

The random free-energy barrier model for ac conduction in disordered solids

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A brief review of the history of ac ionic and electronic conduction in disordered solids is given, followed by a detailed discussion of the simplest possible realistic model: the random free-energy barrier model. This model assumes conduction takes place by hopping, where the hopping charge carriers are subject to spatially randomly varying energy barriers. The model is solved in the continuous time random walk and in the effective medium approximation, and it is shown that the two solutions are almost indistinguishable. In the random free-energy barrier model, the frequency-dependent conductivity is completely determined by the dc conductivity and the dielectric loss strength. The model correctly predicts all qualitative features of ac conduction in disordered solids, and a comparison to experiment on a large number of solids shows that the model is also quantitatively satisfactory.

I. INTRODUCTION

One of the most characteristic properties of electrical conduction in disordered solids is a strong dispersion of the conductivity. At low frequencies one observes a constant conductivity while at higher frequencies the conductivity becomes strongly frequency dependent, varying approximately as a power of the frequency. The increase in conductivity usually continues up to phonon frequencies. This behavior is seen in a wide variety of nonmetallic disordered solids and has been studied extensively during the last 30 years. The classes of disordered solids investigated include amorphous semiconductors,^{1-5,7,5} ionic conductive glasses,⁶⁻⁹ ionic or electronic conducting polymers,^{4,10,11} organic semiconductors,¹² nonstoichiometric or highly defective crystals,¹³ or doped semiconductor single crystals at helium temperatures.¹⁴ Even highly viscous liquids behave as typical disordered solids as regards ac ionic conductivity.

All disordered solids show similar behavior with respect to their ac properties. This is true not only for the frequency dependence of the conductivity but also for the temperature dependence. Here one observes a strongly temperature-dependent (usually Arrhenius) dc conductivity, while the ac conductivity depends much less on temperature and becomes almost temperature independent as $T \rightarrow 0$. This uniform behavior of $\sigma(\omega, T)$ for quite different solids has been pointed out a number of years ago,^{2,3,5,15} but is still not generally appreciated. And indeed, the fact that ionic and electronic conducting solids show similar behavior is quite surprising. Apparently, it means that we cannot expect to learn much about details of the conduction mechanism from measuring the frequency or temperature dependence of the conductivity.

As witnessed by the large number of publications and the continued interest in the field, ac conduction in disordered solids is a subject of interest on its own. More often, however, the focus is on dc transport only. Even then, a proper understanding of ac conduction is important in order to arrive at a correct picture of the dc transport. This is because dc and ac conduction are both due to the same mecha-

nism, as shown in Sec. II. In particular, this implies that a new interpretation of the dc conductivity activation energy is necessary. The dc conductivity activation energy is, it turns out, the *maximum* of a whole range of activation energies needed to account for the frequency dispersion (Sec. IV). We believe this fact is important for a genuine understanding of dc transport in disordered solids. It implies that most present models for dc conduction, thermopower, Hall effect, etc., in disordered solids, are probably too simple to be realistic.

The simplest and indeed the most common explanation for a conductivity which increases with frequency is the existence of one or the other kind of inhomogeneities in the solid. This assumption is consistent with the fact that a strong frequency dispersion of the conductivity is observed only in disordered solids. The inhomogeneities may be of a microscopic or a more macroscopic nature, a question which is not yet settled. In this paper, hopping models will be discussed. In hopping models one makes the assumption of inhomogeneity on the atomic scale by assuming randomly varying jump frequencies for the charge carriers. It is the purpose of the paper to show that a simple hopping model is able to give a qualitatively correct picture of ac conduction in disordered solids. By taking some care in deriving the model, it is hoped that the paper may contribute to make hopping models more popular among experimentalists. The paper, which summarizes, clarifies, and extends recent work by the author,¹⁶⁻¹⁹ has the following outline: Sec. II briefly reviews the history of ac conduction in disordered solids. In Sec. III a general discussion of hopping models is given. It is argued that in order to arrive at realistic hopping models, any effect of a cutoff at large jump frequencies should be eliminated. In Sec. IV we discuss what is probably the simplest possible model consistent with observations, a model based on the assumption of randomly varying free-energy barriers for jumps. The model is solved in the continuous time random walk approximation and in the effective-medium approximation, and it is shown that the two solutions are almost identical. Also, the model is compared to experiments on a number of quite different disordered solids. Finally, in Sec. V a discussion is given.

II. ac CONDUCTION IN DISORDERED SOLIDS: A BRIEF REVIEW

Frequency-dependent conduction in disordered solids is a very broad field and probably nobody has a full general view of it. Different schools have emerged within the field. Though using different terminology, these schools discuss quite similar experimental facts. In reviewing the field, however, it is convenient to ignore this and follow the terminology of the different schools.

Historically one can distinguish two schools depending on the preferred way of presenting data.⁵ The "dielectric" school uses the dielectric constant, $\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$, while the "semiconductor" school prefers to speak about the conductivity, $\sigma(\omega) = \sigma'(\omega) + i\sigma''(\omega)$. These two quantities are related by

$$\epsilon_0\epsilon(\omega) = [\sigma(\omega) - \sigma(0)]/i\omega, \quad (1)$$

where ϵ_0 is the vacuum permittivity. More recently it has become popular, in particular in the field of ionic conduction, to present data in terms of the electric modulus, $M(\omega) = M'(\omega) + iM''(\omega)$, defined²⁰ by

$$M(\omega) = i\omega/\sigma(\omega). \quad (2)$$

The use of $M(\omega)$ has the advantage that there is no contribution to $M''(\omega)$ from electrode capacitances. Also, it is not necessary as in Eq. (1) to subtract $\sigma(0)$ from $\sigma(\omega)$ in order to get peaks in the imaginary part ("loss peaks"). Finally, the impedance, $Z(\omega) = Z'(\omega) - iZ''(\omega)$, is sometimes used for presenting data, usually plotted in a so-called complex impedance diagram where $x = Z'(\omega)$ and $y = Z''(\omega)$.⁷

The first systematic studies of ac conduction in disordered solids were carried out by workers within the dielectric school about 30 years ago. The systems considered were ionic conductive oxide glasses.^{6,21} These solids were studied much because of technological interest; an understanding of the dielectric loss in glass as a function of frequency and temperature became important for the electric industry in the 1950s when one started to construct large transmitting valves, x-ray tubes, and similar products.²² Since dielectric loss in liquids had already been studied for many years, it was natural to report observations in terms of the dielectric loss. In glasses, however, it is necessary to subtract the non-zero dc conductivity in order to get proper dielectric loss peaks [Eq. (1)]. This was done without further justification, although it was soon discovered that there is a close correlation between dc conduction and dielectric loss.²³

The main features of dielectric loss in ionic conductive glasses, as established by the end of the 1950s,^{6,21,23,24} are (1) very broad dielectric loss peaks with a temperature-independent shape and an almost frequency-independent loss at high frequencies, and (2) an Arrhenius temperature-dependent dielectric loss peak frequency ω_m with the same activation energy as the dc conductivity. Point (2) means that ω_m and $\sigma(0)$ are proportional. As pointed out by Isard, the constant of proportionality is almost universal, varying only weakly with temperature and glass composition.²⁴ A closer analysis of the proportionality was carried out by Barton, Nakajima, and Namikawa²⁵⁻²⁷ who found the following equation to be valid for most glasses:

$$\sigma(0) = p\Delta\epsilon\epsilon_0\omega_m. \quad (3)$$

Here $\Delta\epsilon$ is the dielectric loss strength, i.e., $\Delta\epsilon = \epsilon(0) - \epsilon(\infty)$, and p is a temperature-independent numerical constant close to one. At ordinary temperatures $\Delta\epsilon$ is usually not very much different from one, thereby explaining the approximate universality of $\sigma(0)/\omega_m$. Equation (3), which applies also for electronic conducting disordered solids,^{28,29} will be referred to as the BNN relation.¹⁹ It carries very important information, implying that ac and dc conduction are closely correlated and must be due to the same mechanism. A number of models have been proposed to explain the BNN relation but none of these models can explain at the same time the observed very broad dielectric loss peaks.¹⁹ The random free-energy barrier model, to be discussed below, is consistent with both these experimental facts.

Perhaps the earliest model for ac conduction of ionic glasses is Stevels' and Taylor's random potential energy model.^{21,23,30} This model was only qualitative and did not discuss the BNN relation. In the model, it is assumed the ions feel a more or less randomly varying potential energy deriving from the random network structure of the glass. For dc conduction the largest energy barriers have to be overcome, while lower barriers are involved for ac conduction since only a limited distance has to be traveled. Though quite attractive, it was generally believed this model is inconsistent with the experiment. It was thought that, since ω_m is determined from ac properties, the model predicts a lower activation energy for ω_m than for $\sigma(0)$. Also, it was believed that a distribution of activation energies implies a temperature-dependent shape of the loss peak.^{7,8,15} Both things are wrong as becomes evident in Secs. IV and V where the random free-energy barrier model is discussed; this model is essentially nothing but Stevels' and Taylor's old random potential energy model.

Work within the semiconductor school started in 1961 when Pollak and Geballe measured the ac properties of n -type doped crystalline silicon at very low temperatures.¹⁴ They observed an approximate power law for the ac conductivity,

$$\sigma'(\omega) \propto \omega^s, \quad (4)$$

with an exponent s close to 0.8. Since then it has been customary to speak about power-law frequency dependencies, inferred from straight lines in log-log plots. However, even almost perfectly straight lines does not mean that $\sigma'(\omega)$ is an exact power law; log-log plots may be deceptive. This is not always remembered and equations like (4) have created some confusion in the field by being taken literally. To avoid this, one should preferably only speak about *approximate* power laws.

