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Universality of AC conductivity: Random site-energy model with Fermi statistics

W. F. Pasveer, P. A. Bobbert,* and M. A. J. Michels
Group Polymer Physics, Eindhoven Polymer Laboratories and Dutch Polymer Institute, Technische Universiteit Eindhoven, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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The universality of the frequency-dependent (AC) conduction of many disordered solids in the extreme-disorder limit has been demonstrated experimentally. Theoretically, this universality has been established with different techniques and for various models. A popular model that has been extensively investigated and for which AC universality was established is the symmetric random-barrier model without Fermi statistics. However, for the more realistic model of random site-energies and Fermi statistics AC universality has never been rigorously established. In the present work we perform a numerical study of the latter model for a regular lattice in two dimensions. In addition, we allow for variable-range hopping. Our main conclusion is that AC universality appears to hold for this realistic model. The obtained master curve for the conductivity and the one obtained for the random-barrier model in two dimensions appear to be the same.

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I. INTRODUCTION

For a large class of different disordered solids data on the frequency-dependent conductivity exhibit remarkable similarities.1 The real part \( \sigma'(\omega) \) of the complex conductivity \( \sigma(\omega) = \sigma'(\omega) + i\sigma''(\omega) \) is found to be constant below a critical frequency \( \omega_c \), \( \sigma'(\omega) = \sigma(0) = \sigma_{DC} \) for \( \omega < \omega_c \), while for \( \omega > \omega_c \), \( \sigma'(\omega) \) increases monotonously with \( \omega \) until typical phonon frequencies \( \omega_0 \approx 10^{12} \text{s}^{-1} \), above which vibrational contributions become dominant. Throughout this paper we will denote \( \sigma'(0) = \sigma_{DC} = \sigma(0) \). For frequencies far above \( \omega_c \), \( \sigma'(\omega) \) exhibits an approximate power-law behavior \( \sigma'(\omega) \sim \omega^n \), with \( n < 1 \). A more detailed analysis shows a weak temperature and frequency dependence for \( n \).

The critical frequency \( \omega_c \) after which the AC conduction starts to rise can be identified as the frequency of the dielectric-loss peak, which shows up if we plot \( \sigma''(\omega) - \sigma(0)/\omega \) vs \( \omega \). This frequency \( \omega_c \), the dielectric-loss strength \( \Delta e = e(\omega = 0) - e(\omega = \infty) = -\epsilon_0^1 \lim_{\omega \to 0} \sigma''(\omega)/\omega \), and the DC conductivity \( \sigma(0) \) are connected by a relation found by Barton, Nakajima, and Namikawa (Refs. 2–4):

\[
\sigma(0) = p \Delta e \epsilon_0 \omega_c, \tag{1}
\]

where \( \epsilon_0 \) is the permittivity of vacuum and \( p \) a material-dependent constant of order unity. We will refer to this relation as the BNN relation.

At low temperatures the disorder becomes more and more important, and we enter the “extreme-disorder limit.” At such temperatures it turns out to be usually possible to construct a master curve, consisting of the scaled AC conductivity \( \Sigma(\omega) = \sigma(\omega)/\sigma(0) \) as a function of a scaled frequency \( \Omega = \omega/\omega_c \). The fact that the shape of this master curve does not depend on temperature anymore means that the AC conductivity obeys the “time-temperature superposition principle.”\(^5\) Furthermore, this master curve appears not to depend on the specific disordered system considered, hence the name “AC universality.”

