important and well-established experimental fact is
the Barton-Nakajima-Namikawa (BNN) relation, i.e.,
the rule that the characteristic frequency for onset of
ac conduction has the same activation energy as $\sigma(0)$. This
follows directly from Eqs. (9) and (10) [a reduced
frequency definition similar to Eq. (9) was used for hopping
models by Scher and Lax and by Sumnerfield]. It is easy to understand qualitatively why the BNN relation
is valid here. In the dc limit the current follows the
“critical” percolation paths giving the easiest ways between
the electrodes. As the frequency increases there is
little effect until, for $s \sim s_c$, $s$ is of order the lowest
conductivity $\sigma_{\text{min}}$ met on a critical path. On the other hand, the dc conductivity is also determined by $\sigma_{\text{min}}$, and
thus one expects $\sigma(0) \sim s_c$ which is the essence of the
BNN relation.

In three dimensions the EMA has the percolation
threshold somewhat wrong, so the predicted dc
conductivity activation energy is also wrong. However, Eq.
(10) may still be valid in three dimensions at low
temperatures. Sumnerfield has conjectured a “quasiuniversality” for the frequency dependence of the conductivity. This
idea fits nicely into the present work that predicts true
universality only in the zero temperature limit. Comparing
to experiments, it has been shown elsewhere that all
qualitative features of experiment follow the equation

$$\sigma = \bar{\sigma} / \ln(1 + \bar{\sigma})$$

(11)

Equation (11), which clearly is an approximate solution of
Eq. (10), represents the admittance of a single critical path. Both equations predict an approximate power-law
frequency dependence of the real part of the conduc-
tivity where the exponent at the real frequency $\bar{\omega} = -i \bar{z}$
is equal to $1 - 2/\ln(\bar{\omega})$. A few decades above the onset
of ac conduction, the exponent is predicted to be 0.8,
in agreement with most experiments. Thus, there are
certainly no experimental reasons to reject Eq. (10) as a low-
temperature limiting universal frequency dependence of
the conductivity in three dimensions.

Some time ago Pollak and Pike suggested that details of
the conduction mechanism should be contained in deviations from linear frequency dependence of the conductivity. While Eq. (10) approaches proportionality $\sigma \sim z$
for $z \to \infty$, there is a significant nontrivial frequency dependence in a very large frequency range. If the predicted
universality is indeed valid also in three dimen-
sions, there is little information in a conductivity that
follows Eq. (10). It seems therefore that experiments could
naturally be interpreted in terms of deviations from Eq. (10),
representing the low-temperature fix point, rather than in terms of deviations from linear frequency dependence.

The EMA assumes admittances that are uncorrelated
above the lattice spacing, the discretization length $a$. The
present results may be compared to recent simulations of
interacting charged particle hopping on a disordered lat-
tice, where it was found that the dispersive regime is due
to the blocking effect on very short distances. Possibly,
the length $a$ may be identified with this range of
length scales.

In conclusion, it has been shown that the EMA
predicts a universal frequency dependence of the conductivity
for disordered nonmetals at low temperatures. Simula-
tions in two dimensions have confirmed not only the
qualitative universality prediction, but the quantitative
EMA prediction as well. Finally, we note that since hopping
models often follow Eq. (10), one cannot distinguish,
from ac measurements alone, between these two
approaches to the modeling of ac conduction in disordered
solids.

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