During the 1960s, the study of amorphous semiconductors emerged as a new and exciting field within semiconductor physics. As regards ac properties it was soon found that all amorphous semiconductors obey Eq. (4), and for most systems studied, one found values of s close to 0.8.⁴ A simple model for this is the pair approximation which was advanced by Austin and Mott in 1969,³¹ generalizing an idea of Pollak and Geballe.¹⁴ The pair approximation assumes that ac

losses are due to tunneling between pairs of localized states. For a random distribution of tunneling distances one finds an approximate power-law ac conductivity with an exponent given by³¹

$$s = 1 + 4/\ln(\omega\tau_{\text{ph}}) \quad (5)$$

where τ_{ph} is a typical phonon time. For ordinary laboratory frequencies Eq. (5) gives $s \cong 0.8$. Despite this success, it turns out that the pair approximation has a number of problems, and this approach cannot be regarded as a serious candidate for explaining experiments: Eq. (5) predicts s is a weakly decreasing function of frequency whereas experimentally s is, if it varies at all, weakly increasing.³² Also, the pair approximation cannot explain the transition to frequency-independent conduction at low frequencies; an expression of the form $\sigma'(\omega) = \sigma(0) + A\omega^s$ does not fit data at low frequencies where a loss peak appears, showing that ac and dc conduction are due to the same mechanism.^{5,29} Finally, it has been found that $s \cong 0.8$ is not universally valid, for instance, s always converges to one as the temperature goes to zero.^{32,33}

More refined models were suggested in the 1970s and early 1980s when hopping models, i.e., random walks in systems with spatially randomly varying jump frequencies, became popular. This approach was developed by Scher and Lax in 1973,³⁴ building on earlier ideas of Miller and Abrahams.³⁵ Scher and Lax suggested calculating $\sigma(\omega)$ in a hopping model by approximating the spatially inhomogeneous markovian random walk by a homogeneous nonmarkovian Montroll–Weiss-type continuous time random walk (CTRW).³⁶ Today the CTRW approximation is recognized as the simplest possible nontrivial mean-field approximation for calculating $\sigma(\omega)$ in random media, although the original derivation is inconsistent (Sec. III). Around 1980 the coherent potential approximation^{37,38} was introduced into the field independently by several workers, where it became known as the effective-medium approximation (EMA).^{39–42} Attempts were also made to improve the pair approximation. The correlated barrier hopping model is a version of the pair approximation which predicts $s \rightarrow 1$ as $T \rightarrow 0$.^{33,43} Alternatively, by returning to the original Miller–Abrahams equivalent circuit, Summerfield and Butcher in the extended pair approximation (EPA) succeeded in joining the pair approximation smoothly to the dc conduction.⁴⁴ In practical applications the EPA is very similar to the EMA and both approximations lead to self-consistency equations for $\sigma(\omega)$.

Hopping models are markovian, i.e., the charge carrier jump probabilities are assumed to be time independent. This leads to simple exponential decays of the probability for a charge carrier to stay at a given site in the solid. The observed pronounced frequency dispersion of the conductivity is then attributed to spatial disorder in the solid, resulting in a broad distribution of relaxation times (waiting times). A completely different approach to the problem is possible, however, namely to assume the fundamental hopping process is itself nonexponential.^{45,46} Models along these lines have not yet come up with useful predictions about $\sigma(\omega)$. It is important to note that the assumption of nonmarkovian jumps does not in itself imply the conductivity is frequency depen-

dent. Correlations in the directions of subsequent jumps are needed to ensure $\sigma(\omega) \neq \sigma(0)$ (see Sec. III). At present there seems to be no reason to assume nonmarkovian processes to lie behind the ac conduction, and only models based on simple exponential decays will be considered in this paper.

The dielectric and the semiconductor schools not only present data in terms of different quantities but they also have different emphasis.⁵ Workers from the dielectric school were always mainly interested in the loss peaks and did not put much effort into an investigation of the region of frequencies much larger than the loss peak frequency where the dielectric loss is almost constant. In contrast, this region has always been regarded as of main interest by the semiconductor school. This is because no frequency dependence analogous to Eq. (4) is found in single-crystal semiconductors where $\sigma(\omega) = \sigma(0)$ up to microwave frequencies. Also, experimentalists within the semiconductor school traditionally assumed the ac conduction to take place by a mechanism completely different from that behind the dc conduction, thereby making irrelevant any detailed investigation of the frequency region where the transition to dc conduction occurs.

As regards the question of the best way of presenting data, we suggest $\sigma(\omega)$ is to be preferred compared to $\epsilon(\omega)$ or $M(\omega)$. The use of $M(\omega)$ may have serious problems (see Sec. V). The conductivity is the more fundamental quantity, being directly related to equilibrium current-current fluctuations via the Kubo formula⁴⁷

$$\sigma(\omega) = \frac{1}{3k_B T V} \int_0^\infty \langle \mathbf{J}(0) \cdot \mathbf{J}(t) \rangle e^{-i\omega t} dt, \quad (6)$$

where \mathbf{J} is the total current in volume V , and k and T have their usual meaning. Reflecting also the fundamental nature of the conductivity is the fact that the dissipation per unit time and unit volume is $\sigma'(\omega)/2$ times the absolute square of the current density. Finally, because of the nonzero dc conductivity there is no simple interpretation of $\epsilon(\omega)$ in terms of fluctuating dipole moments. A focus on the dielectric loss does have some merit, though. The very fact that peaks in $\epsilon''(\omega)$ are seen at all is very important since this, in conjunction with the BNN relation, demonstrates that dc and ac conduction are both due to the same mechanism. Thus, the early discovery of the BNN relation for ionic glasses was due to the dielectric school while the analog for amorphous semiconductors only much more recently has been firmly established.^{28,29,48}

We end this section by listing the general features of ac conduction in disordered solids which are observed almost without exception and which a satisfactory model should explain^{1–6,29,32,75}: (1) For $\sigma'(\omega)$ one observes at high frequencies an approximate power law with an exponent s less than or equal to one, and usually close to one. If any deviation from a power law is seen, it corresponds to a weakly increasing $s(\omega)$. (2) At lower frequencies there is a gradual transition to a frequency-independent conductivity. The transition takes place around the loss peak frequency. (3) Whenever the dc conductivity is measurable there is always a dielectric loss peak. The loss peak frequency satisfies the

BNN relation [Eq. (3)]. When there is no measurable dc conductivity the exponent s is very close to one. (4) As regards their temperature dependence, $\sigma(0)$ and ω_m are usually Arrhenius with the same activation energy although more complicated temperature dependencies are occasionally observed, e.g., in group-IV amorphous semiconductors. (5) The shape of the loss peak is temperature independent. (6) The ac conductivity is much less temperature dependent than the dc conductivity (when considered in the usual log-log plot of Fig. 1). For s very close to one the ac conductivity is practically independent of temperature. (7) The exponent s increases as the temperature decreases, and for $T \rightarrow 0$ one finds $s \rightarrow 1$. Thus, the ac conductivity becomes almost temperature independent as $T \rightarrow 0$. (8) Even though $\sigma(0)$ may vary by many orders of magnitude, the ac conductivity varies only relatively little (one or two orders of magnitude) for different solids and different temperatures. In Sec. IV a simple hopping model will be considered which can explain these facts, but first a general discussion of hopping models is given.

III. HOPPING MODELS

Though a complete model for glass ionic conductivity does not exist today, it is seldom questioned that the basic transport mechanism is thermally activated hopping across an energy barrier, a process described by Eyring's rate theory.⁴⁹ Being a stochastic theory, rate theory leads to a simple exponential decay for the probability for an ion to stay at an energy minimum. Conductivity described by rate theory is usually referred to as hopping conductivity. While ionic conductivity is a classical thermally activated process, electronic conductivity is of quantum-mechanical nature. The fact that the two kinds of conduction in disordered solids are quite similar in their frequency and temperature dependence, is surprising and must provide an important piece of

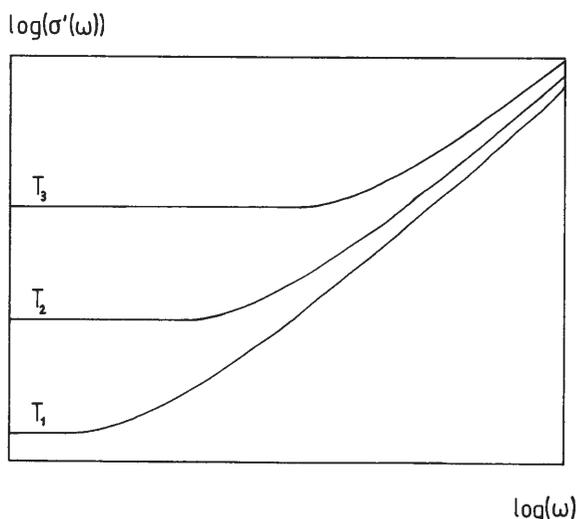


FIG. 1. Sketch of the real part of the frequency-dependent conductivity in a disordered solid at three different temperatures $T_1 < T_2 < T_3$. At low frequencies the conductivity is constant and equal to the dc conductivity, while at higher frequencies the conductivity obeys an approximate power law. The characteristic frequency marking the onset of ac conduction, the dielectric loss peak frequency ω_m , increases with increasing temperature. Note that in this logarithmic plot, the ac conductivity is less temperature dependent than the dc conductivity.

information. The simplest explanation is that even electronic conduction in disordered solids is to be described by hopping models. Actually, hopping between pairs of localized states has always been assumed to account for ac conduction in amorphous semiconductors, while dc transport, with the important exceptions of impurity conduction and Mott's variable range hopping model,⁴ traditionally is assumed to take place via extended state conduction. But since dc and ac conduction are due to the same mechanism (Sec. II), it seems that this approach must be abandoned and one has to assume dc conduction is due to hopping as well. The transport mechanism is probably quantum-mechanical tunneling between localized states. To ensure energy conservation the tunneling must be phonon assisted, thus destroying any quantum coherence effects. Accordingly, electronic hopping is of a stochastic nature just as ionic hopping.

