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Electronic Transport in Organic Materials: Comparison of Band Theory with Percolation/(Variable Range) Hopping Theory

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Percolation theory or hopping theory, used to describe the electronic behavior of devices, is very popular in the chemistry-dominated research area of organic electronics. The reason is that chemists think in units ("moieties") such as the phenyl ring in a polymer, with specific energy levels (for instance the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO)), and conduction of charge is considered a perturbation to the molecular electronic levels. A typical organic semiconductor consists of a one-dimensional chain — the conjugation backbone — along which current is visualized. Thinking in terms of conduction paths seems very natural and three-dimensional conduction in terms of "hopping" to neighboring conjugation segments seems an obvious approach. Charges reside on specific sites and only occasionally make a jump to neighboring units. This way of thinking has successfully described the low-conductivity end of the spectrum of organic materials, those materials that people imagine when they think of "plastics".

The success of the percolation/hopping theory manifests itself in the easy explanation of some often observed phenomena, such as the following: i) Temperature-dependent charge-carrier mobility, see for instance the work of Mott (and his famous variable-range hopping equation: conductivity proportional to $\exp[-(T_0/T)^{1/4}]$, with T the absolute temperature and T_0 — like all T_i in this work — a constant),[1] Shklovskii[2] (who changed the exponent in the Mott equation to $\exp[-(T_1/T)^{1/2}]$), and Aharony et al. (any exponent in between).[3] See also the numerical simulations by Bässler.[4] ii) Bias-dependent mobility, or, better, field-dependent mobility. iii) Anomalous transients, described as the observation that the as-measured time-of-flight (ToF) carrier mobility depends on the sample thickness, also explained as the power-law behavior (to be discussed later). Indeed, these observations are often seen as proof of the validity of the percolation/hopping theory. However, consistency of a certain model to the data alone is not good enough to prove the model, since there can be many models that do the trick. We have to highlight the divergence between the existing models and design a way to arbitrate between them. Moreover, the winning model has to make sense and be simple, and not only be a set of mathematical equations, never mind how powerful in describing reality. For that we have to discuss them a little more. There is no use in going into a lot of detail, also because there are nearly as many models as there are publications in the literature or measurement sets, but also because we will get bogged down in equations. Yet, it is useful to introduce the models globally, the families of models that is. That is the scope of this Essay. The equations will be kept here to a minimum.

The (variable range) hopping (VRH) theory is based on the idea that charges are localized but can every now and then jump ("hop") to another localized state. The probability of hopping between two states of spatial separation R and energy separation W is given by[5]

$$P(R, W) = \exp\left(-a R - \frac{W}{kT}\right) \qquad (1)$$

with k Boltzmann's constant, and a a constant. The total conduction can then be found as the integral over all energy states and distances, which can be worked out into the previously mentioned Mott equation or Shklovskii and Éfros equation when a particular state distribution and dimensionality is used. Note that the original theory was not intended to be used for conductive materials. Mott had a dilute system in mind, or based it on such a system. As he himself wrote: "The process is similar to 'impurity conduction'",[1] or Shklovskii and Éfros: "we use mainly hopping conductivity of weakly doped semiconductors".[6] Such materials are of low conductivity, where the conduction takes place by hopping between distant, localized states. It is questionable whether the theory can be transposed to any low-mobility material — materials that superficially seem to behave the same, but intrinsically are very different — as is conventionally done by the organic materials community. The localized states — conjugated segments in organics — are in fact adjacent in amorphous materials and conduction takes place between states of the host, not via dilute impurity levels. It is questionable whether the application of Mott's idea to amorphous materials, as done by Ambegaokar et al.[7] and picked up by many others, is justified, even if it is mathematically correct and is consistent with the experimental data.

Percolation theory is closely related to VRH theory and is often mentioned in one breath ("the transport of current in a disordered system with localized states, which is realized by hopping of electrons from one state to another, should be regarded as a percolation process"[6]), something that we will also do here in this Essay. The reason is obvious when we take a look at what goes on in the hopping regime. The effective hopping radius, the distance R where the hopping for available energies is still reasonably possible for a certain temperature T, can be calculated, and this thus results in a sphere around the impurity that is effectively conductive. There then exists a critical radius where the spheres marginally touch each other, thereby forming a network of interconnected conductive material spanning the entire sample through which current can marginally percolate,[8] just like water can percolate through

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the marginally interconnected pores in a ground-coffee-bean powder. For this reason, the names percolation theory and VRH theory are often fused. See for instance the pioneering work of Shklovskii and Éfros[6] or the review by Tessler et al.[9] on percolation/hopping theory.

