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Universality of ac conduction for generalized space-charge transport in ordered solids

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On numerous nonmetallic systems, the ac conductivity is observed to follow an approximate power law behavior \( \sigma(\omega) \propto \omega^s \) with \( 0 < s \leq 1 \). We show that the presence of nonlimiting, i.e., ohmic, contacts on the sample necessarily leads to these characteristics. The ac conductivity curves are obtained by the numerical solution of the complete set of time-dependent drift-diffusion equations. The calculated ac conductivity curves can be converted into quasuniversal master curves by application of the Taylor-Isard scaling law for an arbitrary temperature dependence of the mobility. Our results demonstrate that space-charge transport can lead to the commonly observed power law and scaling behaviors without incorporating disorder. Nevertheless, the implications of disorder are discussed and they are expected to increase the range over which the power law behavior extends.

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I. INTRODUCTION

The literature on ac conductivity in disordered solids and its scaling properties with temperature and composition is extensive and experiments have been performed on a wide range of semiconducting and insulating materials.1–14 The frequency dependent conductivity is characterized by an approximate power law behavior \( \sigma(\omega) \propto \omega^s \) in which \( s \) is observed to be \( 0 < s \leq 1 \). By rescaling the frequency dependent conductivity at various temperatures following Taylor-Isard scaling, master curves can be created that appear to be independent of the actual disordered material. In order to explain this ac conductivity and its universal character, many theories have been proposed in which disorder plays a leading role.14–16 As disorder on a microscopic level necessarily varies with material and preparation conditions, it is striking that these master curves seem to be independent of the details of the disorder. This is indeed a subject of controversy, though in the limit of extreme disorder14 and near the threshold of percolation,15 the validity of this proposition has been proven by theoretical modeling. Nevertheless, this merely shifts the argument of striking generality as either of these critical limits thus always seems to be achieved experimentally, despite the wide range of sample parameters for which the universality is observed.1–14

Although the implications of space charge are commonly included in the interpretation of \( I-V \) characteristics on insulating materials, this seems not to be the case in the field of ac conduction and only a few papers have pointed in this direction.3,17

In this paper, we will demonstrate that the use of the drift-diffusion equations in combination with a realistic model for the ohmic contact is in fact sufficient to obtain an ac conductivity that follows \( \sigma(\omega) \sim \omega^s \) with \( 0 < s \leq 1 \) and that obeys Taylor-Isard scaling. We will refer to this as the generalized space-charge limited conductivity \( (gSCLC) \) to contrast with conventional SCLC, in which diffusion is commonly neglected. As we only consider the case of constant mobility here, we tacitly assume the absence of disorder and conclude that the universality in ac conductivity on dielectric materials may be extended. However, as these result do not dispute the presence of disorder in the investigated materials, we discuss its implications and argue that both space charge and disorder are needed to provide a complete description.

II. DRIFT DIFFUSION

The drift-diffusion equations are widely used to describe semiconductor devices. The set of coupled partial differential equations is given by

\[ \nabla \cdot (\varepsilon \nabla \phi) = q(n - p - C), \]

\[ \nabla \cdot J_n = q(\partial_n, n + R), \]

\[ \nabla \cdot J_p = q(- \partial_p, p - R), \]

\[ J_n = q(D_n \nabla n - \mu_n n \nabla \phi), \]

\[ J_p = q(- D_p \nabla p - \mu_p p \nabla \phi), \]

where \( \phi \) denotes the electric potential, \( n \) and \( p \) are the free carrier concentrations of electrons and holes, and \( J_n \) and \( J_p \) are the electron and hole current density, respectively. \( D_n, D_p, \mu_n, \) and \( \mu_p \) are the diffusion coefficients and the mobilities of electrons and holes, respectively. \( C \) is the net doping concentration, \( R \) is the recombination rate, \( \varepsilon = \varepsilon_r \varepsilon_0 \) the permittivity of vacuum, and \( \varepsilon_r \) the relative permittivity that is assumed constant. Often, the Einstein relation for diffusion, \( D_{np} = k_B T / q \mu_{np} \), is assumed to hold, where \( k_B \) is the Boltzmann constant, \( T \) the temperature, and \( q \) the elementary charge.