Electrons are fermions, of course, but even ions behave as fermions as regards their hopping properties. This is because the Coulomb repulsion between ions and the finite ion size imply there is only room for one ion in each potential energy minimum in the solid. In the equation describing hopping fermions, it is usually assumed that transitions involve only hops of a single fermion. Even then, the equation is very complicated and further simplifications must be introduced to arrive at a tractable model. By assuming the site occupation numbers do not fluctuate in time it is possible to "project" the equation into three dimensions, in effect getting rid of all interactions between the particles, including that induced by fermistatistics.⁵⁰ The resulting equation, to be discussed below [Eq. (7)], describes hopping of noninteracting "quasi-particles" and this is what is usually meant by a hopping model. It is important to remember, however, that hopping models are built on mean-field assumptions which are far from obvious and cannot be justified in general.⁵¹ Hopping models have recently been reviewed by Niklasson in a paper emphasizing fractal aspects of conduction in disordered solids.⁵²

The very basic fact about ac conduction in disordered solids is that $\sigma'(\omega)$ is an increasing function of frequency. Any hopping model has this feature.⁵³ This is not surprising, since by hopping backwards and forwards at places with high jump probability a quasi-particle may sizably contribute to the ac conductivity, while the dc conductivity is determined by overcoming of unfavorable places in the solid for the formation of a continuous "percolation" path between the electrodes. The higher the frequency of the electric field, the larger is the ac conductivity because better use is made of the places with very large jump probability. As illustrated in Fig. 2, the increase in conductivity continues as long as the frequency of the field is lower than the maximum quasi-particle jump frequency (jump probability per unit time) in the solid. For larger field frequencies the conductivity stabilizes and becomes constant.

In order to arrive at a conductivity which increases for many decades of frequency, one must assume the jump frequency distribution also covers many decades. In comparison, the jump distances vary only relatively little. For nearest-neighbor hopping, for instance, the jump distance typically varies a factor of 2 or 3. It is commonly believed

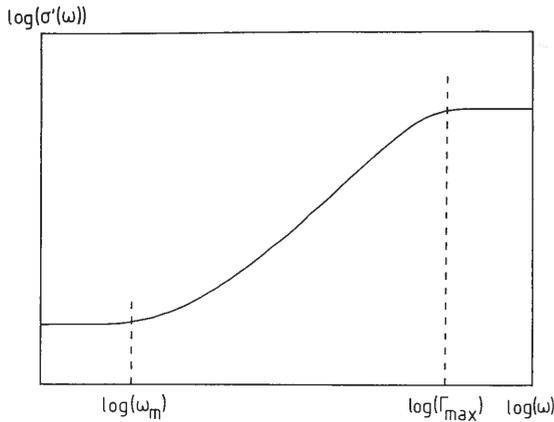


FIG. 2. Typical behavior of $\sigma'(\omega)$ in a hopping model. In hopping models $\sigma'(\omega)$ is always an increasing function of frequency (Ref. 53), just as in experiment. The saturation of $\sigma'(\omega)$ at high frequencies takes place when ω is close to the maximum jump frequency Γ_{\max} . Only in this region, typically close to 10^{12} Hz, is the pair approximation valid. The onset of ac conduction at low frequencies takes place around the loss peak frequency ω_m , which is the lowest effective jump frequency of the system, corresponding to the longest waiting time at a lattice site.

that this variation is insignificant. Following this, all jump distances may be assumed to be equal by considering the quasi-particle random walk to take place on a simple cubic lattice. The stochastic "equation of motion" for a quasi-particle is now the following master equation:

$$\frac{\partial P(\mathbf{s}, t)}{\partial t} = -\gamma_s P(\mathbf{s}, t) + \sum_{\mathbf{s}'} \Gamma(\mathbf{s}' \rightarrow \mathbf{s}) P(\mathbf{s}', t), \quad (7)$$

where $P(\mathbf{s}, t)$ is the probability to find the particle at the lattice site \mathbf{s} at time t , $\Gamma(\mathbf{s}' \rightarrow \mathbf{s})$ is the jump frequency for jumps from site \mathbf{s}' to \mathbf{s} (Γ is usually assumed to be nonzero only when \mathbf{s}' and \mathbf{s} are nearest neighbors), and

$$\gamma_s = \sum_{\mathbf{s}'} \Gamma(\mathbf{s} \rightarrow \mathbf{s}'). \quad (8)$$

To mimic the disorder of the solid, the Γ 's are assumed to vary randomly according to some probability distribution $p(\Gamma)$. The problem of calculating $\sigma(\omega)$ from $p(\Gamma)$ is not easy and suitable approximations have to be done. Below, the derivation of the CTRW and the EMA approximations is briefly sketched.

Adopting the bra and ket notation of quantum mechanics, Eq. (7) can be rewritten as

$$\frac{\partial}{\partial t} |\psi\rangle = H |\psi\rangle, \quad (9)$$

where $|\psi\rangle = \sum_{\mathbf{s}} P(\mathbf{s}) |\mathbf{s}\rangle$ is the state with probability $P(\mathbf{s})$ of finding the particle at site \mathbf{s} , and the "Hamiltonian" H is given by

$$H = - \sum_{\mathbf{s}} \gamma_s |\mathbf{s}\rangle \langle \mathbf{s}| + \sum_{\mathbf{s}, \mathbf{s}'} \Gamma(\mathbf{s}' \rightarrow \mathbf{s}) |\mathbf{s}\rangle \langle \mathbf{s}'|. \quad (10)$$

The formal solution of Eq. (9) is $|\psi(t)\rangle = \exp(Ht) |\psi(t=0)\rangle$. By two partial integrations, the Kubo formula for $\sigma(\omega)$ [Eq. (6)] reduces to

$$\sigma(\omega) = - \frac{nq^2\omega^2}{6k_B T} \int_0^\infty \langle \Delta \mathbf{R}^2(t) \rangle e^{-i\omega t} dt, \quad (11)$$

where q and n are charge respective density of the quasi-particles and $\langle \Delta \mathbf{R}^2(t) \rangle$ is the mean-square displacement of a particle in time t . A convergence factor $\lim_{\epsilon \rightarrow 0} \exp(-\epsilon t)$ is implicitly understood in the integral. If all sites are equally populated in thermal equilibrium, i.e., have the same free energy, Eq. (9) in conjunction with Eq. (11) implies

$$\sigma(\omega) = - \frac{nq^2\omega^2}{6k_B T} \frac{1}{N} \sum_{\mathbf{s}, \mathbf{s}'} (\mathbf{s} - \mathbf{s}')^2 \langle \mathbf{s} | G(i\omega) | \mathbf{s}' \rangle, \quad (12)$$

where N is the number of lattice sites and G is the resolvent or Green's function operator for H :

$$G = 1/(i\omega - H). \quad (13)$$

The Green's function depends on the actual values of the Γ 's. Hopping systems in three dimensions are believed to be self-averaging, implying that different samples with different H 's have the same bulk $\sigma(\omega)$. This property simplifies matters considerably since only the average of G over all possible H 's, $\langle G \rangle$, needs to be evaluated in order to find $\sigma(\omega)$. $\langle G \rangle$ is translationally invariant and we now make the ansatz

$$\langle G \rangle = 1/(i\omega - H_c), \quad (14)$$

where $H_c = H_c(\omega)$ is a "coherent" Hamiltonian determined by a coherent jump rate $\Gamma_c(\omega)$ in the following way:

$$H_c(\omega) = \Gamma_c(\omega) \left(-6 \sum_{\mathbf{s}} |\mathbf{s}\rangle \langle \mathbf{s}| + \sum_{\mathbf{s}, \mathbf{s}'} |\mathbf{s}\rangle \langle \mathbf{s}'| \right),$$

where the double sum is over nearest neighbors only. It is not hard to show from Eqs. (12) and (14), and is indeed intuitively obvious, that $\sigma(\omega)$ is proportional to $\Gamma_c(\omega)$.⁵⁴ For simplicity from now on we adopt the unit system in which the constant of proportionality is one, i.e., where $\sigma(\omega) = \Gamma_c(\omega)$.

To derive the CTRW approximation we write $H = H_0 + V$ where H_0 is the diagonal part and V the off-diagonal part of H . If G_0 is the Green's function for H_0 , the standard perturbation expansion is³⁷

$$G = G_0 + G_0 V G_0 + G_0 V G_0 V G_0 + \dots \quad (15)$$

The CTRW approximation is now to assume that all averages of products in G are equal to products of averages, i.e.,

$$\langle G \rangle = \langle G_0 \rangle + \langle G_0 \rangle \langle V \rangle \langle G_0 \rangle + \dots, \quad (16)$$

which implies $\langle G_0 \rangle \langle G \rangle^{-1} + \langle G_0 \rangle \langle V \rangle = 1$. Taking a diagonal element of this operator identity we get the CTRW approximation for $\sigma(\omega)$ in our rationalized unit system^{34,42,54,55}

$$\frac{1}{6\sigma(\omega) + i\omega} = \left\langle \frac{1}{\gamma + i\omega} \right\rangle. \quad (17)$$

The original derivation of the CTRW approximation was made for a nonmarkovian random walk in a homogeneous medium characterized by a so-called waiting time distribution function.³⁴ This derivation is inconsistent, however, since the assumption of spatial homogeneity implies the current autocorrelation function is a delta function, and thus $\sigma(\omega) = \sigma(0)$ from Eq. (6).^{56,57} Note that this criticism applies to any nonmarkovian hopping in a homogeneous medium; a nontrivial frequency dependence of the conductivity only comes about if there are correlations in the directions of subsequent jumps. The derivation of Eq. (17) given above is

due to Odagaki and Lax^{42,54}; here the CTRW approximation appears as the simplest possible nontrivial mean-field approximation which is also referred to as the Hartree approximation.