Serious doubt was already shed on the validity of these theories for conductive organic materials by Rakhmanova and Conwell[10] (energies need to be correlated), Waragai et al.[11] (exponent is simple Arrhenius behavior, $\exp[-(T_2/T)^1]$, that is, outside Aharony range), Nelson et al.[12] (not thermally activated, $\exp(T^0)$, i.e., outside Aharony range), among others, who prefer, for various reasons, the Poole–Frenkel formalism, which consists of (conduction and valence) bands supplemented with trap states. As an example, the Vissenberg VRH/percolation analysis of the transistor[13] is predated by the Shur and Hack analysis using band theory,[14] which yields more-or-less the same results. This sheds some doubt on hopping theory for conductive materials.

Indeed, modern conductive organic electronic materials are not necessarily also best described by low-conductivity theories. An alternative to percolation/hopping theory is band theory, which is in fact much older. In this theory the individual energy levels of the unit cells — as they are now called — are irrelevant and only the band diagram of the entire crystal is of importance. The Schrödinger equation is solved for the crystal, which has Bloch waves as solutions, as we know from solid-state physics lectures. Because of the high level of delocalization and reduction of time spent on individual sites, a charge no longer belongs to a unit but rather to the entire crystal, resulting in an energy band structure. Moreover, for describing electronic conduvction, this entire band structure is summarized by two discrete levels (and an effective mass). We call this semiconductor-(device)-physics band theory; see for example the book by Sze.[15] The first battle is thus won by band theory: Where there are often many theories that can explain data, the simplest model should be preferred. Without doubt, band theory is the simplest of them all. According to page 14 of the above book, electronic levels of the host are summarized as N_V (full) levels at energy E_V and N_C (empty) levels at energy E_C, the valence and conduction bands, respectively. Yet, in spite of its simplicity, it explains the workings of all semiconductor devices as shown in the next 800-plus pages of the book. The question is, can the same theory also be used for organic (amorphous) electronic materials? Yes, it can. With some modifications, namely the addition of trap states.

As a direct bonus of band theory, the often observed field-dependent mobility of the form

$$\mu \propto \exp\left(\frac{1}{kT}\sqrt{\frac{E}{E_0}}\right) \tag{2}$$

(E is electric field, $E_0 = \pi\varepsilon/q$, ε the permittivity of the material, and q the elementary charge) results directly, since placing the effective-mass hydrogen-like Coulomb potential of a discrete trap on an inclined potential slope of a constant field will lower its thermal ionization barrier on one side by exactly $\sqrt{E/E_0}$, as shown by Frenkel nearly a century ago in a one-page comment,[16] beautiful for its sheer simplicity.

Figure 1 and **Table 1** summarize the various conduction models, ranging from hopping, where only trap states exist and charge has a small mobility in the form of infrequent hops, to the Poole–Frenkel formalism, where traps states capture a large part of the charge, fixing it in place, and conduction occurs by temperature- and field-assisted excitation from the trap to conductive bands (the model is also often called multi-trap-and-release, MTR for short), and to the pure crystal models that have no impurities and where the mobilities reach the upper-limit value of the bands. For completeness sake, also the hybrid-model dual-formalism of a (distant) band combined with direct (variable range) hopping is given, which is often used in low-conductive inorganic semiconductors such as non-stoichiometric GaAs.[17]

The band theories were derived for crystalline materials because, apart from their superior performance, by using crystals science progressed more rapidly; crystal-growing communities could spend their time on optimizing the crystalline quality and purity, while a community of experimental researchers and theoreticians worked on describing them, with the interaction between these groups essential for the accumulation of knowledge. In fact, this focus on pure and crystalline materials initially meant putting semiconductors aside as being of no interest to the solid-state physics community because their behavior, as we all know, depends too much on the purity of the material. Important to note, the fact that the theories were developed and tested with crystalline materials does not mean that they are valid *only* for crystalline materials. It had already been pointed out long before the advent of the new wave of organic research that crystallinity is in no way needed to give a material semiconducting (band) properties. As shown by Ioffe, Regel, and Gubanov: "A periodic electric field of the lattice is not essential for the occurrence of typical semi-conducting properties and the band model may be applied also in the case in which there is a loss of periodicity of the lattice" (a citation from the work of Caserta et al.[18]). In other words, the fact that most organic electronic materials are in the amorphous state does not by itself warrant them a special treatment. Obviously the non-crystallinity lowers their performance, but the electrical description can remain basically the same. In our research we have thought along these lines: "It walks like a duck, it talks like a duck, so it is a duck". In practice we have worked out that using band theory, with the inclusion of traps in the model, as in Poole–Frenkel/MTR, gives no problem whatsoever in describing all the organic electronic materials and devices, summarized in
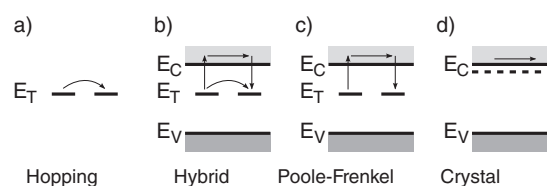