The construction of a master curve has been discussed quite extensively in literature\(^6–11\) and basically starts from the following expression, which is often called the Taylor-Ilsard scaling relation (Refs. 12 and 13):

\[
\Sigma(\omega) = F \left( \frac{\omega}{\sigma(0)} \right), \tag{2}
\]

with \( F \) a universal function. From the above definition of the scaled frequency \( \Omega \) it follows that Taylor-Ilsard scaling implies \( \omega_\text{ph} = \sigma(0)/C \). Via the BNN relation Eq. (1), which relates \( \omega_c \) and \( \sigma(0) \), the constant \( C \) can be identified: \( C = p \Delta e \epsilon_0 \). The first proof of the BNN relation was given by Sidebottom.\(^14\) He supported his arguments by considering the hopping motion within a Debye model for the rotation of permanent dipoles. Later, the relation \( C = \Delta e \epsilon_0 \) was proven mathematically by Schröder and Dyre.\(^15\) However, the relevance of the small-frequency Taylor expansion to the scaling properties was questioned by Dieterich and Maass.\(^16\) That the issue about how to scale correctly is a subtle one is clear from literature. Sometimes it is found that \( \Omega \propto \omega/\sigma(0) \)\(^17–19\) drastically increases the quality of the scaling curve as compared to \( \Omega \propto \omega/\sigma(0) \).\(^6,8\) The latter finding, \( \Omega \propto \omega/\sigma(0) T \), can be interpreted as a manifestation of the “Curie law” with \( C = \Delta e \sim 1/T \).\(^1\) However, it has been shown that \( \Delta e \) can decrease with temperature much more rapidly than \( 1/T \).\(^20\)

In order to describe the frequency-dependent conductivity with quantitative models, the processes governing the response to an AC field are, in literature, distinguished in three different frequency regimes (Ref. 21): Regime I is the high-frequency pair-hopping regime, \( \omega_0 < \omega < \omega_{ph} \) where conduction is between isolated pairs of sites. Regime II is the multiple-hopping regime, \( \omega_s < \omega < \omega_0 \) conduction occurs in isolated clusters of sites. Regime III is the low-frequency regime, approaching DC, \( 0 < \omega < \omega_s \); conduction takes place in large clusters consisting of up to an infinite amount of sites.

The crossovers between these three regimes are gradual. The reason why it is possible to distinguish these three different regimes is the following. By considering frequencies \( \omega > \omega_0 \) such that only hopping between pairs of isolated sites
needs to be considered, one immediately arrives at the so-called pair-hopping approximation. This approximation logically breaks down if the transition rates are such that a charge carrier can hop across more than two sites during a period of the applied field, which happens at lower frequencies. This defines the frequency $\omega_0$. For frequencies $\omega < \omega_0$, a carrier can make multiple hops, which explains the name of this so-called multiple-hopping regime. Finally, if the frequency is so low that hopping on basically infinite clusters starts to occur regime I is encountered.

The first who developed a theory to deal with the frequency-dependent conductivity using the pair-hopping approximation were Pollak and Geballe in 1961.\textsuperscript{22} In their approach they assumed thermally activated hopping between pairs of sites with a random distribution of pair spacings to describe impurity conduction at high temperatures. As a result they found a frequency-dependent conductivity independent of temperature. Later (1969), Austin and Mott\textsuperscript{23,24} addressed the same approximation, but they considered variable-range hopping between sites, with energy differences of the order of $kT$ or less from the Fermi energy. The equation derived by these authors predicts the slope $n$ in a double-logarithmic plot of conductivity vs frequency to be a decreasing function of frequency. However, as pointed out first by Jonscher in 1977,\textsuperscript{25} the slope tends to increase with increasing frequency if monitored from the onset $\omega_0$ till the frequency $\omega_0$. Because such an increasing slope as a function of frequency cannot be understood within the pair-hopping approximation, another theory, valid for frequencies $\omega_s < \omega < \omega_0$, a “multiple hopping” theory, is required. In this regime $n$ is known to develop with temperature as $1-n \propto (T/T_0)^{1/(d+1)}$ (Refs. 21 and 26), where $d$ is the dimensionality of the system (without variable-range hopping one can formally put $d=0$ in this equation). Such a behavior of $n$ is a direct consequence of the Taylor-Isard scaling relation Eq. (2) and the fact that for variable-range hopping $\sigma(0)$ is proportional to $\exp[-(T/T_0)^{1/(d+1)}]$, apart from an algebraic dependence on temperature.\textsuperscript{27} Assuming that $F(x) \propto x^n$ for large argument $x$ of the universal function in Eq. (2) we have

$$\sigma(\beta,\omega) \propto \sigma(\beta,0) \left( \frac{\omega}{\sigma(\beta,0)} \right)^n \propto \left[ \sigma(\beta,0) \right]^{1-n} \omega^n \propto \exp[-(1-n)(T_0/T)^{1/(d+1)}] \omega^n,$$

with $\beta = 1/kT$ and $k$ Boltzmann’s constant. Since for finite frequency $\sigma(\beta,\omega)$ should be finite if $T \to 0$, we find $1-n \propto (T/T_0)^{1/(d+1)}$ (excluding the trivial solution $n=1$).