The magnitude of the dc conductivity is usually quite wrong in the CTRW approximation, throwing doubt on this approach.⁵⁸ A more reliable way of evaluating $\sigma(\omega)$ is the EMA.³⁹⁻⁴² Here the idea is to focus on a particular link of the lattice, say the link between sites \mathbf{s} and \mathbf{s}' . Assuming, as above, that all site free energies are equal, the principle of detailed balance implies $\Gamma(\mathbf{s} \rightarrow \mathbf{s}') = \Gamma(\mathbf{s}' \rightarrow \mathbf{s})$. The link is considered to be embedded in an average medium described by the $\langle G \rangle$ of Eq. (14) and one now requires self-consistency so that, on the average, the system of link plus average medium is described by $\langle G \rangle$: Writing the effective Hamiltonian for the system, H_{eff} , as $H_{\text{eff}} = H_c + V$ where $V = [\sigma(\omega) - \Gamma(\mathbf{s} \rightarrow \mathbf{s}')] |a\rangle \langle a|$ with $|a\rangle = |\mathbf{s}\rangle - |\mathbf{s}'\rangle$, the standard perturbation expansion Eq. (15) yields for the Green's function for H_{eff}

$$G_{\text{eff}} = \langle G \rangle + \langle G \rangle T \langle G \rangle, \quad (18)$$

where

$$T = V + V \langle G \rangle V + \dots = V(1 - \langle G \rangle V)^{-1}. \quad (19)$$

The self-consistency requirement, $\langle G_{\text{eff}} \rangle = \langle G \rangle$, now leads to $\langle T \rangle = 0$. A straightforward calculation with 2×2 matrices referring to site \mathbf{s} and \mathbf{s}' shows that $\langle T \rangle = 0$ is equivalent to^{40,42}

$$\left\langle \frac{\Gamma - \sigma(\omega)}{1 - 2(\langle \mathbf{s} | \langle G \rangle | \mathbf{s} \rangle - \langle \mathbf{s} | \langle G \rangle | \mathbf{s}' \rangle)(\sigma(\omega) - \Gamma)} \right\rangle = 0. \quad (20)$$

This is the EMA equation for $\sigma(\omega)$; it can be simplified somewhat by noting that

$$\langle \mathbf{s} | \langle G \rangle | \mathbf{s} \rangle - \langle \mathbf{s} | \langle G \rangle | \mathbf{s}' \rangle = \frac{1 - i\omega \langle \mathbf{s} | \langle G \rangle | \mathbf{s} \rangle}{6\sigma(\omega)}, \quad (21)$$

which follows from evaluating the diagonal element of Eq. (14) written as $(i\omega - H_c) \langle G \rangle = 1$.

As mentioned already, the real part of the conductivity is always an increasing function of frequency. The increase continues until one reaches the region of frequencies around the maximum jump frequency of the model, where the conductivity stabilizes (Fig. 2). In experiments the conductivity usually increases until $\omega \approx 10^{12}$ Hz. At these high frequencies the stochastic assumption of hopping models cease to be valid and one enters a region characterized by various resonance effects. At even higher frequencies the conductivity starts decreasing. The stabilization of Fig. 2 predicted by hopping models is thus seldomly observed in experiment which suggests that, for the construction of realistic hopping models, one should try to eliminate completely all effects of the maximum jump frequency. This philosophy is followed below.

IV. THE RANDOM FREE-ENERGY BARRIER MODEL

Equipped with the tools of Sec. III we now address the problem of formulating the simplest possible realistic model for ac conduction in disordered solids. For most solids the dc conductivity is thermally activated: $\sigma(0) \propto \exp(-\Delta E_{\text{dc}}/k_B T)$.

As illustrated in Fig. 1, the ac conductivity is less temperature dependent than $\sigma(0)$, suggesting that ac conduction is dominated by processes with activation energies smaller than ΔE_{dc} . A closer analysis shows that the ac conductivity activation energy depends on frequency and temperature so it is natural to assume that, consistent with the disorder of the solid, a whole range of activation energies is involved. This idea goes back in time at least to 1946 (Refs. 30 and 59) and it is the basic ingredient in Stevels' and Taylor's model from 1957.^{21,23} It should be emphasized that, even without any microscopic picture of the transport mechanism, results like Fig. 1 strongly suggest that any model for ac conduction should somehow be built on the assumption of a distribution of energy barriers. Hopping models, of course, fit nicely into this since it is realistic to assume the quasi-particle jumps are thermally activated over an energy barrier. More generally, one speaks about free-energy barriers⁴⁹ and writes

$$\Gamma = \Gamma_0 \exp\left(-\frac{\Delta F}{k_B T}\right), \quad (22)$$

where Γ_0 is the so-called attempt frequency, and the free-energy barrier, $\Delta F = \Delta E - T\Delta S$, is composed of an energy barrier ΔE and an entropy barrier ΔS . Quantum-mechanical tunneling may be thought of as providing a negative entropy barrier proportional to the tunneling distance. In this terminology it is possible to speak about ionic and electronic conduction in a unified language which, incidently, also covers the possibility of thermally activated electron or polaron jumps over energy barriers.

In modeling a disordered solid, the simplest possible assumption is that all free-energy barriers are equally likely. Since $p(\Gamma) = p(\Delta F)(d\Delta F/d\Gamma)$ this implies

$$p(\Gamma) \propto \Gamma^{-1}. \quad (23)$$

The model defined by Eq. (23) will be referred to as the random free-energy barrier model. To solve this model within the CTRW approximation [Eq. (17)], the distribution of γ 's needs to be calculated. Since γ is a sum of Γ 's [Eq. (8)], $p(\gamma)$ is a convolution of $p(\Gamma)$ with itself a number of times. The result is a complicated function, equal to γ^{-1} times some logarithmic terms. These terms are not very important compared to the γ^{-1} term, so we approximate $p(\gamma)$ simply by γ^{-1} . Substituting this now into Eq. (17) leads to

$$\sigma(\omega) = \frac{1}{6} \left(-i\omega + \frac{i\omega \ln \lambda}{\ln[(1 + i\omega/\gamma_{\min})/(1 + i\omega/\gamma_{\max})]} \right), \quad (24)$$

where two cutoffs have been introduced, and $\lambda = \gamma_{\max}/\gamma_{\min}$. According to the philosophy of Sec. III any influence of the high-frequency cutoff should be eliminated. For $\gamma_{\max} \rightarrow \infty$ the second term of Eq. (24) dominates, and for frequencies $\omega \ll \gamma_{\max}$ we thus have

$$\sigma(\omega) = \frac{1}{6} [i\omega \ln \lambda / \ln(1 + i\omega\tau)], \quad \tau = \gamma_{\min}^{-1}. \quad (25)$$

From this we get

$$\sigma(0) = \ln \lambda / 6\tau, \quad (26)$$

which substituted into Eq. (25) finally gives¹⁶

$$\sigma(\omega) = \sigma(0) [i\omega\tau / \ln(1 + i\omega\tau)]. \quad (27)$$

By regarding this expression as a formula for $\sigma(\omega)$ with two free parameters, $\sigma(0)$ and τ , any influence of γ_{\max} has now been formally eliminated.

The random free-energy barrier model predicts a universal shape of the conductivity curve plotted in the usual log-log plot.¹⁶ In Fig. 3 the model is compared to experiments on a number of different solids.⁶⁵⁻⁷¹ Though exact universality is not observed, the model is in rough agreement with experiment. The model implies a high-frequency behavior which is very close to a power law, reminding us of the danger of deducing fundamental power laws from log-log plots. For $10^3 < \omega\tau < 10^6$ one finds $s \cong 0.8$, which offers a possible explanation for the frequently observed exponents around 0.8.⁴ For $\omega\tau \gg 1$ the exponent s is given by the expression

$$s = 1 - 2/\ln(\omega\tau). \quad (28)$$

This can be easily proved from $\sigma'(\omega) \propto \omega\tau/\ln^2(\omega\tau)$, which is valid whenever $\omega\tau \gg 1$. In general, the model predicts ex-