Numerical solution of the above system of equations is far from trivial. In the 1980s, many conferences (NASECODE and SISDEP/SISPAD series) were held on the topic. The system of equations is singularly perturbed10 and highly nonlinear. Dedicated numerical methods have been developed to
solve the system, and they turn out to be essential for a robust and efficient solution. The Scharfetter-Gummel discretization scheme must be used to discretize the current densities, whereas damped Newton methods\textsuperscript{20} or nonlinear variable transformations\textsuperscript{20} are essential for the solution of the extremely nonlinear systems of discretized equations. A thorough description of all numerical methods used for semiconductor device simulation is given in Ref. 21, the simulations described in this paper have been performed using the software package CURRY, developed within the Philips electronics company.

In the calculations presented here, we consider only single carrier transport, a constant mobility, and $C$ equal to zero. Therefore, we are not obliged to assume any model for the recombination process, the field or density dependence of the mobility, the shape of the doping profile, and the temperature dependence of its ionization, which could limit the generality of our conclusions.

As only a small harmonic modulation is generally applied in admittance spectroscopy, we may linearize the time-dependent problem in the following manner:

$$
\frac{\partial}{\partial t}\vec{\nabla}^2 \phi_i = D \vec{\nabla}^4 \phi_i + \mu \vec{\nabla} (\vec{\nabla}^2 \phi_0 \cdot \vec{\nabla} \phi_i + \vec{\nabla}^2 \phi_i \cdot \vec{\nabla} \phi_i),
$$

where $\phi(x,t) = \phi_0(x) + \phi_1(x,t)$, $\phi_1(x,t) = \phi_1^0(x) \exp(i\omega t)$ for the case of single carrier (hole) transport and $\phi_0$ is derived from

$$
D \vec{\nabla}^4 \phi_0 + \mu \vec{\nabla} (\vec{\nabla}^2 \phi_0 \cdot \vec{\nabla} \phi_0) = 0.
$$

In the discussion below, we will refer to the terms in Eq. (2) (left to right) as the displacement term, the diffusion modulation, velocity modulation, and density modulation.

Similar equations, though with the diffusion terms omitted, have been solved analytically by Kassing\textsuperscript{22} and Shao and Wright.\textsuperscript{23} In the resulting analytical expression, the conductance drops to 2/3 of its steady state value at frequencies much higher than $1/\tau_t$, the reciprocal transit time. This has been called the transit time effect, and we will refer to this as the SCLC solution.

The boundary values that we choose to remain constant in following discussion are $\phi_0=0$ V and $\rho_0=1$ cm$^{-3}$ at the noninjecting contact and $\phi_i=1$ V at the injecting contact. Commonly, admittance spectra are determined at zero bias. However, comparison with the analytical description of the transit time effect becomes meaningless as the actual transit time is then defined as infinite. Below, we will show that taking $\phi_0=0$ V yields very similar results.

In case the diffusion currents are neglected, the logical second boundary condition at the injecting contact for SCLC is $-\vec{\nabla} \phi_i = E(0) = 0$. When including diffusion, it is more realistic to apply the free carrier density at the interface, $-\varepsilon/\varepsilon_0 \vec{\nabla}^2 \phi_i = \rho_i$, as the boundary condition

$$
\rho_i = n_{\text{metal}} \exp \left( -\frac{\Delta \phi}{kT} \right)
$$

with $\Delta \phi$ as the effective barrier height for carrier injection from the metal Fermi level into the transport level of the dielectric and $n_{\text{metal}}$ as the carrier density in the metal.\textsuperscript{25} As an ohmic contact is required to probe the bulk properties, $\Delta \phi$ must be small ($\leq 0.2$ eV) and $\rho_i$ may become unrealistically large, i.e., larger than the density of states (DOS) of the dielectric. Therefore, we set $\rho_i$ equal to the DOS. The temperature is set to 300 K.