In the low-frequency regime the conductivity shows a flattening, which at first appearance might look uninteresting. Nevertheless, it is in this regime where differences between theoretical predictions from effective-medium theories by Ganter and Schirrmacher,\textsuperscript{28} $\sigma(\omega) = \sigma(0)(1 + \Omega^{d/2})$, and from percolation-based theories by Hunt,\textsuperscript{29} $\sigma(\omega) = \sigma(0)(1 + 1/\Omega^{d-1/2} + (l'/l)^{d} \Omega^{d/2})$ appear, where $l$ is the separation of critical resistances and $l'$ the correlation length of the percolation cluster (which only slightly differ). In this regime there is the ongoing discussion about the issue whether the conductivity should have the term with the power $(d-1)/2$, as predicted by the latter theory, or not.\textsuperscript{21}

To study the above-mentioned dependencies and especially the discussion about the universal behavior of the AC conductivity, computer simulations have been carried out in the past, of which we mention in particular those by Dyre and Schröder.\textsuperscript{1,15} They have investigated the AC conductivity for a model with only energy disorder and symmetric transition rates, the so-called symmetric hopping model or random-barrier model. These authors studied the low-temperature limit, which is equivalent to the extreme-disorder limit. Their results clearly point to the existence of a universal master curve.\textsuperscript{15} However, it would be more realistic to take into account the Pauli exclusion principle for the charge carriers, and to allow the carriers to hop over variable distances and with asymmetric transition rates, instead of considering only nearest-neighbor hopping with symmetric transition rates. In Fig. 1 we have drawn a schematic picture indicating the differences between the random-barrier model and the site-energy disorder model. A logical question is then: does a model with asymmetric transition rates and Fermi statistics also show AC universality? First attempts toward treating this more realistic model have been made by Baranovskii and Cordes, and Porto et al., who included Fermi statistics and site-energy disorder, but at relatively high temperatures and taking nearest-neighbor hopping only.\textsuperscript{30,31} Within effective-medium theory, the site-energy disorder model with Fermi statistics and nearest-neighbor hopping has been treated by Maas, Rinn, and Schirrmacher.\textsuperscript{32,33} Another question is: how does this AC master curve (if it exists) compare with the one obtained for the symmetric hopping model? These two open questions\textsuperscript{1,34} are the main focus of this work.

The present work is a numerical study of AC universality for the more realistic model of Fig. 1(b). We will examine the case of a two-dimensional system, because calculations for a three-dimensional system turned out to be unfeasible computationally. A drawback of studying a two-dimensional system is that the knowledge about two-dimensional systems is not as large as that about three-dimensional systems. In particular, the scaling properties of two-dimensional systems have not been analyzed.\textsuperscript{35} However, by comparing our results with a numerical study of the two-dimensional symmetric hopping model\textsuperscript{36} we can still draw very useful conclusions. We want to make the important remark that, although
the discussion about AC universality has been stimulated very much by (nearest-neighbor) ionic conduction in disordered solids, we focus here on electronic conduction, for which variable-range hopping is important at low temperatures.

