Low temperature universality in computer simulations of the macroscopic model for ac conduction in disordered solids

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Abstract

A new method is presented for computer simulation of the macroscopic model for ac conduction, a model that considers Maxwell's equations for conduction in an inhomogeneous medium. The method iterates a small network. In this way, the overall admittance of the large RC-network, that one obtains by discretizing Maxwell's equations, is computed. Results are presented that confirm the universality prediction of the effective medium approximation in three dimensions. According to this prediction, all systems with a thermally activated local conductivity have the same frequency dependence of the conductivity, independent of the activation energy distribution.

1. Introduction

AC conduction in various types of disordered solids has been studied for many years. The studies in the 1950s were concerned with ionic conductive "classical" oxide glasses [1]. It was later found that the same ac features are seen in electronically conducting systems, such as amorphous semiconductors [2,3], polymers [4], doped single crystals of silicon at helium temperatures [5], or metal-cluster compounds [6]. The almost universally observed features of ac conduction in disordered solids are the following. At low frequencies the conductivity is constant. Around a characteristic frequency, ω_m, the conductivity starts to increase, following an approximate power-law, $\sim \omega^s$, where the exponent

s is between 0.7 and 1.0. This increase in conductivity continues up to phonon frequencies. A slight increase in s, if any, as the frequency increases is observed. As regards the temperature dependence of the conductivity, the dc conductivity is strongly temperature-dependent (usually thermally activited) while the ac conductivity depends less on temperature. Finally, one always observes the Barton–Namikawa–Nakajima (BNN) relation [7]. This relation implies that the dc conductivity has the same temperature dependence as the characteristic frequency, ω_m, for onset of ac conduction.

2. The macroscopic model for ac conduction

The standard model for ac conduction in disordered solids is the hopping model. This model considers a classical random walk of particles (electrons, polarons or ions) in a random environment.

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The transition rates for jumps between two sites are usually assumed to be thermally activated. In the case of hopping electrons there is in most cases an extra exponential tunneling factor. The hopping model assumes, in its simplest form, *non-interacting* particles. This assumption means that 'self-exclusion' is not taken into account (that there is only room for one particle at each site) nor is Coulomb repulsion between the charge carriers. These simplifications raise the question whether it is possible to have a more realistic model, while still retaining the simplicity of the non-interacting hopping model.

In recent work by one of us [8,9] a macroscopic approach to ac conduction in disordered solids was advocated. The model considered, below referred to as the macroscopic model, is not new, but in the past it has been studied mainly in regard to dc conduction and percolation. The macroscopic model assumes a spatially varying [frequency independent] conductivity, $g(r)$. The overall macroscopic conductivity becomes frequency-dependent, because charges gradually accumulate at the boundaries between conducting and less conducting regions, creating a time-dependent polarization. To calculate the frequency-dependence one refers directly to Maxwell's equations. This is how Coulomb interactions are taken into account in the macroscopic model (remember that Coulomb's law is contained in Gauss's law). When Maxwell's equations are discretized, one arrives at the electrical equivalent circuit shown in Fig. 1 [9]. The resistors have values that are given by the local resistivities, $1/g(r)$, while all capacitors are equal, having a value given by the [infinite-frequency] dielectric constant. The currents through the capacitors are the well-known displacement currents, while the resistor currents are the sought for free charge currents.

It is possible in this model to solve the relevant equations in the effective medium approximation (EMA). If one considers an admittance network in D dimensions with randomly distributed admittances, Y, the EMA predicts an effective average admittance, Y_m, given by [10]

$$\left\langle \frac{Y - Y_m}{Y + (D - 1)\, Y_m} \right\rangle = 0. \tag{1}$$

In Ref. [9] a detailed comparison was made between the EMA predictions for the network in Fig. 1 and computer simulations in 2 dimensions. It was assumed that the local conductivities are given by an activation energy randomly chosen according to some probability distribution. The overall admittance was then calculated by means of the Frank–Lobb algorithm [11]. There was an excellent agreement between the simulations and the EMA predictions. This agreement was observed even at low temperatures where the admittance distribution covers ~ 100 decades. Here, the EMA in the prevailing general opinion was *not* expected to do very well (because the EMA usually is derived from a weak disorder perturbation expansion). As the temperature goes to zero, the EMA predicts a frequency dependence of the conductivity that is independent of the activation energy probability distribution. In this limit one finds that, if $\tilde{\sigma} = \sigma/\sigma(0)$ and $\tilde{s} = i\tilde{\omega}$ with $\tilde{\omega}$ being a suitably scaled frequency, $\tilde{\sigma}$ is given as the solution [9] of

