

## Rapid Communications

*Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in Physical Review B should be no longer than four printed pages and must be accompanied by an abstract. Page proofs are sent to authors.*

### Universal ac conductivity of nonmetallic disordered solids at low temperatures

Jeppe C. Dyre

*Institute of Mathematics and Physics, Roskilde Universitetscenter, Postbox 260, DK-4000 Roskilde, Denmark*

(Received 11 January 1993)

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.<sup>1-8</sup> 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.<sup>9-13</sup> While hopping models are rather successful, the importance of Coulomb interactions has recently come into focus.<sup>14,15</sup> 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.<sup>16-20</sup> 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  $\phi$

$$\nabla \cdot [(i\omega\epsilon + g)\nabla\phi] = 0. \quad (1)$$

This equation is discretized<sup>21,22</sup> 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  $a$  is the lattice constant and  $D$  the dimension, the correct continuum limit is ensured if each link admittance  $y$  is given by

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

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<sup>23</sup> by

$$\sigma(\omega) = \frac{G(\omega)}{L^{D-2}} - i\omega\epsilon. \quad (3)$$

If the discretization length  $a$  is chosen to be the correlation length for  $E(\mathbf{r})$  and correlations beyond  $a$  are ignored,<sup>21,24</sup> the effective-medium approximation (EMA) may be applied to calculate  $G$ .<sup>16,21</sup> The EMA equation for the effective-link admittance,  $y_m$ , is  $\langle (y - y_m) / [y + (D-1)y_m] \rangle_y = 0$  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  $s \equiv i\omega\epsilon$ )

$$\frac{1}{D(\sigma + s)} = \left\langle \frac{1}{g(E) + (D-1)\sigma + Ds} \right\rangle_E. \quad (4)$$

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

$$E_g(s) = -\frac{1}{\beta} \ln \left[ \frac{(D-1)\sigma + Ds}{g_0} \right]. \quad (5)$$

If  $p(E)$  is the activation-energy probability distribution, Eq. (4) at low temperatures becomes

$$\frac{1}{D(\sigma+s)} = \frac{1}{(D-1)\sigma + Ds} \int_{E_g(s)}^{\infty} p(E) dE \quad (6)$$

or

$$\frac{D-1}{D} + \frac{s}{D(\sigma+s)} = \int_{E_g(s)}^{\infty} p(E) dE \quad (7)$$

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

$$\begin{aligned} \frac{s}{D(\sigma+s)} &= \int_{E_g(s)}^{E_g(0)} p(E) dE \\ &= p(E_g(0)) \frac{1}{\beta} \ln \left[ \frac{\sigma}{\sigma(0)} + \frac{D}{D-1} \frac{s}{\sigma(0)} \right]. \end{aligned} \quad (8)$$

Introducing the dimensionless variables

$$\bar{\sigma} = \frac{\sigma}{\sigma(0)}, \quad \bar{s} = \frac{\beta}{Dp(E_g(0))\sigma(0)} s, \quad (9)$$

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

$$\bar{\sigma} \ln(\bar{\sigma}) = \bar{s}. \quad (10)$$

Equation (10) was derived by Fishchuk for the uniform energy barrier distribution with cutoffs where the average in Eq. (4) can be calculated explicitly.<sup>20</sup> 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.<sup>25,26</sup> 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.<sup>27</sup> For simplicity the simulations were carried out for real  $\bar{s}$ ; 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<sup>23</sup> 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  $T \rightarrow 0$  all energy distributions effectively tend to the uniform distribution so the conductance distribution be-