III. RESULTS AND DISCUSSION

A. Approximate power law behavior

The solutions for the electric field and charge concentration divided by the relative dielectric constant, $\rho/\varepsilon_0$, for a dielectric layer of 10 $\mu$m in the space-charge configuration. The legend in (a) is identical to that in (b). The boundary conditions are shown in the inset: $\phi_{\text{app}} = \phi_i - \phi_0 = \phi_i$ and for $E(0) = 0$ and $E(0) < 0$, we choose $\rho_i = 3 \times 10^{13}$ cm$^{-3}$ and $\rho_i = 1 \times 10^{21}$ cm$^{-3}$, respectively. $E$ and $\rho/\varepsilon_0$ derived from the Mott-Gurney square law, $J_0 = 9/8 \varepsilon_0 \varepsilon_0 \phi_{\text{app}}^2 L^3$, are denoted as SCLC, with $J_0$ the steady state current density, $L$ the layer thickness.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1.png}
\caption{(a) Electric field, $E$, and (b) charge concentration divided by the relative dielectric constant, $\rho/\varepsilon_0$, for a dielectric layer of 10 $\mu$m in the space-charge configuration. The legend in (a) is identical to that in (b). The boundary conditions are shown in the inset: $\phi_{\text{app}} = \phi_i - \phi_0 = \phi_i$ and for $E(0) = 0$ and $E(0) < 0$, we choose $\rho_i = 3 \times 10^{13}$ cm$^{-3}$ and $\rho_i = 1 \times 10^{21}$ cm$^{-3}$, respectively. $E$ and $\rho/\varepsilon_0$ derived from the Mott-Gurney square law, $J_0 = 9/8 \varepsilon_0 \varepsilon_0 \phi_{\text{app}}^2 L^3$, are denoted as SCLC, with $J_0$ the steady state current density, $L$ the layer thickness.}
\end{figure}
As the gradient in charge density increases toward the injecting contact beyond the value given by the MG law, the diffusion current must be opposed by a drift current toward the injecting contact, which requires a negative electric field.

In Fig. 2, the normalized conductance and capacitance is shown as a function of normalized angular frequency \(\omega \tau\). The solid curve is calculated for SCLC and the dotted and dashed curve for gSCLC with boundary conditions as indicated in the inset and with \(\phi_{0\text{app}}=1\). In (c), the conductance for gSCLC and \(E(0)<0\), as in (a), is shown again on double logarithmic scale.

FIG. 2. Normalized conductance, \(G(\omega)/G_0\), and capacitance, \(C(\omega)/C_0\). (b) versus normalized angular frequency \(\omega \tau\). \(G_0=G(0)=9/4, \mu e \epsilon_0\Phi_{\text{app}}^{-3}\), the geometrical capacitance \(C_0=\epsilon_\infty \epsilon_0/L\) and the transit time \(\tau=(2L)^2/(3\mu\Phi_{\text{app}})^{1/3}\), where \(\Phi_{\text{app}}\) is set to 1 V. In (a) and (b), the solid curve is calculated for SCLC and the dotted and dashed curve for gSCLC with boundary conditions as indicated in the inset and with \(\Phi_{0\text{app}}=1\). In (c), the conductance for gSCLC and \(E(0)<0\), as in (a), is shown again on double logarithmic scale.

In order to gain more insight in the frequency dependence of the conductance, the solution for the time-dependent Eq. (2) is given for three frequencies in terms of \(-\nabla \Phi_{1} = E_{1}\) = \(E_{\infty}\) and \((-e/q)\nabla^2 \Phi_{1} = \rho_{1} = \rho_{\infty}\) in Fig. 3. With increasing frequency, the real and imaginary contributions to \(E_{1}\) and \(\rho_{1}\) start to diminish at the noninjecting side. Physically, this behavior results from the finite velocity of the charge carriers, which causes a decreasing penetration depth and, hence, a decreasing ability to screen external fields with increasing frequency. This ultimately leads to a charge response that is restricted to the injecting contact and, hence, a constant electric field \((\phi_{1}/L)\) in the remaining dielectric layer. Therefore, at high frequencies, the in-phase velocity modulation near the injecting contact \((-\nabla^2 \Phi_{1} \Phi_{\phi,1})\) is much higher in case of \(\rho_{1}=10^{21} \text{ cm}^{-3}\) than for \(\rho_{1}=3 \times 10^{13} \text{ cm}^{-3}\). Since the density modulation and the diffusion modulation decrease and finally vanish with increasing frequency, the velocity modulation becomes the dominating term in the conductance near the injecting contact at sufficiently high frequencies. This velocity modulation simultaneously induces a displacement current that becomes the dominating term away from the injecting contact.