Figure 1. (N-type) conduction models from Table 1. a) Hopping/percolation. Conduction consists of infrequent jumps from one localized state to another. b) Hybrid (hopping + Poole - Frenkel). c) Poole - Frenkel (MTR). Conduction consists of charge being promoted to delocalized levels, where it can move freely. d) Crystal/band theory. Conduction occurs in the conduction band (for electrons). The dashed line is a donor level that supplies the surplus of electrons but plays no further role.

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Model	Band		Trap	
	DoS	mob.	DoS	mob.
VRH/percolation	0	–	N_T	μ_t
Hybrid	N_C	μ_n	N_T	μ_t
Poole - Frenkel/MTR	N_C	μ_n	N_T	0
Crystal	N_C	μ_n	0	–

the book *Electrical Characterization of Organic Electronic Materials and Devices*.[19] This includes the phenomena mentioned above: temperature-dependent mobility, bias-dependent mobility, and anomalous transient effects. A temperature-dependent mobility, for instance, is caused by the temperature-dependent thermal-equilibrium ratio of trapped and free charge. The effective mobility is the weighted average of band mobility and trapped mobility: If 10% of the charge is free and 90% trapped, then, because the mobility of trapped charge is, by definition, zero, this results in a reduction of a factor of ten relative to the band mobility. Similarly, bias and associated Fermi-level shifts can have a different effect on the occupancy of traps and conductive states, because they are differently distributed in energy, and hence a bias-dependent mobility results. Moreover, all kinds of transient effects on all time scales occur because the relaxation times for establishing thermal equilibrium depend exponentially on the energy gap being bridged by the capture and emission of charge at and from traps. **Figure** 2 shows the modified band diagram presented by Shur and Hack,[14] which includes trap states and conduction states exponentially distributed in energy, that was successfully used to describe the electronic behavior of amorphous materials such as a-Si and most organic materials.

Now that the theories are introduced, the reader will probably ask the very pertinent question that easily springs to mind: If crystalline materials are irrefutably described by band
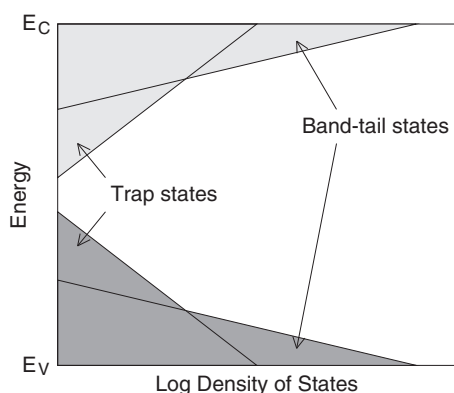

Figure 2. Band diagram of amorphous semiconductors (after Shur and Hack[14]) with conduction levels ("tail states" of conduction and valence bands, arbitrarily positioned at E_C and E_V, respectively) and trap levels exponentially distributed in energy. This results in bias- and temperature-dependent as-measured mobilities[19,20]