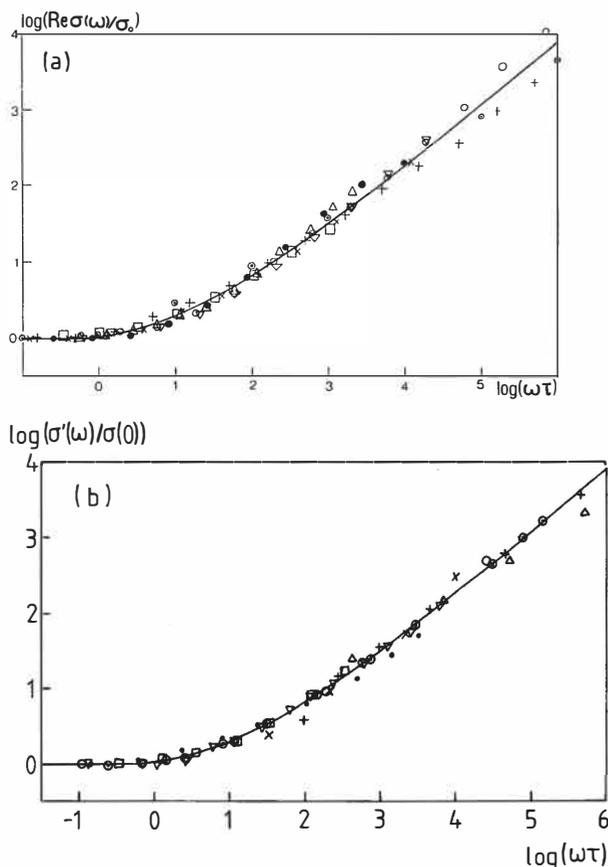


FIG. 3. CTRW solution of the random free-energy barrier model [Eq. (27)] compared to experiment on a number of solids [(a) is reproduced from Ref. 16]. The data represent conduction in (a) n -doped crystalline silicon (\times), sputtered films of arsenic (\bullet), sodium silicate glasses (\odot), glow-discharge silicon (Δ), silicon monoxide ($+$), amorphous germanium (\square), $\text{Mn}_{1.8}\text{Ni}_{0.6}\text{Co}_{0.6}\text{O}_4$ (∇), monolayer of stearic acid (\circ); and (b) a - As_2Se_3 at 370 K (\times) (Ref. 65), viscous $0.4\text{Ca}(\text{NO}_3)_2 \cdot 0.6\text{KNO}_3$ at 338.5 K (\bullet) (Ref. 66), viscous $\text{HZnCl}_3 \cdot 4\text{H}_2\text{O}$ at 154.5 K (\odot) (Ref. 67), illuminated polycrystalline zinc oxide (Δ) (Ref. 63), vanadium phosphate glass at 167 K ($+$) (Ref. 68), AsF_5 -doped polyphenylacetate at 271 K (\square) (Ref. 69), flux-grown single-crystal alumina in c direction at 873 K (∇) (Ref. 70), 81% tungsten phosphate glass at room temperature (\circ) (Ref. 71). For all data the characteristic time τ has been adjusted to fit the theory as well as possible; τ varies between 10^{-7} and 10^3 s.

ponents between 0.7 and 1.0, which is exactly the interval in which one finds the vast majority of reported exponents.³² Also in agreement with experiments is the fact that $s(\omega)$ is a weakly increasing function of ω .

For the dielectric loss one finds by substituting Eq. (27) into Eq. (1),

$$\epsilon''(\omega) = 2\Delta\epsilon \left(\frac{\arctan(\omega\tau)}{[\ln\sqrt{1 + (\omega\tau)^2}]^2 + [\arctan(\omega\tau)]^2} - \frac{1}{\omega\tau} \right), \quad (29)$$

where $\Delta\epsilon$ is the dielectric loss strength given by

$$\epsilon_0\Delta\epsilon = \frac{1}{2}\sigma(0)\tau. \quad (30)$$

Equation (29) implies a very broad loss peak with a temperature independent shape. The loss peak is shown in Fig. 4 together with data for a typical sodium silicate glass. There is a qualitative, but not exact, agreement between theory and experiment. The BNN relation is satisfied by the model. A numerical analysis of Eq. (29) shows that the loss peak frequency is given by $\omega_m\tau = 4.71$.¹⁹ Combining this with Eq. (30) and the definition of the BNN p parameter in Eq. (3) we get

$$p_{\text{CTRW}} = 0.42. \quad (31)$$

This number is not as close to one as required by experiment, but in comparison to the many orders of magnitude variations in $\sigma(0)$ and ω_m for the solids where the BNN relation has been found,²⁷ this is not a serious objection to the model.

Writing Eq. (30) in the form

$$\tau = 2\epsilon_0\Delta\epsilon/\sigma(0), \quad (32)$$

implies an interesting scaling principle which has recently been discussed by Summerfield⁴⁸ and which was also used by Scher and Lax in their 1973 papers.³⁴ The scaling principle, which is just the BNN relation in conjunction with the time-temperature superposition principle (i.e., the existence of a universal conductivity curve), allows one to plot different experiments onto a master curve. To make use of the scaling principle, one may use, e.g., experiments on one solid at different temperatures, as illustrated by Pollak and Geballe's original experiments replotted in Fig. 5(a)¹⁴ and a similar

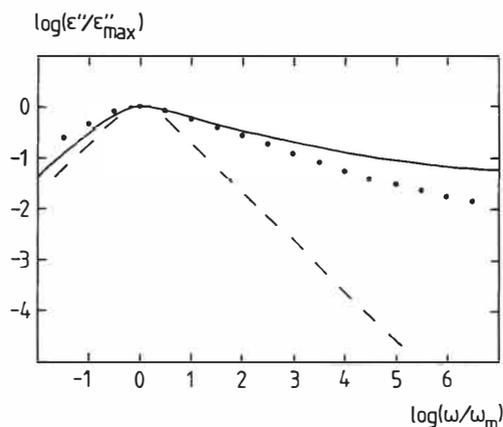


FIG. 4. Dielectric loss of the random free-energy barrier model according to Eq. (27) and data for a typical sodium-silicate glass (reproduced from Ref. 19). The dashed curve is the Debye dielectric loss peak. There is a qualitative, but not exact, agreement between theory and experiment.

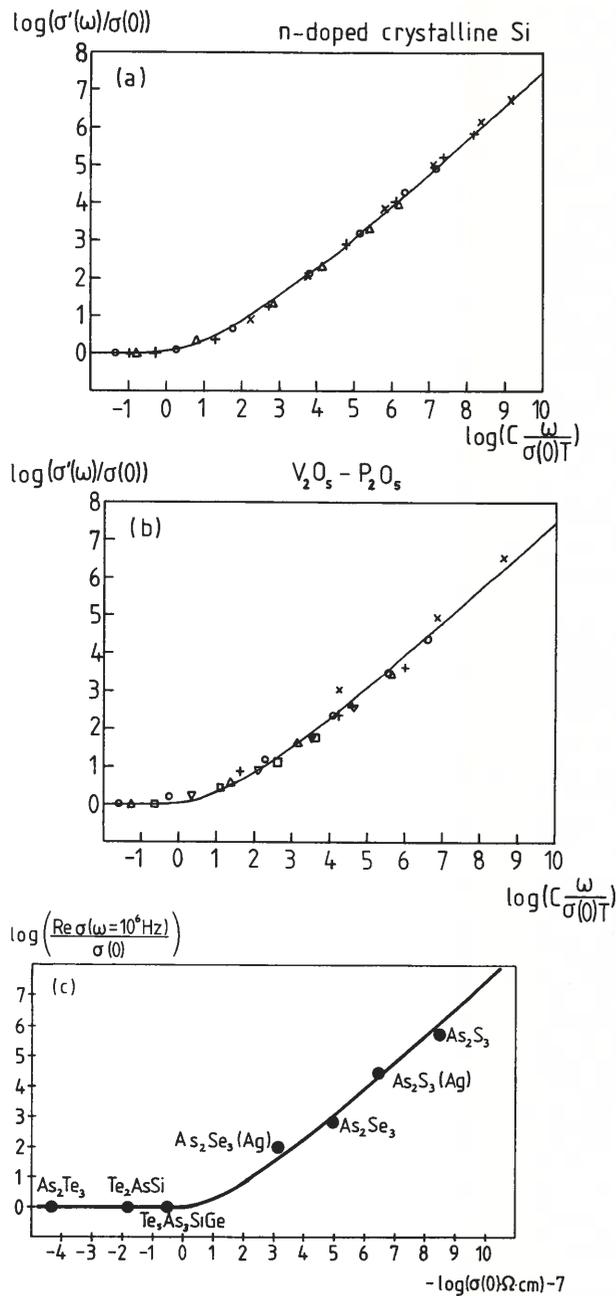


FIG. 5. Applications of the scaling principle, i.e., the BNN relation in conjunction with the time-temperature superposition principle. In the model, the scaling principle is expressed by Eq. (32) and the fact that the conductivity relative to $\sigma(0)$ is a function only of $\omega\tau$. In (a) and (b) data for a single sample at different frequencies and temperatures are plotted, making use of Eq. (32) and the Curie law equation (33). The data are compared to the CTRW solution of the random free-energy barrier model [Eq. (27)]. (a) considers the original data by Pollak and Geballe on heavily *n*-doped crystalline silicon at low temperatures, taken from Fig. 5 of Ref. 14. The data were obtained at the following temperatures: 2, 2.5, 3, 3.5, 4.5, 5.5 K at 0.1 kHz (Δ), 1 kHz (\circ), 10 kHz ($+$), 100 kHz (\times). (b) considers data on a vanadium phosphate glass taken from Fig. 2 of Ref. 72. The data was obtained at 83, 100, 125, 167, and 250 K at 0.1 kHz (\square), 1 kHz (∇), 10 kHz (Δ), 100 kHz (\circ), 8 MHz ($+$), 3.6 GHz (\times). The gigahertz data deviates from the master curve, signaling a breakdown of the theory at very high frequencies. In both (a) and (b) the constant C is a fitting parameter, $C = 1.9 \times 10^{12}$ for (a) and $C = 2.1 \times 10^{10}$ for (b) in units of $(\Omega \text{ cm})^{-1} \text{ K/Hz}$. In (c) data for different chalcogenide glasses at a fixed frequency are compared to Eq. (27). It is assumed that the different samples have the same dielectric loss strength $\Delta\epsilon$ which becomes a fitting parameter ($\Delta\epsilon = 0.6$). The data were obtained at 300 K by several workers [see the references in the paper by Davis and Mott who compiled the data (Ref. 73)].