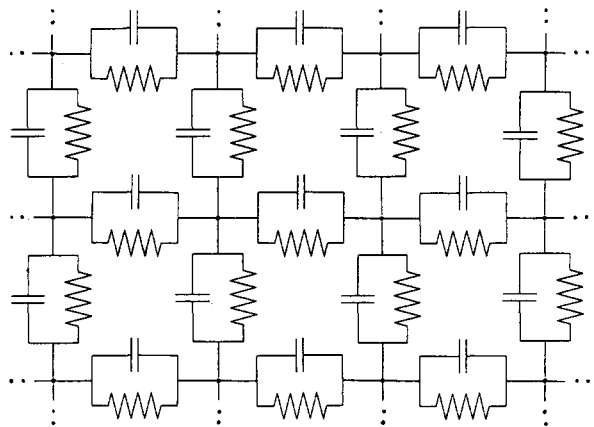$$\tilde{\sigma}\, \ln(\tilde{\sigma}) = \tilde{s}. \tag{2}$$

Fig. 1. Electrical equivalent circuit of Maxwell's equations for an inhomogeneous conductor, discretized in two dimensions. All capacitors are equal while the resistors vary, reflecting the spatially varying conductivity of the solid. The resistor currents are the free charge currents of interest here; the capacitor currents are the displacement currents [9]. Because of the Maxwell–Wagner effect (giving rise to a time-dependent polarization due to charge accumulation) the conductivity becomes frequency dependent.

As an illustration of this 'universality', Fig. 2 shows the results of computer simulations in two dimensions of several activation energy distributions at $\beta = 160$, where β is the inverse temperature in dimensionless units.

The universality qualitatively corresponds quite well to the conductivity observed in disordered solids. Thus, when Eq. (2) is converted into real frequencies it predicts an approximate power-law frequency dependence of the conductivity with an exponent given by $s = 1 - 2/\ln(\omega\tau)$ where τ is the characteristic time giving the onset of ac behaviour. A few decades above $\omega_m = 1/\tau$ this gives $s \cong 0.8$. As the temperature is decreased, the universal conductivity curve is displaced towards lower frequencies in the log–log plot. If one measures in a fixed frequency range, in effect one measures further and further out on the universal curve as the temperature is decreased. Therefore, the theory predicts that the exponent goes to one as the temperature goes to zero. This effect is observed in experiment.
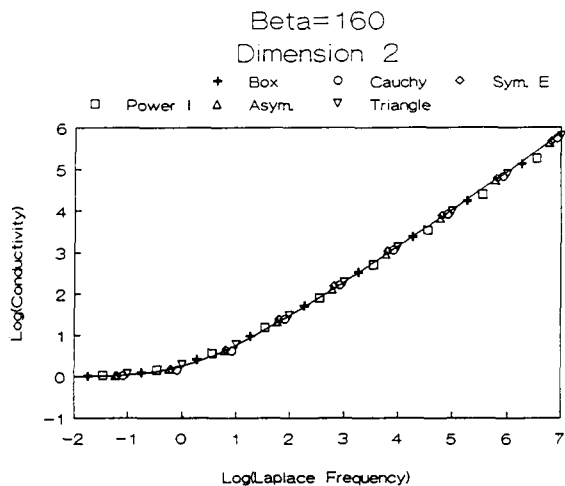

Fig. 2. Test in two dimensions of the EMA prediction (Eq. (2)) for the low temperature universal conductivity (full curve) in a log–log plot (base 10) at $\beta = 160$ (reproduced from Ref. [9]). The x-axis denotes the real dimensionless 'Laplace' frequency $\tilde{s} = i\tilde{\omega}$, corresponding to an imaginary frequency, while the y-axis is the normalized conductivity $\tilde{\sigma} = \sigma/\sigma(0)$. The symbols refer to various activation energy distributions. This figure was obtained by averaging 10 simulations of 200 × 200 lattices solved by using the Frank–Lobb algorithm.

3. A new recursive 'renormalization' method for simulations

Computer simulations of the model in three dimensions are difficult. In three dimensions there is no algorithm which is as efficient as the Frank–Lobb algorithm in 2-D. Furthermore, at low temperatures corresponding to β's of order 100 or more, large lattices are needed to average out the large conductance fluctuations of the model. Therefore the problem becomes extremely complicated; if for instance one wants to solve Kirchhoff's equations this corresponds to solving 10^6 or more sparse linear equations. Today an efficient algorithm is available for doing this, the algebraic multigrid algorithm (AMG) [9], but even with this algorithm it was difficult to obtain reliable answers in a reasonable computer time. This failure is because it is not only neccesary to solve a huge number of equations, but it is also neccesary to obtain the solution with an accuracy of very many digits. Some 3-D AMG simulations were presented in Ref. [9], but results were inconclusive. We have therefore developed an alternative method for dealing with the problem.