II. NUMERICAL APPROACH

The incoherent motion of noninteracting charge carriers on a lattice of sites can be described by the Pauli master equation:

$$\frac{\partial n_i}{\partial t} = -\sum_{j \neq i} [W_{ij} n_j(1 - n_j) - W_{ji} n_i(1 - n_i)],$$

(4)

where $n_i$ is the occupational probability of site $i$ with position vector $\mathbf{R}_i$ and energy $e_i$, and $W_{ij}$ is the transition rate for hops from site $i$ to $j$. The factors $1 - n_i$ account, in a mean-field approximation, for the fact that only one carrier can occupy a site (implying Fermi statistics). For the case of interest, $W_{ij}$ is suggested by Miller and Abrahams as

$$W_{ij} = \begin{cases} v_0 \exp[-2\alpha R_{ij} - \beta (e_j - e_i)], & e_j > e_i, \\ v_0 \exp[-2\alpha R_{ij}], & e_j < e_i. \end{cases}$$

Here $v_0$ is an intrinsic rate and $e_i - e_j$ includes a contribution $-e \mathbf{E} \cdot \mathbf{R}_{ij}$ from an external time-dependent electrical field $\mathbf{E} = \hat{x} E_0 \exp(i\omega t)$, which we apply in the $x$ direction; $\mathbf{E}$ is the particle charge and $\alpha$ is the inverse decay length of the wave functions of the localized states involved in the hopping. In the above-stated form the master equation is nonlinear and thus difficult to handle. However, upon linearization in the electric field and the change in the occupational probabilities $n_i' = (n_i - n_i^0)\exp(-i\omega t)$, with $n_i^0$ the equilibrium Fermi-Dirac distribution, one arrives at the following equation:

$$\sum_{j \neq i} [W_{ij}^0(1 - n_j^0) + W_{ji}^0 n_j^0] n_i' = \sum_{j \neq i} [W_{ij}^0(1 - n_j^0) + W_{ji}^0 n_j^0] + i\omega n_i^0 = \sum_{j \neq i} [W_{ij}^0 n_j^0(1 - n_j^0) - W_{ji}^0 n_j^0(1 - n_j^0)],$$

(6)

where $W_{ij}^0 \exp(i\omega t)$ is the change in the transition rate to first order in the applied field. In our numerical calculations, we first generate randomly distributed energies $e_i$ on each site of a two-dimensional square array of lattice constant $R_0$ and size $N = L^2$, by sampling from an interval $-\epsilon_0/2 < e_i < \epsilon_0/2$, with $\epsilon_0/2 = (2R_0^2 e^\epsilon)^{-1}$, $\epsilon$ being the density of states (DOS). Charges are introduced by setting the chemical potential in the Fermi-Dirac distribution equal to zero. This means that our DOS is always half-filled, independent of the temperature. For comparison, we also consider the case of a Gaussian DOS where we sample from a normalized Gaussian distribution with a width $\sigma$ and introduce charges by setting the chemical potential equal to a desired value. We perform our simulations on a $200 \times 200$ array. We use periodic boundary conditions, taking a “circular” electric field in the $x$ direction. We choose $\alpha = 3.5/R_0$. For this value of $\alpha$ and for the temperatures we have considered, it is sufficient to take into account hopping to 624 neighbors in a square area of $25 \times 25$ sites around a central site. We solve Eq. (6) for $n_i'$ with standard matrix routines, after which the total current and the frequency-dependent conductivity can be straightforwardly determined. We apply an averaging over different realizations of the disorder such that the error bars are always smaller than or equal to the symbol size in the figures presented in the next section. In recent work we studied the DC conductivity of the present model. We checked that the AC conductivity in the limit $\omega \rightarrow 0$ agrees with the DC conductivity found in that work. For very low temperatures we could not always reach the DC limit, because of numerical instabilities. For these cases we calculated the DC limit from an extrapolation of the higher-temperature data.

The use of the master equation (4) is the standard way in literature to consider hopping transport in disordered solids (see, e.g., Ref. 27). However, an important question is whether the mean-field approximation inherent to the master equation properly takes into account the Pauli exclusion principle, since correlations between the occupational probabilities of different sites are neglected. For the situation of a Gaussian DOS we recently calculated the DC charge-carrier mobility as a function of charge-carrier density with the same master equation. More recently, we considered the validity of the mean-field approximation in this context by taking into account the correlations between nearest-neighbor pairs. We found that these correlations suppress the mean-field mobility by only a few percent, even at charge-carrier concentrations of 0.5 per site, which is the situation considered here. We expect that this result also gives an indication for the (un)importance of correlations for the present case of AC transport in a constant DOS.