figure for measurements by Mansingh and co-workers [Fig. 5(b)].⁷² Alternatively, measurements at the same frequency on different solids assumed to have the same $\Delta\epsilon$ [Fig. 5(c)] may be used.⁷³

In connection with the scaling principle we remind that $\Delta\epsilon$ experimentally varies with temperature according to the Curie law

$$\Delta\epsilon \propto T^{-1}, \quad (33)$$

a fact which is also predicted by the CTRW treatment though here, it has been hidden by the rationalized unit system. Figure 6 illustrates the use of the scaling principle in conjunction with Eq. (33) for measurements by Long and Balkan on amorphous germanium.⁷⁴ Except for the weak temperature dependence of $\Delta\epsilon$, Eq. (32) predicts the universal conductivity curve of Eq. (27) to be displaced in the direction 45° to the $\log(\omega)$ axis when the temperature is changed. As the temperature is lowered, $\sigma(0) \rightarrow 0$, which implies that measurements at a fixed frequency in effect probes larger and larger $\omega\tau$ on the universal conductivity curve. Since $s \rightarrow 1$ as $\omega\tau \rightarrow \infty$, the model thus predicts $s \rightarrow 1$ as $T \rightarrow 0$, which is in agreement with experiment. Substituting $\sigma(0) \propto \exp(-\Delta F_{dc}/k_B T)$ via Eq. (32) into Eq. (28) we find as $T \rightarrow 0$ for the exponent s , measured in a fixed range of frequencies,

$$s = 1 - T/T_0, \quad k_B T_0 = \frac{1}{2} \Delta E_{dc}. \quad (34)$$

According to the theory, the temperature dependence of the ac conductivity is much weaker than that of the dc conductivity. Note that the temperature dependence almost vanishes whenever s approaches one. This is predicted and observed for all systems at low temperatures, but $\sigma'(\omega)$ may also become almost temperature independent at room tem-

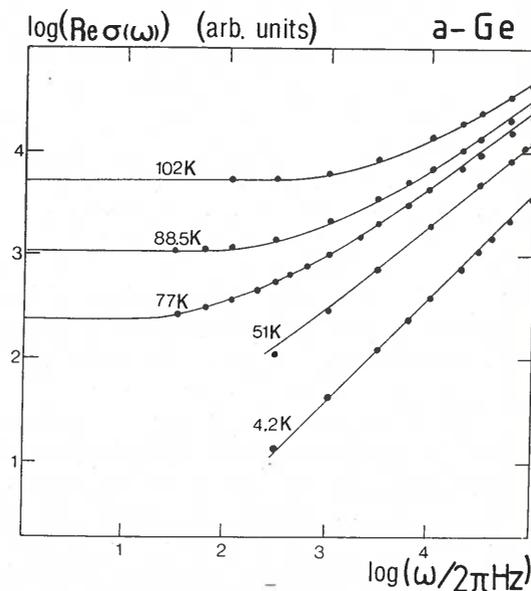


FIG. 6. Comparison between the prediction of Eq. (27) and measurements on amorphous germanium at various temperatures by Long and Balkan (Ref. 74) (reproduced from Ref. 16). The data were fitted by Eq. (27) at 77 K and then displaced according to the scaling law [Eq. (32)] taking into account Eq. (33). At the two lowest temperatures the dc conductivity is unknown and was treated as a fitting parameter.

perature for solids with a very low, perhaps unmeasurable, dc conductivity.

In experiment one finds that, while $\sigma(0)$ may vary many orders of magnitude between different solids, the ac conductivity varies only relatively little (one or two orders of magnitude).² This can be understood from the model: For two different solids, (1) and (2), we find from Eqs. (27) and (30)

$$\lim_{\omega \rightarrow \infty} \frac{\sigma^{(1)}(\omega)}{\sigma^{(2)}(\omega)} = \frac{\sigma^{(1)}(0)\tau^{(1)}}{\sigma^{(2)}(0)\tau^{(2)}} = \frac{\Delta\epsilon^{(1)}}{\Delta\epsilon^{(2)}}. \quad (35)$$

Since the dielectric loss strength varies only relatively little between different solids, Eq. (35) explains the small spread in ac conductivity.

Turning now to the problem of solving the random free-energy barrier model by the effective-medium approximation, we first substitute Eq. (21) into Eq. (20) and get

$$\langle (\Gamma - \sigma)/(\Gamma + \chi\sigma) \rangle = 0 \quad (36)$$

where

$$\chi = 3/(1 - i\omega \langle \mathbf{s} | \langle G \rangle | \mathbf{s} \rangle) - 1. \quad (37)$$

It is straightforward to calculate the average appearing in Eq. (36) when the distribution of Γ 's is given by Eq. (23); the result is

$$(1 + \chi) \ln \left(\frac{\Gamma_{\max} + \chi\sigma}{\Gamma_{\min} + \chi\sigma} \right) = \ln \left(\frac{\Gamma_{\max}}{\Gamma_{\min}} \right), \quad (38)$$

which is a rather complicated equation for $\sigma(\omega)$. However, according to the philosophy of Sec. III we are only interested in the limit of very large Γ_{\max} . In this limit an important simplification occurs, as pointed out by Bryksin.³⁹ In the whole range of frequencies much smaller than Γ_{\max} we have $\omega \ll |\sigma(\omega)|$. In this region one may therefore expand χ to first order in $\omega/\sigma(\omega)$:

$$\chi = 2 + \xi[i\omega/\sigma(\omega)] + \dots, \quad (39)$$

where ξ is a numerical constant given by^{39,60}

$$\xi = \frac{1}{6\pi^3} \int_0^\pi \int_0^\pi \int_0^\pi \frac{dx dy dz}{1 - \frac{1}{3}[\cos(x) + \cos(y) + \cos(z)]} = 0.253. \quad (40)$$

The expansion in Eq. (39) is only possible in three or more dimensions where the Green's function for diffusion is well behaved as $\omega \rightarrow 0$. By putting $\chi = 2$ in Eq. (38) it is easy to see that in the frequency region of interest $\Gamma_{\min} \ll |\sigma(\omega)| \ll \Gamma_{\max}$. Thus, the \ln term on the left-hand side of Eq. (38) may be replaced by $\ln(\Gamma_{\max}/\chi\sigma)$. Equation (38) now becomes, by equating the $\omega = \omega$ and the $\omega = 0$ on the left-hand side,

$$\left(3 + \xi \frac{i\omega}{\sigma(\omega)} \right) \ln \left(\frac{\Gamma_{\max}/2\sigma(\omega)}{1 + \frac{1}{2}\xi [i\omega/\sigma(\omega)]} \right) = 3 \ln \left(\frac{\Gamma_{\max}}{2\sigma(0)} \right), \quad (41)$$

which expanded to first order in $\omega/\sigma(\omega)$ reduces to

$$3 \ln \left(\frac{\sigma(0)}{\sigma(\omega)} \right) + \xi \frac{i\omega}{\sigma(\omega)} \ln \left(\frac{\sigma(0)}{\sigma(\omega)} \right) + \xi \frac{i\omega}{\sigma(\omega)} \ln \left(\frac{\Gamma_{\max}}{2\sigma(0)} \right) - \frac{3}{2} \xi \frac{i\omega}{\sigma(\omega)} = 0. \quad (42)$$

The second term is unimportant compared to the first term and may be ignored, leading to

$$\frac{\sigma(\omega)}{\sigma(0)} \ln \left(\frac{\sigma(\omega)}{\sigma(0)} \right) = i\omega\tau, \quad (43)$$

where

$$\tau = \frac{\xi}{3\sigma(0)} \left[\ln \left(\frac{\Gamma_{\max}}{2\sigma(0)} \right) - \frac{3}{2} \right]. \quad (44)$$

Equation (43) was first derived by Bryksin for electrons tunneling between nearest neighbors in a solid with electron sites randomly located in space.³⁹ The jump frequency probability distribution of this model is more complicated than Γ^{-1} , but in the limit $\Gamma_{\max} \rightarrow \infty$ the frequency-dependent conductivity is the same in the two models. It is quite unusual that the EMA leads to such a simple equation. This equation will henceforth be referred to as Bryksin's equation.

In Fig. 7 the solution to Bryksin's equation is compared to the CTRW solution of the random free-energy barrier model [Eq. (27)]. The two are quite similar, lending some credit to the simple CTRW expression for $\sigma(\omega)$. All features of the CTRW solution are shared by the solution of Bryksin's equation. In particular, the BNN relation is satisfied by the EMA solution, although Eq. (30) is now replaced by

$$\epsilon_0 \Delta\epsilon = \sigma(0)\tau. \quad (45)$$

The loss peak frequency is given by $\omega_m \tau = 1.709$ and for the BNN p parameter one finds

$$p_{\text{EMA}} = 0.59. \quad (46)$$

This value is in better agreement with the experimentally found $p \cong 1$ than the $p_{\text{CTRW}} = 0.42$. But for other purposes the two solutions are practically identical and one may use

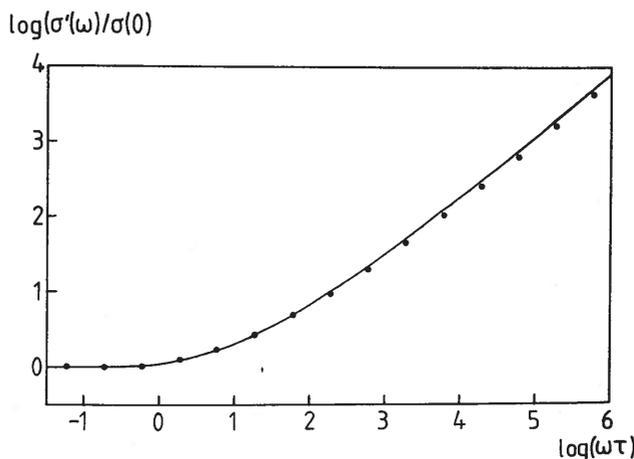


FIG. 7. Comparison between the CTRW and the EMA solution of the random free-energy barrier model. The full curve is the CTRW solution [Eq. (27)] and the dots mark the EMA solution [Eq. (43)]. The two solutions are shown for the same value of $\sigma(0)$ and $\Delta\epsilon$ which, according to Eqs. (30) and (45), implies $\tau_{\text{EMA}} = 2\tau_{\text{CTRW}}$. The CTRW and EMA solutions are almost indistinguishable, lending credit to the simpler CTRW approach from the more reliable but also more involved EMA.