The method, which will be described in detail elsewhere [12], consists in *recursively iterating a small network*. The idea is inspired by earlier work by Stinchcombe and Sahimi and coworkers on real-space renormalization of random resistor networks [13,14]. Here, however, we adopt a phenomenological approach and do not refer to the renormalization group. Suppose one has a small RC-network; we used a $4 \times 4 \times 4$ network, with short-circuited end-faces. A phenomenological constant is multiplied to the calculated overall admittance so that equal admittances between all nodes produces the same overall $4 \times 4 \times 4$-network admittance. This trick makes it possible to avoid the total admittance running away upon iterating and thereby it becomes easier to identify the interesting frequency range [12]. But the trick means that one probably does not get a numerically accurate estimate of the conductivity. However, plots as Fig. 2 of the *relative* conductivity are still possible – and this is the focus of the present work. The network is iterated by replacing each admittance by the total admittance of a similar $4 \times 4 \times 4$ network, etc, to some depth – in the present case depth 4. At the

"lowest" level the network admittances are each a capacitor in parallel with a resistor determined by a randomly chosen activation energy. Finally, when the entire iterative calculation is finished, we subtract s, the capacitor contribution to the overall admittance. Thus, one is left with the free charge conductivity. In this way one 'simulates' a very large 3-dimensional lattice; the present case corresponding to a side length of almost 300.

In our simulations we found that it was neccesary to go to some depth (here 4) to obtain 'self-averaging'. This means that many calculations are necessary. The calculation of the admittance of each single 4 × 4 × 4 network is a non-trivial problem that must be solved in a short time and with great accuracy. One can always find the overall admittance of a network by removing nodes one by one; whenever a node is removed a number of new admittances are introduced. This process is sometimes referred to as the Fogelholm algorithm [15]; it utilizes the general star-mesh transformation well-known from electrical engineering [16]. To speed up the calculation of the 4 × 4 × 4-network admittance we wrote a *program* that generates Turbo Pascal code for doing this calculation,

a code which uses only simple array operations. In this way we eleminated the linked lists of neighbour points connected to a given admittance, that are present in the original Fogelholm algorithm. The generated Turbo Pascal code was then compiled and the compiled code is called by another program. The details of the method will be given elsewhere [12], but we note here that this way of solving the iteration speeds up the calculation by a factor of about one hundred compared to our first program that directly used the Fogelholm algorithm.

Typical results of the calculations are given in Fig. 3. This figure shows results for $\beta = 120$. The full curve is the prediction of Eq. (2). On the basis of Fig. 3 and other similar figures it is now possible to conclude that even in three dimensions the predicted universality is valid and well fitted by the EMA prediction.

4. Discussion

Does the universal EMA function fit experiment accurately? Certainly, experiments do not point to an exact universality at finite temperatures, but
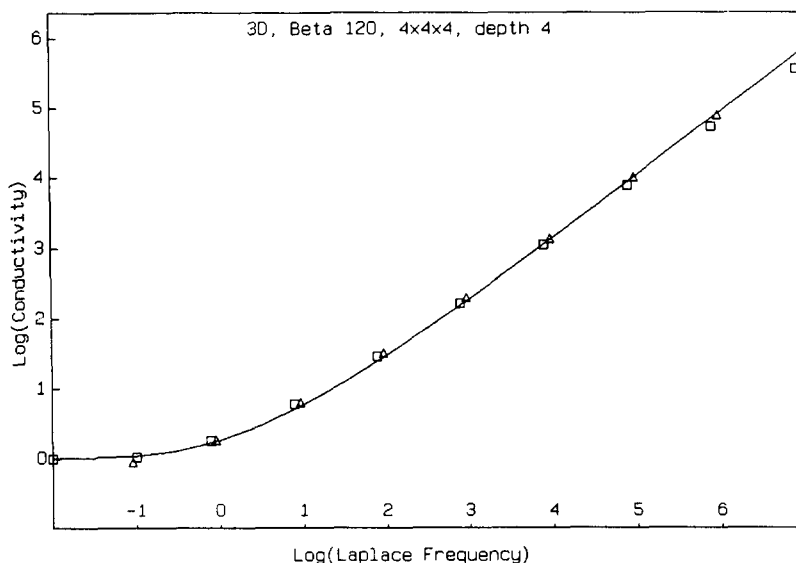

Fig. 3. Test in three dimensions of the EMA prediction (Eq. (2)) for the low temperature universal conductivity (full curve) at $\beta = 120$. The results were obtained by the new method presented here that iterates a 4 × 4 × 4 lattice to depth 4. At this level the system becomes self-averaging so it is not neccesary to average over several simulations. □ denotes results for the box distribution of energy barriers; △ denotes results for the triangle distribution (for details of the generation of these distributions, see Ref. [9]).

a comparison to a number of experiments [17] has shown that this function does capture all qualitative features and sometimes provides a quantitatively accurate fit. Below the loss peak, however, the universal EMA function becomes Debye-like (using now the dielectric language), which does not correspond well to experiment. In this region, which deserves further experimental investigations, the well-known 'long time tails' inherent in any random walk become important. This phenomenon goes beyond the EMA.

5. Conclusion

This paper has shown how to study the macroscopic model numerically by a new iterative method. The results give new and convincing evidence that the EMA universality is also valid in three dimensions.

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