theory and amorphous materials supposedly by hopping theory, then where is the magic delimitation? What is the degree of amorphousness (randomness) that will make us need to use hopping theory instead of band theory? While the scientific community likes to express this demarcation in a value for the mobility (say about 10^{-5} cm^2 V^{-1} s^{-1}, a number that makes sense somehow, since the mobility is related to average time spent on a site and via Heisenberg's Uncertainty Principle to the width of the energy levels — yet, Heisenberg does not relate time Δt to space Δx), the question is whether this demarcation is needed. How can it be, for instance, that the same material pentacene when crystalline has high mobility and in amorphous form has low mobility (some six orders of magnitude different). If charge is trapped on pentacene's benzene rings, as hopping theory tells us, it is trapped on the benzene rings regardless of the crystallinity of the material. The long-range order should not matter (hopping to a rotated, differently oriented molecule is not expected to be of significantly lower probability, certainly not six orders of magnitude). It cannot be the amorphicity that lowers the mobility. Let us take this thought a little further. Amorphous materials differ only very slightly from their crystalline counterparts, chemically. Take the example of amorphous and crystalline silicon. *Both* have covalent bonds, formed by sp^3 hybridization. In amorphous silicon there is some sp^2 hybridization, but this is not even very common. As Clark writes in his analysis of ab initio amorphous silicon and carbon calculations: "It is found that most atoms are four-fold coordinated [...] while only a few atoms are either 3 or 5 fold coordinated."[21] The material is less dense, but only slightly so (about 5%,[22] not enough to seriously reduce wave function overlap), nor has the density a large impact on the electronic structure: "A relatively large change in density and structure does little to change the electronic nature [band structure] of the samples".[21]

If they are chemically similar, why not physically (electrically) as well? Remember that those covalent bonds, the interactions between atoms, are the origin of the formation of band structure and delocalization. Where have the bands in hopping theory gone? The description of amorphous materials without the inclusion of bands does not make sense. Nor did the originators of hopping theory neglect them. The classical work of Mott, for instance, included, apart from the dilute hopping levels, also the conduction and valence bands.[1] By treating only extreme low temperatures, these bands were made irrelevant by the fact that thermal excitation to these conductive band states becomes energetically too expensive at these low temperatures. This treatment cannot be applied to amorphous materials, not to the intrinsic conduction of amorphous materials themselves. This needs further explanation.

What makes the amorphous materials differ from crystalline materials is that, apart from the covalent bonds, the material also has unbonded — or rather under-bonded and over-bonded — atoms with unpaired electrons. Or, in other words, apart from the existence of delocalized states it also possibly has localized states, traps, and they can be very abundant indeed (on the order of percents). This is the idea of modified band theory (Poole–Frenkel, or MTR). Also, both types of states can be distributed ("randomized") in energy, as in Figure 1, based on the ideas of Shur and Hack.[14] In this theory, the degradation of mobility is explained by the continuous increase in trapping

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centers caused by the introduction of non-perfect interaction bonds between moieties, viz. the dangling bonds in amorphous silicon, well known to be electrically active mid-gap trapping centers. Whereas a crystal has 100% conductive states and 0% trap states, resulting in a high effective mobility equal to the unperturbed band-mobility given by effective mass theory, amorphous material has more trap states, with the band getting less weight in the effective mobility, and the band mobility itself is also lower because of the increased defect scattering; the overall mobility can be orders of magnitude smaller, *without* a necessary change in conduction model. It is a continuous effect, easily spanning many orders of magnitude.

Note the very important feature of the energy diagram of amorphous materials (Figure 1) that the trap states are resonant and overlapping with the conductive states. It is thus not possible for *any* temperature to neglect one or the other, as is done in hopping theory. The band states are there *and* they play a role in amorphous materials. The work of Mott and hopping theory in general have been taken out of its scope and erroneously applied to intrinsic conduction of amorphous materials.

We can now look at some devices and measurement techniques. The most popular device in organic electronic research is the thin-film transistor (TFT). The reason for its popularity — apart from the need for full-plastic electronics that necessarily include a switching ("control") element — is that on the one hand it is the most easily fabricated (just smack your active material on top of a pre-structured FET substrate of gate, insulator, and drain–source electrodes and you're off) and on the other the device works for seemingly all materials (actually, we have argued that a TFT *does* work for virtually all materials[23]) and is thus an ideal developer's playground and material testbed. While the devices behave very much like a metal-oxide-semiconductor field-effect transistor (MOS-FET) and MOS-FET modeling for TFTs is common in the literature, upon closer scrutiny they merit their own treatment (the main topic of my book on the subject of organic electronic materials and devices[19]). The fact is that they are very easily described by band theory. Both non-linearities in transfer curves (current vs. gate bias, I_{ds}–V_g) and output curves (current vs. drain bias, I_{ds}–V_{ds}) can be explained in the framework of band theory if (abundant) traps are included.