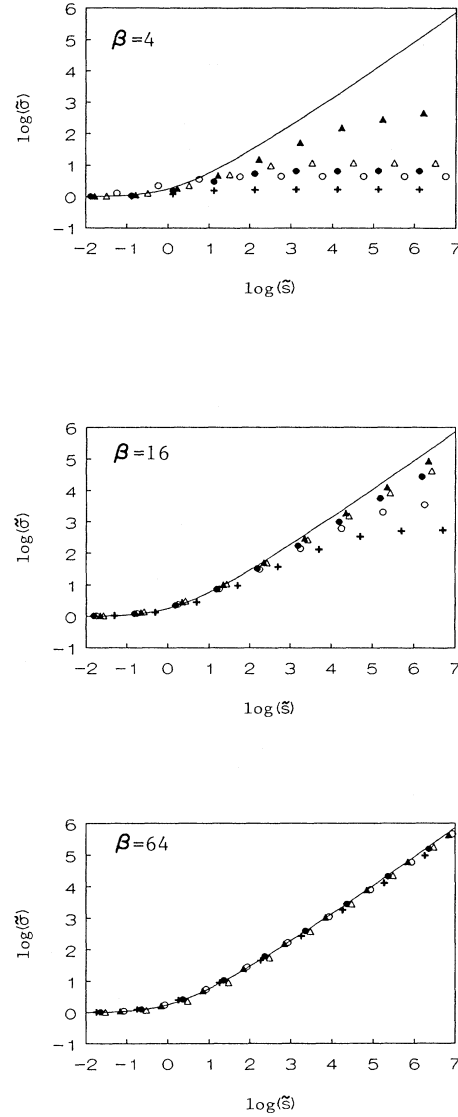


FIG. 1. Log-log plot (base 10) of the dimensionless conductivity  $\bar{\sigma}$  as function of the real dimensionless Laplace frequency  $\bar{s}$  [both quantities defined in Eq. (9)] at different temperatures. The full curve is the EMA prediction for the low-temperature limit of  $\bar{\sigma}(\bar{s})$  [Eq. (10)], while the symbols represent simulations in two dimensions for different activation energy probability distributions.  $\beta$  is the inverse dimensionless temperature. Each point represents the average of 20 simulations of a  $100 \times 100$  lattice. The total admittance was determined by the Frank-Lobb algorithm (Ref. 27) and  $\bar{\sigma}$  subsequently found from Eq. (3). Results are shown for the following activation energy probability distributions: ( $\blacktriangle$ ),  $p(E) = (1/\sqrt{2\pi})e^{-E^2/2}$  ( $-\infty < E < \infty$ ); ( $\bullet$ ),  $p(E) = \frac{1}{2}$  ( $-1 < E < 1$ ); ( $\triangle$ ),  $p(E) = (2/\pi)(1+E^2)^{-1}$  ( $0 < E < \infty$ ); ( $\circ$ ),  $p(E) = e^{-E}$  ( $0 < E < \infty$ ); (+),  $p(E) = 2E$  ( $0 < E < 1$ ). In each case the distribution should be thought of as centered around an energy  $E_0$ ; this gives an extra factor  $e^{-\beta E_0}$  to both conductivity and frequency without changing  $\bar{\sigma}$  or  $\bar{s}$ . The quantity  $E_g(0)$  in Eq. (9) is the dc conductivity activation energy [Eq. (5)] which is easily determined from the fact that the percolation threshold is  $\frac{1}{2}$  in two dimensions (Refs. 21, 23, 35, and 36).

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  $\sigma \sim \bar{\tau}$  found for  $\bar{\tau} \rightarrow \infty$  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 Bryksin for a model of noninteracting electrons tunneling between positionally disordered sites;<sup>28</sup> it has also been shown to apply for a hopping model with a box-type distribution of energy barriers.<sup>5</sup> 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,<sup>29-31</sup> i.e., the rule that the characteristic frequency for onset of ac conduction has the same activation energy as  $\sigma(0)$ .<sup>32</sup> 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<sup>33</sup> and by Summerfield<sup>34</sup>]. 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.<sup>35</sup> As the frequency increases there is little effect until, for  $s \sim s_c$ ,  $s$  is of order the lowest conductivity  $\sigma_{\min}$  met on a critical path. On the other hand, the dc conductivity is also determined by  $\sigma_{\min}$ ,<sup>35,36</sup> 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,<sup>21</sup> so the predicted dc conductivity activation energy is also wrong. However, Eq. (10) may still be valid in three dimensions at low temperatures. Summerfield has conjectured a "quasiuniversality" for the frequency dependence of the conductivity.<sup>34</sup> 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<sup>5</sup> that all qualitative features of experiment follow the equation

$$\bar{\sigma} = \bar{\tau} / \ln(1 + \bar{\tau}) . \quad (11)$$

Equation (11), which clearly is an approximate solution of Eq. (10), represents the admittance of a single critical path.<sup>23</sup> Both equations predict an approximate power-law frequency dependence of the real part of the conductivity where the exponent at the real frequency  $\bar{\omega} = -i\bar{\tau}$  is equal to  $1 - 2/\ln(\bar{\omega})$ .<sup>5,28</sup> 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.<sup>37</sup> While Eq. (10) approaches proportionality  $\bar{\sigma} \propto \bar{\tau}$  for  $\bar{\tau} \rightarrow \infty$ , there is a significant nontrivial frequency dependence in a very large frequency range. If the predicted universality is indeed valid also in three dimensions, 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 lattice, where it was found that the dispersive regime is due to the blocking effect on very short distances.<sup>15</sup> 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. Simulations 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.

The author wishes to thank N. B. Olsen and P. V. Christiansen for useful discussions and I. H. Petersen for technical assistance. This work was supported by the Danish Natural Science Research Council.

<sup>1</sup>A. E. Owen, *J. Non-Cryst. Solids* **25**, 372 (1977).