III. RESULTS

In the numerical results shown in this section we have taken units such that $e = R_0 = \nu_0 = \epsilon_0 = 1$ for the particle charge $e$, the lattice constant $R_0$, the intrinsic rate $\nu_0$, and the width of the DOS $\epsilon_0$ ($\epsilon_0$ should not be confused with the vacuum permittivity $\epsilon_0$). In particular, this implies the redefinition $\beta = \epsilon_0/kT$. In Fig. 2 we give a typical example of the “raw” data for the real part of the AC conductivity as a function of frequency for different temperatures in the case of a constant
The overall behavior of $\sigma'(\omega)$ compares fairly well with the universal trend as found in experiments. There is a crossover from $\sigma'(\omega) \approx \sigma(0)$ to a regime where $\sigma'(\omega)$ increases monotonously as a function of frequency, showing an approximate power-law behavior with power $n$. One can clearly see that $n$ is a function of temperature. In the case of two-dimensional variable-range hopping a temperature dependence of $n$ of the form $1-n \approx \beta^{-1/3}$ should develop, if a fixed frequency range is considered [see Eq. (3)]. In Fig. 3 we check this, and it is seen to be well obeyed. In the inset we show an extrapolation to zero temperature, which is compatible with $n$ approaching 1 in the $T=0$ limit.\(^1\)

The influence of finite-size effects was checked by considering the result for the case $\beta=350$ and $\omega=10^{-14}$ in Fig. 2. For this case these effects are expected to have the largest influence. We checked that reducing the square area within which we allow hopping from $25 \times 25$ to $21 \times 21$ sites changes the result for the conductivity by only 0.2%. Averaging over 50 different disorder configurations, we checked that reducing the system size from $200 \times 200$ to $150 \times 150$ or $100 \times 100$ sites leads to the same results within the error bar of about 20%. We can therefore say that the error bar due to finite-size effects is smaller than the symbol size in Fig. 2.

As mentioned in the Introduction, there has been a debate in literature about how to scale the frequency in order to find the proper master curve. Sometimes it is said that $\Omega \approx \omega/\sigma(0)$ gives better results,\(^17-19\) but in other cases $\Omega \approx \omega/\sigma(0)T$ does.\(^5,8\) We show in Fig. 4 the effect of scaling the frequency with $\sigma(0)$ only. The result is unambiguous: we do not find a proper master curve. It is also evident, however, that in order to obtain a common onset of the AC conductivity a further scaling of the horizontal axis is needed.

We will now discuss how we obtain a better scaling. We use the method discussed in Ref. 41 to obtain $\omega_r$; $\omega_r$ is chosen to be the characteristic frequency defined by $\log_{10}(\sigma(\omega_r)/\sigma(0))=0.5$ (the value 0.5 is somewhat arbitrary). In Fig. 5 we show the results for both the real and imaginary part of the scaled conductivity $\Sigma'$ and $\Sigma''$ at low temperatures, obtained with this definition of $\omega_r$. The results suggest that both the real and imaginary part of the conductivity approach a master curve. Regarding the imaginary part, this demonstrates that the BNN relation Eq. (1) is indeed obeyed. For comparison, we have also included the real part of the scaled conductivity for the case of Gaussian disorder, with $\sigma/kT=9$ ($\sigma$ is the width of the Gaussian) and the chemical potential at $-2\sigma$. The fact that the data fall on the same curve (for not too high frequencies) demonstrates the existence of real universality, since the master curves for different types of onsite energy disorder are apparently the same. This indicates that the mean carrier concentration does not appear to play an important role in this context, since this concentration is 0.023 per site for this case, whereas it is 0.5 per site for the half-filled square-shaped DOS. The inset in Fig. 5(a) shows the dependence of $\omega_0$ on temperature: $\omega_0$ is proportional to $\sigma(0)$ times a power-law dependence on temperature with a power close to two. In terms of the dependence of the dielectric-loss strength $\Delta \epsilon$ on temperature (see the Introduction) this is in agreement with the finding that $\Delta \epsilon$ can have a stronger dependence on temperature than $1/T$.\(^20,41\)