In Fig. 4, we demonstrate the variation of the high frequency conductivity with charge density at the injecting contact. This shows that the occurrence of the calculated power law behavior does not critically depend on the charge concentration at the electrodes. However, the dependence of the saturation value of the ac conductivity on the charge concent-
Injection at the electrodes implies that admittance spectroscopy can, in principle, be used as a probe for the density of states.

**B. Taylor-Isard scaling and the BNN relation**

Taylor-Isard scaling has been applied in a number of experiments and reflects the time-temperature superposition that appears to hold generally\(^1\)–\(^14\).

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

Here, \(C\) is the Taylor-Isard constant and \(\sigma(0)\) is the conductivity at low frequencies. It is found that \(C\) is determined by the Barton-Nakajima-Namikawa (BNN) relation\(^{14}\)

\[
\sigma(0) = \rho \Delta \varepsilon \varepsilon_0 \omega_m,
\]

which gives \(C = \Delta \varepsilon \varepsilon_0\). This relation was observed for electric conduction on both ionically and electronically conducting oxide glasses.\(^{26}\) Here, \(\omega_m\) is the angular frequency at the relaxation peak, \(\varepsilon_0\) is the permittivity of vacuum, \(\Delta \varepsilon\) is the magnitude of the dielectric relaxation, and \(\rho\) is a numerical constant experimentally determined to be of order one. Recently, Sidebottom\(^3\) proposed a scaling that combined both laws.\(^{14}\)

The complex conductivity \(\sigma(\omega) = \sigma'(\omega) + i \sigma''(\omega)\) [both \(\sigma'(\omega)\) and \(\sigma''(\omega)\) are real valued functions of \(\omega\)] is calculated for increasing mobility and the real part, \(\sigma'(\omega)\), is shown at normal and scaled axes for zero bias in Fig. 5. This figure should emphasize the similarity with experimental curves typically obtained with increasing temperature. The proportionality of both \(\sigma(0)\) and \(\omega_m\) with \(T\) is clearly visualized and will be derived below. The typically observed Arrhenius temperature dependence in both \(\sigma(0)\) and \(\omega_m\) with similar activation energies is thus readily explained as in gSCLC, both quantities are proportional to \(\mu\), which normally follows an Arrhenius law. This implies that the time-temperature superposition property is obtained for any temperature dependence of \(\mu\) in the case of gSCLC transport. Here, we did not choose the scaling constant \(C\) to be proportional to \(1/T\) as is sometimes applied. In case the temperature range is limited \((T_{min}/T_{max} < 0.5)\), this will not affect the scaling property severely, and in this manner, we are not obliged to assume a Curie law for \(\Delta \varepsilon\).\(^{14}\)
Because of the various conventions used in the literature, it is interesting to recalculate our data as complex relative permittivity, which is defined as \( \varepsilon(\omega) = [\sigma(\omega) - \sigma(0)]/\omega \varepsilon_0 \). Here, \( \varepsilon(\omega) \) and \( \varepsilon'(\omega) \) are real valued functions of \( \omega \). This enables one to estimate the dielectric relaxation, also known as the dielectric loss peak, from the imaginary part of \( \varepsilon(\omega) \), \( \varepsilon''(\omega) \). In the lower panels of Fig. 5, \( \varepsilon''(\omega) \) is plotted on both the normal and scaled axes, in correspondence to Ref. 26. From this, we conclude that \( \Delta \varepsilon \) is independent of the mobility as can be readily understood since both \( \omega_m \) and \( \sigma(0) \) are observed to be linear in \( \mu \). From Fig. 5, we obtain \( \omega_m = 66/\tau_r = 5 \mu \phi_{\text{app}} L^{-2} \), when we use \( \phi_{\text{app}} = 1 \).