Eq. (27) just as well as Bryksin's equation, which has to be solved numerically before it can be compared to experiment.

V. DISCUSSION

Looking back on the history of ac conduction in disordered solids, it strikes one that a handful of glass technologists established very early the general features of glass ionic conductivity, while only much more recently the same features have been established also for electronic conductive disordered semiconductors. A likely explanation for this is the fact that electronic conductivity was always thought to be much more complicated than transport in ionic conductive solids, which obviously proceeds via thermally activated charge carrier jumps over barriers. The pair approximation, which seems to have delayed a proper understanding of electronic transport, was never really applied to ionic glasses, where one also needs a mechanism for the dc conduction which very early was known to be closely related to the ac conduction. On the other hand, the traditional ion glass researchers never managed to explain both the BNN relation and the broad dielectric loss peaks,¹⁹ and the more successful random walk models were first solved by workers within the semiconductor school. Despite extensive theoretical work, these models have not yet become popular among experimentalists. This is perhaps because the models usually end up with complex equations which have to be solved numerically and which are far from transparent in their interpretation. But this is not necessarily the case, and one purpose of this paper has been to show that simple random walk models do exist and to encourage their use.

The justification of hopping models comes from the fact that dc and ac conduction are both due to the same mechanism. This is the message of the BNN relation which is central to the whole subject. It is of crucial importance that genuine loss peaks are observed. Otherwise, even when ac and dc conduction are totally unrelated, one may find a BNN-like relation of the form $\sigma(0) \propto \omega_m$ where ω_m is the characteristic frequency for the onset of ac conduction; this is the case, e.g., if $\sigma'(\omega) = \sigma(0) + A\omega$. In experiments one does indeed find loss peaks in all disordered solids, though this is not always as carefully checked as one might wish.

Given that conduction in disordered solids is to be described by hopping models, the only possible explanation for the ion-electron analogy is that the same jump frequency distribution applies for both cases. The simplest guess for the common distribution is that corresponding to randomly varying free-energy barriers for jumps, Eq. (23). One may argue for this distribution directly from experiments¹⁸: Since the shape of the $\sigma'(\omega)$ curve is temperature independent and $s \rightarrow 1$ as $T \rightarrow 0$, it can be concluded that $s \rightarrow 1$ as $\omega \rightarrow \infty$ on the master curve; the simplest jump frequency distribution consistent with this is $p(\Gamma) \propto \Gamma^{-1}$.¹⁸ At low frequencies, when the cutoff at ω_m starts to play a role, one expects it to decrease the frequency dependence of the conductivity slightly, i.e., to push s below one. This is exactly what happens in the random free-energy barrier model [Eq. (28)]. While the assumption of completely randomly varying free-energy barriers is probably the simplest realistic choice, other barrier distributions may also be useful. This has been discussed

in detail by Macdonald in recent papers.⁶¹ He adopts a more macroscopic point of view to ac conduction but the mathematics developed by him is quite similar to that of hopping models.

In hopping models it is possible to distinguish different characteristic regions of frequency.^{39,50} At low frequencies the conductivity is constant. Here transport takes place on infinite "percolation" paths. Then comes a region of frequencies where the conductivity increases strongly with frequency (compare Fig. 2); here transport is dominated by contributions from hopping in finite clusters. Finally one encounters the region where the high-frequency cutoff starts to play a role and $s(\omega)$ decreases to zero with increasing frequency. This is where the pair approximation gradually becomes valid, i.e., where the conductivity is made up of contributions from independent pairs of sites connected by a link with a particularly large jump rate. The division into three regions of frequency is suggestive but not really based on exact theory. The validity of the pair approximation at high frequencies is an exact result, though.⁵⁰ To estimate where the pair approximation sets in, let us use the jump frequency distribution of Sec. IV [Eq. (23)] which gives equal weight to each decade of jump frequencies. In order for a link to be "isolated" from its surroundings, its jump rate must be larger than those of the 10 other links which it is directly connected to on the cubic lattice. Since the random free-energy barrier model weighs all decades of jump frequency equally, on the logarithmic frequency axis the pair approximation will be valid in the final 10% of the interval between Γ_{\min} and Γ_{\max} . Equation (38) implies for the dc conductivity $\sigma(0) \propto \Gamma_{\min}^{1/3} \Gamma_{\max}^{2/3}$ which via the BNN relation implies $\omega_m \propto \Gamma_{\min}^{1/3} \Gamma_{\max}^{2/3}$. Thus the pair approximation is valid only in the final third of the (logarithmic) interval between ω_m and Γ_{\max} . In order to fit experiment Γ_{\max} must be at least 10^{12} Hz, so the pair approximation is seldom of relevance at typical laboratory frequencies (unless at very low temperatures), and we may safely follow the philosophy of Sec. III and eliminate any influence of Γ_{\max} . In the resulting "renormalized" hopping models, the physics is a consequence of the low-frequency cutoff at Γ_{\min} . This is complementary to the pair approximation where the physics is a consequence of the high-frequency cutoff [Eq. (5)].¹⁸

When applying the renormalization philosophy to the random free-energy barrier model, one finds in the CTRW approximation a simple formula for $\sigma(\omega)$ [Eq. (27)] and in the EMA a simple transcendental equation for $\sigma(\omega)$ [Eq. (43)]. As illustrated in Fig. 7, these two solutions are almost identical. Since the dc conductivity in the CTRW approximation generally may be wrong by several orders of magnitude,⁵⁸ while the EMA value is probably much more accurate, the similarity between the two solutions is far from obvious and must be regarded as an empirical fact. Apparently, the CTRW is saved by our prescription of eliminating Γ_{\max} , which leaves $\sigma(0)$ as a free parameter in the model.

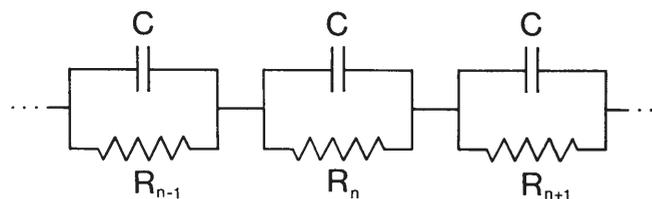
Recently, it has been shown by Summerfield that several different models solved in the EPA have almost the same frequency dependence in the region of frequencies where the high-frequency cutoff is irrelevant.⁴⁸ He refers to this phenomenon as "quasi-universality." The solutions of the mod-

els discussed by Summerfield are quite close to the solution of the random free-energy barrier model. This supports a hypothesis of “quasi-universality” among all models and not only among EPA models as originally suggested. Though further investigation of this hypothesis is necessary, a preliminary conclusion is that all realistic models in the $\Gamma_{\max} \rightarrow \infty$ limit gives more or less the same frequency-dependent conductivity. Equation (27) provides a simple analytical representation of the quasi-universal conductivity.

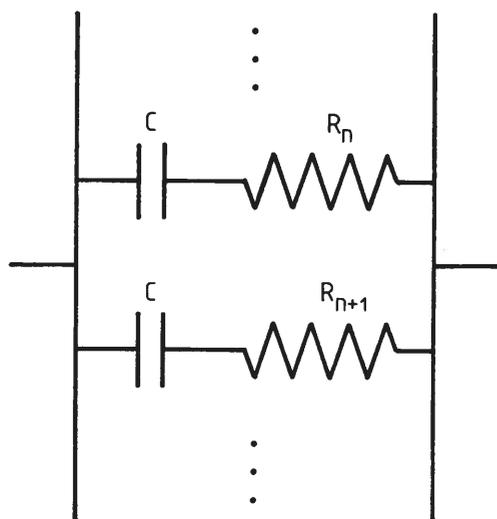
In the limit $\Gamma_{\max} \rightarrow \infty$, the CTRW approximation is represented by the electrical equivalent circuit shown in Fig. 8(a).¹⁷ In the circuit all capacitances are equal while the resistances vary. The impedance $Z(\omega)$ is given by

$$Z(\omega) = \langle 1/(R^{-1} + i\omega C) \rangle, \quad (47)$$

where the average is over the distribution of resistances. Corresponding to randomly varying free-energy barriers, the resistance probability distribution varies as R^{-1} , the analog of Eq. (23), and thus, the characteristic time $t = RC$ is distributed according to t^{-1} . If the maximum value of t is denoted by τ and the minimum value is zero, we now get



(a)



(b)

FIG. 8. Electrical equivalent circuits for (a) the CTRW approximation in the $\Gamma_{\max} \rightarrow \infty$ limit and (b) the pair approximation. Note that the pair approximation does not have any dc conduction. This figure shows that the two approaches are, in a sense, complementary. This is also reflected by the fact that the exponent s in the pair approximation is a function of the logarithmic distance from ω to the *high*-frequency cutoff [Eq. (5)], while s in the CTRW case is a function of the logarithmic distance to the effective *low*-frequency cutoff at ω_m [Eq. (28)].

$$Z(\omega) = \frac{K}{C} \int_0^\tau \frac{1}{t^{-1} + i\omega} \frac{dt}{t} = \frac{K}{C} \int_0^\tau \frac{1}{1 + i\omega t} dt. \quad (48)$$

Since t^{-1} is not normalizable, the constant K is unknown and must be determined self-consistently. When this is done after the integration has been carried out, Eq. (48) reduces to Eq. (27). Note that it is straightforward to actually build the equivalent circuit in the laboratory, since the ordinary resistance scale is logarithmic just as the distribution used in Eq. (48).