The gate-bias-dependent mobility (empirically determined to be of the form $\mu \propto V_g^\gamma$, with γ a temperature-dependent constant) is a good example. If both the trap states and band states are exponentially distributed in energy (although with different energy constants), and the *total* gate-induced charge (both trapped and free) is a linear function of the gate bias ($\rho = -V_g C_{ox}$, with C_{ox} the oxide capacitance), the *free* charge (and thus the current in the "linear" regime) follows a power law.[20] The mobility, being defined as the derivative of this transfer curve, is then also a power law (with exponent 1 less).

Moreover, the non-linearities in the output curves (current vs. drain-source bias) are the direct result of the previously mentioned Poole-Frenkel concept that mobility depends on the electric (drain–source) field in the presence of traps. An exponential (supralinear) rise in current is observed in the linear regime. There is no need for the philosophically difficult-to-justify[24] "contact effects" that percolate the literature. The conclusion is

that the thin-film-transistor behavior is very well described by band theory.[25]

We move on to the next topic. A powerful tool for the determination of the conduction model is the transient effect, or the "evolution" of the system. In crystals, a simple transient following the first-order differential "master equation", for instance the system with 100% of the charge at time zero trapped on a discrete trap, will show an exponential decay of trapped charge with a time constant that is thermally activated, approximately $\tau \propto \exp(E_A/kT)$, with E_A related to the trap depth. This is the basis for transient techniques to obtain the "fingerprint" of impurities, such as the deep-level transient spectroscopy (DLTS) technique,[26] that are very popular in semiconductor characterization.

Organic materials do not follow nice exponential transients. Theoretically derived, or empirically determined, they are either power-law or stretched exponential,

$$\propto t^{-\alpha} \tag{3}$$

$$\propto \exp[-(t/\tau)^\beta] \tag{4}$$

respectively. The observation of the stretched exponential goes as far back as 1847, when Rudolf Kohlrausch started writing his papers on the subject.[27] The problem with the stretched exponential (and related functions) is that they are basically only empirical; all the functions are the result of empirical fitting rather than theoretical analysis. Note that the same applies when the relaxations are measured in the frequency domain, that is, in admittance spectroscopy: "Almost all the experimental data has been represented in terms of empirical fitting functions. Two such [functions] are the Cole–Davidson and Williams–Watts function."[28] On the other hand we have the power law (or Pareto distribution or Zipf's law, the more common names in economics and sociology), which seems to be related to "countable" stochastic objects (number of earthquakes with certain magnitude, citations of papers, etc.), but also finds theoretical examples for more continuous phenomena.[29] With these two classes of functions seemingly mutually excluding each other, this offers us the prospect of shedding light on the conduction mechanism. However, nature has more tricks up its sleeve to confuse us.

Let us go back one step to explain this. In my book I made a strong case for the power law, since this more-or-less follows from the simple idea of making a convolution of simple mono-exponential transients;[19] the same band theory, with exponential distributions of the relevant energy levels that proved to be highly effective in explaining the behavior of nonlinear transfer and output curves in TFTs[25] presented above, was used to describe the transient behavior and the overall idea was that power laws should result. See also the work of Newman[29] describing the power law, where he explains how the power law results from a combination of exponentials. In other words, a simple continuation of the band theory readily explains power-law transient behavior. A single formalism of band theory with abundant traps manages to explain a wide range of phenomena in a wide range of devices and measurement techniques.

Yet, here percolation theory also predicts power-law transients (see for instance the time-of-flight theory of Scher and

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Montroll[30]) or the excellent percolation description in the work of Newman.[29] Thus, we have a stand-off and the unfortunate situation where experiments cannot arbitrate between models. This is especially unfortunate given the fact that in *practice* stretched exponentials are more commonly observed in evolution experiments. See for instance the transistor reliability summary by Sirringhaus, that reports a stretched exponential.[31] It seems that in this case both theories fail instead of both being correct.

However, there is an easy explanation that puts everything into place. At least for the band-theory approach. Remember that in band theory the convolution of simple exponential transients results theoretically in a power-law transient. Now, for the power law to result, we need an infinitely ideal system.[32] For instance, it needs a mathematically perfect distribution of levels that stretch from plus to minus infinity in energy. It needs the system in a well-defined "steady state", etc. In practice this is not attainable. Such systems do not exist in nature. "In any finite critical system, it is well known that the power-law description must give way to another regime".[32]

This is also represented in our power law. The underlying idea is that for instance the "average" energy of the levels, as found by an integral over all energies, should be converging ("alpha stable") to result in a finite value. The density of states used in the work of Shur and Hack (Figure 1) is far from alpha stable; the integral of the DoS is infinite. In the more-realistic non-mathematically-ideal case, the power law is transformed into a stretched exponential, as reasoned by Trzmiel et al.[33] In fact, *any* distribution of relaxation times will result in a stretched exponential, as a result of the central-limit theory: for large numbers of samples, any distribution will behave as a Gaussian distribution. Only those that are not integrable will escape this fate. This explains why stretched exponentials are experimentally observed and power laws theoretically predicted. Most theoretical scientists work with "ideal" systems that easily include energy distributions and relaxation-time spreads that go to infinity. In practice, the convolution of mono-exponential relaxations, as used in band theory, will wind up being measured as a stretched exponential.