Now, starting from \( \sigma(0) = L d I_0/d \phi_{\text{app}} = L G(0) \) and by application of the MG square law, we obtain \( \sigma(0) = 9/4 \varepsilon_r \varepsilon_0 \mu \phi_{\text{app}} L^{-2} \). We observe that \( \Delta \varepsilon \varepsilon_r \), as the maximum of the dielectric relaxation scales with the high frequency conductivity by definition, which in turn scales with \( \varepsilon_r \) in the case of gSCLC. By combination of these results with \( \omega_m \sim \mu \phi_{\text{app}} L^{-2} \), Eq. (5) is derived for \( p \) equal to some numerical value.

One difficulty remains for SCLC though, as at zero bias the dielectric layer is entirely depleted and \( \sigma(0) \) becomes zero. However, for gSCLC, the diffusion causes the steady state charge density \( \sim -\nabla^2 \phi_0 \) to converge to a positive and finite valued function of \( x \), even when the applied bias is zero (see Fig. 1). Consequently, the conductance as calculated from the solution for \( \phi_1 \) in Eq. (2) for \( \phi_{\text{app}} = 0 \) resembles that for \( \phi_{\text{app}} = 1 \) V as can be seen by comparing \( G \) in Fig. 2(c) with \( \sigma \) in Fig. 5.

From Fig. 5, \( \phi \) is determined to be 2.1. This value is far from general as a variety of mechanisms may change the conductivity at both low and high frequencies as will be explained in the subsequent paragraphs. Only in the case of one blocking and one ohmic contact with well-defined sharp interfaces on microscopic level, injecting charge carriers in an otherwise completely depleted dielectric layer, this can be taken as a limiting value for \( \phi \).

So far, gSCLC transport has been considered, which gives rise to quadratic \( I-V \) characteristics, in contrast to the ohmic behavior that is typically observed for most disordered materials. By increasing the background and/or impurity doping concentration to the order \( \varepsilon_r \times 10^{12} \) cm\(^{-3} \), the ohmic contribution to \( \sigma(0) \) becomes dominant, while the high frequency behavior remains unchanged. Simultaneously, \( \phi \) is thus found to increase.

According to these calculations, the universality of ac conductance should include ordered solids as well. The somewhat stringent requirement is that the reciprocal transit time is in the probed frequency range \( 10^3-10^6 \) Hz. For organic crystals, typically having \( \mu \sim 10^{-3} \) cm/Vs, \( 10^3-10^6 \) Hz this means the sample thickness should be \( \gg 10^{-3} \) cm, which seems feasible.

In the calculations described above, we employ a constant mobility to demonstrate the ac conductance and scaling behavior in an ordered medium. However, disorder is known to have a significant effect on the mobility. In a number of publications, it was recently demonstrated that disorder may lead to a mobility that increases with charge concentration,\(^{27-29}\) Consequently, disorder, if present, leads to a mobility that increases toward the injecting contact, where the carrier densities are highest. The ac conductivity, which we have shown to be dominated by the velocity modulation in this region, may, in that case, extend over a larger frequency domain and cover a larger conductivity range than calculated here.

Finally, we should emphasize that the present results do not limit the validity of previous, disorder-based models for the ac conductivity. However, we feel that the space-charge effects discussed in this paper should be incorporated in a full description of the fascinating phenomena associated with ac conductivity.

### IV. CONCLUSIONS

In conclusion, we have demonstrated that space-charge dynamics can explain the approximate power law behavior that is commonly observed in ac conductance experiments on dielectric materials. Moreover, the numerically calculated ac conductance curves are shown to obey the experimentally observed scaling laws. For this, no specific mobility model nor any parameters reflecting unknown disorder need to be assumed. Therefore, the applied generalized SCLC model has general validity for admittance spectroscopy on dielectric materials, irrespective of the presence of disorder. However, we expect that a full understanding of ac transport in dielectrics requires a simultaneous description of both space charge and disorder.

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J. C. Dyre and T. B. Schröder, Rev. Mod. Phys. 72, 873 (2000), and references therein.