The physical interpretation of the circuit is not quite obvious. Intuitively, one may argue that the one-dimensional circuit gives a satisfactory representation of conduction in three dimensions because the broad distribution of jump rates implies that conduction is dominated by contributions from certain optimal paths, the “percolation” paths.¹⁸ Usually, the circuit of Fig. 8(a) is not related to hopping models but applied to conduction in a solid with macroscopic inhomogeneities with different dc resistances.^{20,62,63} In such models the frequency dispersion of the conductivity is described by a generalization of the Maxwell–Wagner theory of inhomogeneous dielectrics, as first suggested by Isard.²⁴ The reduction from three to one dimension has never really been justified.

The equivalent circuit of the renormalized CTRW approximation is complementary to the equivalent circuit of the pair approximation shown in Fig. 8(b). In the pair approximation conduction takes place in parallel channels corresponding to additive *admittances*, while in the CTRW case the *impedances* are additive, intuitively expressing the fact that charge carriers on the percolation paths have to overcome a sequence of barriers.

The random free-energy barrier model is essentially identical to Stevels’ and Taylor’s 1957 “random potential energy model” for glass ionic conductivity.^{21,23} This model was never generally accepted because it was thought to contradict experiment on two important points^{7,8,15}: It was believed that a model based on a distribution of energy barriers can never give temperature-independent loss peaks, and also that the BNN relation implies the ac conducting ions to have the same activation energy as those behind dc conduction. These objections are incorrect, however.¹⁹ If all barriers are equally likely, the jump frequency distribution is proportional to Γ^{-1} at all temperatures, yielding a temperature-independent loss peak, and there is certainly no problem in having a whole range of activation energies involved in the conduction process. Actually, from figures like Figs. 1 and 6 one can conclude that ac conduction *must* have a smaller activation energy than dc conduction. Thus, the experimental facts seem to more or less force one to base the theory for ac conduction on a distribution of energy barriers, where the dc conductivity activation energy is the maximum activation energy involved in the conduction process. Correspondingly, the loss peak frequency, which marks the onset of ac conduction, must be essentially the minimum jump rate in the solid: On a time scale larger than ω_m^{-1} the conductivity is frequency independent so the solid “looks” homogeneous to the quasi-particles. This can only come about if ω_m is the effective minimum jump frequency so that many jumps necessarily are involved for times $\gg \omega_m^{-1}$. Note that, since both

dc conduction and loss peak frequency are determined by the maximum energy barriers, the proportionality between $\sigma(0)$ and ω_m in the BNN relation becomes obvious from this analysis of experimental facts, without any calculation.

The random free-energy barrier model predicts a frequency dependence of $\sigma'(\omega)$ that is very close to a power law (Fig. 3). This may seem surprising since there is no power law hidden in Eq. (27), but it is just another illustration of the old truth that "anything is a straight line in a log-log plot." Because of this, care must be taken in deducing power laws from apparently straight lines in log-log plots, though it may still be convenient to discuss measurement and theory in terms of the "exponent" s .

At the end of Sec. II was listed in eight points the universally found experimental facts on ac conduction in disordered solids, and in Sec. IV it was shown that the random free-energy barrier model explains all eight points. Here we want to point out that these facts are not independent but closely interrelated, as becomes evident when they are discussed in light of the model. The fact that $\sigma'(\omega)$ has a temperature-independent shape implies that, at lowering the temperature, one measures further and further out on the master curve which is known to exist. Consequently, since $s(\omega) \rightarrow 1$ as $\omega\tau \rightarrow \infty$, the exponent s measured in a fixed range of frequencies converges to one as $T \rightarrow 0$. The BNN relation implies that $\sigma(0)$ and ω_m are proportional [apart from the factor of T^{-1} in $\Delta\epsilon$ (Eq. (33))]. Thus, if the temperature is lowered, the conductivity curve is displaced in direction 45° to the x axis in the log-log plot. It is now obvious that the ac conductivity is less temperature dependent than the dc conductivity and that, for exponents very close to one, the ac conductivity must be practically temperature independent. In particular, this is always the case at low temperatures.

The BNN relation implies a convenient scaling principle which allows one to construct a master curve from measurements at different temperatures at a fixed frequency. In the random free-energy barrier model, the scaling principle is reflected by the fact that the whole of $\sigma(\omega)$ is determined from a knowledge of the two numbers $\sigma(0)$ and $\Delta\epsilon$. Note that, experimentally, $\Delta\epsilon$ is usually not very far from one so it is possible to get a rough idea of the magnitude of $\sigma'(\omega)$ just from a knowledge of the dc conductivity: Putting $\Delta\epsilon \simeq 1$ in Eq. (30) we get $\tau \simeq \epsilon_0/\sigma(0)$ which, when substituted into Eq. (27), determines $\sigma'(\omega)$. In particular, at large frequencies Eq. (27) implies $\sigma'(\omega) \simeq \sigma(0) [\omega\tau/\ln^2(\omega\tau)]$ so a rough estimate of $\sigma'(\omega)$ here is

$$\sigma'(\omega) \simeq \epsilon_0\omega/\ln^2(\omega\epsilon_0/\sigma(0)). \quad (49)$$

To summarize the paper, an important point is the irrelevance of Γ_{\max} for $\sigma(\omega)$ in realistic situations. Letting Γ_{\max} go to infinity, one arrives at "renormalized" hopping models for which the pair approximation never becomes valid at high frequencies. In a sense the pair approximation is complementary to the renormalized CTRW approximation, as illustrated in Fig. 8. The frequency-dependent conductivity of the random free-energy barrier model is quite similar to that of a number of models discussed by Summerfield.⁴⁸ This supports the hypothesis of quasi-universality: All models based on a broad jump frequency distribution yield almost

identical $\sigma(\omega)$ in the $\Gamma_{\max} \rightarrow \infty$ limit. Thus, Eq. (27) is representative for many models. This equation is in reasonably good agreement with experiment. It seems, however, that the spread among experiments is larger than among theories and one cannot really say quasi-universality applies to experiments. More work has to be done to explain this. Since quasi-universality seems to apply among the hopping models described by Eq. (7), it is possible that these linearized models are too simple and that interactions have to be taken into account, including that due to Fermi statistics, to explain experimental deviations from quasi-universality.

The fact that all disordered solids have similar ac properties means that only little can be learned about a solid from measuring its frequency-dependent conductivity.^{32,48,64} Pollak and Pike have suggested that details of any particular conduction mechanism should be contained in deviations from linearity in the frequency dependence, i.e., from $s = 1$.⁶⁴ But as is clear from the model discussed in this paper, there are significant deviations from linearity 10 or more decades above the loss peak frequency, deviations that are solely a consequence of the low-frequency cutoff and which provide no important microscopic information. Tentatively, we instead suggest that details of any particular conduction mechanism in principle could be inferred from deviations from Eq. (27), which may be regarded as a zero-order approximation to reality, but more theoretical work is needed before microscopic details about the conduction mechanism can be inferred from the measured $\sigma'(\omega)$.

As regards the question of the best way to present data we recommend the use of $\sigma'(\omega)$. This quantity is fundamental, being directly related to the equilibrium current-current fluctuations.⁶¹ The use of the frequency-dependent dielectric constant has one virtue, though: namely, that it reveals loss peaks, the existence of which is crucial to prove that dc and ac conduction are indeed due to the same mechanism. The electric modulus is not recommended because this quantity mixes in effects of ϵ' which, if the ideas advanced here are correct, are independent of and unrelated to the ac conductivity. In the present approach, the total admittance is a sum of a hopping contribution and a purely imaginary dielectric contribution from the atomic polarizability (Fig. 9).

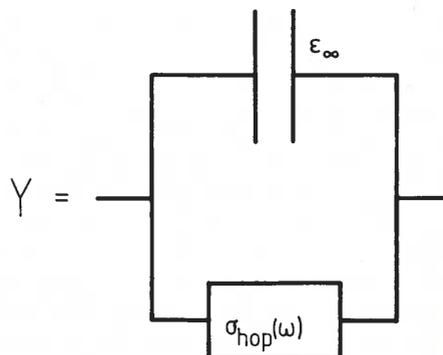


FIG. 9. Total admittance Y for a semiconducting disordered solid according to hopping models. The admittance is a sum of the hopping contribution discussed in the present paper, and a totally unrelated purely imaginary contribution from the atomic polarizability given by the high-frequency dielectric constant ϵ_∞ . If this picture is correct, the use of the electric modulus in representing data is inconvenient since it mixes in effects of ϵ' that are independent of, and unrelated to, the hopping admittance.

Finally, it should be emphasized again that an understanding of ac conduction and its relation to dc conduction is important, even if one is only interested in steady-state transport properties like dc conductivity, Hall resistance, thermopower, etc. From the present paper it seems it can be concluded that a whole distribution of energy barriers is involved in dc transport in disordered solids. Theories which do not take this into account are incomplete.

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