<sup>2</sup>A. Mansingh, *Bull. Mater. Sci. (India)* **2**, 325 (1980).

<sup>3</sup>A. K. Jonscher, *Dielectric Relaxation in Solids* (Chelsea Dielectric Press, London, 1983).

<sup>4</sup>M. D. Ingram, *Phys. Chem. Glasses* **28**, 215 (1987).

<sup>5</sup>J. C. Dyre, *J. Appl. Phys.* **64**, 2456 (1988).

<sup>6</sup>C. A. Angell, *Chem. Rev.* **90**, 523 (1990).

<sup>7</sup>S. R. Elliott, *Physics of Amorphous Materials*, 2nd ed. (Longman, London, 1990).

<sup>8</sup>M. P. J. van Staveren, H. B. Brom, and L. J. de Jongh, *Phys. Rep.* **208**, 1 (1991).

<sup>9</sup>M. Lax and T. Odagaki, in *Macroscopic Properties of Disordered Media*, edited by R. Burrigge (Springer, Berlin, 1982), p. 148.

<sup>10</sup>H. Böttger and V. V. Bryksin, *Hopping Conduction in Solids* (Akademie Verlag, Berlin, 1985).

<sup>11</sup>J. W. Haus and K. W. Kehr, *Phys. Rep.* **150**, 263 (1987).

<sup>12</sup>G. A. Niklasson, *J. Appl. Phys.* **62**, R1 (1987).

<sup>13</sup>J.-P. Bouchaud and A. Georges, *Phys. Rep.* **195**, 127 (1990).

- <sup>14</sup>J. O. Isard, *Philos. Mag. B* **62**, 139 (1990).
- <sup>15</sup>P. Maass, J. Petersen, A. Bunde, W. Dieterich, and H. E. Roman, *Phys. Rev. Lett.* **66**, 52 (1991).
- <sup>16</sup>R. Landauer, in *Electrical Transport and Optical Properties of Inhomogeneous Media*, edited by J. C. Garland and D. B. Tanner, AIP Conf. Proc. No. 40 (AIP, New York, 1978), p. 2.
- <sup>17</sup>A. H. Clark, *Thin Solid Films* **108**, 285 (1983).
- <sup>18</sup>T. Nagatani, *J. Appl. Phys.* **54**, 5132 (1983).
- <sup>19</sup>*Impedance Spectroscopy*, edited by J. R. Macdonald (Wiley, New York, 1987).
- <sup>20</sup>I. I. Fishchuk, *Phys. Status Solidi A* **93**, 675 (1986).
- <sup>21</sup>S. Kirkpatrick, *Rev. Mod. Phys.* **45**, 574 (1973).
- <sup>22</sup>I. Webman, J. Jortner, and M. H. Cohen, *Phys. Rev. B* **11**, 2885 (1975).
- <sup>23</sup>J. C. Dyre and T. Riedel (unpublished).
- <sup>24</sup>I. Webman, J. Jortner, and M. H. Cohen, *Phys. Rev. B* **15**, 5712 (1977).
- <sup>25</sup>J. Koplik, *J. Phys. C* **14**, 4821 (1981).
- <sup>26</sup>S. Tyc and B. I. Halperin, *Physica A* **157**, 210 (1989).
- <sup>27</sup>D. J. Frank and C. J. Lobb, *Phys. Rev. B* **37**, 302 (1988).
- <sup>28</sup>V. V. Bryksin, *Fiz. Tverd. Tela* **22**, 2441 (1980) [*Sov. Phys. Solid State* **22**, 1421 (1980)].
- <sup>29</sup>J. L. Barton, *Verres Réfr.* **20**, 328 (1966).
- <sup>30</sup>T. Nakajima, in *1971 Annual Report, Conference on Electric Insulation and Dielectric Phenomena* (National Academy of Sciences, Washington, DC, 1972), p. 168.
- <sup>31</sup>H. Namikawa, *J. Non-Cryst. Solids* **18**, 173 (1975).
- <sup>32</sup>J. C. Dyre, *J. Non-Cryst. Solids* **88**, 271 (1986).
- <sup>33</sup>H. Scher and M. Lax, *Phys. Rev. B* **7**, 4502 (1973).
- <sup>34</sup>S. Summerfield, *Philos. Mag. B* **52**, 9 (1985).
- <sup>35</sup>V. Ambegaokar, B. I. Halperin, and J. S. Langer, *Phys. Rev. B* **4**, 2612 (1971).
- <sup>36</sup>D. Berman, B. G. Orr, H. M. Jaeger, and A. M. Goldman, *Phys. Rev. B* **33**, 4301 (1986).
- <sup>37</sup>M. Pollak and G. E. Pike, *Phys. Rev. Lett.* **28**, 1449 (1972).