A very sensitive way to study the slopes of the curves is by plotting $n=d\log_{10}(\Sigma')/d\log_{10}(\Omega)$ as a function of $\Sigma'$. The result is shown in Fig. 6. Again we see a tendency to universal behavior when lowering the temperature. Some structure develops at low temperatures and large values of $\Sigma'$. This structure can be attributed to the crossover to resonant pair hopping and is caused by the discreteness of our system. The two different peaks that develop can be traced back to resonant pair hopping between nearest and next-nearest neighbors. Probably, more structure would be observed if we could reach even lower temperatures in our simulations.

We will now address the interesting issue of how the concept of universality enters in the very-low frequency regime. To get a better view of the behavior of $\Sigma(\Omega)$ at low frequencies, we plot $(\sigma'(\omega)-\sigma(0))/\sigma(0)$ as a function of $\Omega$ in Fig. 7. The universality is seen to hold very well at low frequencies. A recent derivation for the conductivity based on effective-medium theory\(^28\) leads to a low frequency behavior of the form $\Omega^{d/2}$. Figure 7 shows that this is fully in agreement with our findings for $d=2$. We also conclude that we do not appear to find any dependence of the form $\Omega^{(d-1)/2}$ as
predicted by percolation-based theories. On the other hand, such a dependence would not be easily observable in systems with variable-range hopping, since it would require very low frequencies.

IV. COMPARISON WITH THE SYMMETRIC HOPPING MODEL

Nowadays, one of the standard works about AC universality is that of Schröder and Dyre. These authors performed computer simulations of the AC conductivity for a random-barrier model and demonstrated AC universality for this model in $d=3$ and $d=2$. We now focus on the question whether the random-barrier model and our more realistic model have the same AC master curve. We can only make a comparison for $d=2$, but it is reasonable to assume that the conclusions reached for $d=2$ can be transferred to $d=3$. In Fig. 8 we show the comparison. The AC conductivity results for the two-dimensional simulations of a random-barrier model are taken from Ref. 36.

It is found that in the regime up to $\omega/\omega_c \approx 10^5$ the agreement is very good for the lowest temperature that we could reach. For higher frequencies the correspondence becomes worse: our curve has a smaller slope. However, from the extrapolation shown in Fig. 3 we see that for lower temperatures our slope would be larger. This means that also at high frequencies we tend to retrieve the same universal curve as found for the random-barrier model. There is also a theoretical reason to expect that the universal curves for the random-barrier model and the present model should be the same. Very recently, we studied the structure and conductivity of clusters generated by variable-range hopping percolation, for basically the same model as the present one. The main conclusion from that work is that the structure of the percolation clusters of the present model is the same as that following from “ordinary percolation,” such as obtained with the random-barrier model.
It is an experimental finding, reproduced by simulations for the random-barrier model, that the AC conductivity in two dimensions is very similar to that in three dimensions, with a slightly smaller frequency dependence in two dimensions than in three. In Ref. 15 a comparison is made between a three-dimensional master curve obtained for the random-barrier model and experiments, showing a good correspondence. Given the good agreement between the master curve of this model and our more realistic model, it can therefore be expected that simulations for our model in three dimensions would also be in agreement with the experiment.

V. CONCLUSIONS

We have numerically investigated the existence of scaling for the AC conductivity of a model with variable-range hopping on a two-dimensional regular lattice with random site energies and Fermi statistics, leading to asymmetric hopping rates. A clear trend toward a universal AC conductivity master curve is observed in the extreme-disorder limit at low temperatures. The master curve of this model appears to be the same as that of the less realistic random-barrier model with symmetric hopping rates. At low frequencies we find a frequency dependence in agreement with predictions from effective-medium theory. At the frequencies and temperatures studied we do not find a term in the frequency dependence that was predicted from percolation theory.

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