Interestingly, the conclusion that any system that has distributed properties (relaxation times, energies, etc.) will behave as a Gaussian-distributed system is relevant in view of the work of Bässler, who described all organic materials as "Gaussian" and manages to explain everything with his stochastic models. In view of the above, the behavior as a Gaussian system does not mean that the system is normally distributed. It just means that the distribution is alpha stable and has a finite integral. In other words, that it is a physically real system and not just somebody's analytical thought product; any real, tangible, measured object is finite in all respects. It should be noted also that the resulting theoretical behavior, the power law $t^{-\alpha}$, does not itself have an integral from zero to infinite time, making it an awkward beast in any case (imagine the time-of-flight current that does not integrate to a finite charge), whereas the stretched exponential does have a nicely converging integral. The integral of Equation 4 is[34]

$$\int_0^\infty \exp[-(t/\tau)^\beta] \mathrm{d}t = \frac{\tau}{\beta} \Gamma\left(\frac{1}{\beta}\right) \tag{5}$$

which is finite for positive β, while the integral of Equation 3 is infinite,

$$\int_0^\infty t^{-\alpha} \, \mathrm{d}t = \infty \tag{6}$$

The above discussion explains why the stretched exponential has only empirical and stochastic (i.e., Monte Carlo simulations) observations, where necessarily finite systems are used, since there is no clean theoretical or analytical justification for it. Yet, it follows easily if we treat the behavior as a convolution of transients, that is, band theory with abundant traps, and consider the above formalism presented by Trzmiel et al.: "The stretched-exponential function is equal to the weighed average of an α-stable effective relaxation rate. The latter is a consequence of the broad distribution of individual rates."[33] It remains to be seen if the theoretical power-law behavior can also easily be converted into a stretched exponential in the framework of percolation theory. For the moment this can be seen as a good argument for band theory.

On closer inspection, there seems to be a general problem with the transients in the framework of hopping theory. Note that there are basically two kinds of transients: i) "movement transients", where charge is created on one side of the sample (for instance by a light pulse) and the charge moves across the device, and ii) "relaxation transients", where the current slowly dies out under DC conditions. The first type of transients are easily explained by hopping theory (and band theory alike), for instance in the ToF measurements.[30] However, for the second type of transients there is a fundamental problem. Why should hopping theory give a relaxation transient at all? In band theory it is obvious why. Charge is injected into the material and this is necessarily into delocalized states (well, it moved, didn't it?). These charges, starting off in the delocalized states ("bands") are slowly captured by localized states ("traps") from where they cannot contribute to current anymore; the current is ever decreasing until thermal equilibrium is reached with trapped charge and mobile charge following a Fermi–Dirac distribution. For hopping theory, there are no delocalized states and charge is directly inserted into the localized states, that is, there is never going to be a relaxation. At best there will be relocation of the charge from one type of localized state to another, but this is exactly the same phenomenon as the transport of charge; transport in energy is transport in space. While hopping theory can explain the behavior of the bulk in the steady state, it cannot easily explain the behavior of the entire device (with contacts and injection) and the relaxation effects.

Also interesting to note, and relevant for the current discussion on relaxation transients, is the Weibull statistics. This is a distribution function that is often used to characterize failure rate, for instance in electronic components. In fact, Weibull is the most widely used distribution in reliability and risk assessment.[35] The distribution is given by

$$f(x) = \frac{k}{\lambda} \left(\frac{x}{\lambda}\right)^{k-1} \exp\left[-(x/\lambda)^k\right] \tag{7}$$

for $x > 0$ (and 0 otherwise), with x for example representing time t and λ a scaling parameter.[36] This has three possibilities: If $k = 1$, the failure probability is constant, and the "survivors"

follow an exponential decay, as in nuclear decay processes; a specific surviving member has a probability of failure that is constant over time. For $k < 1$ there is "infant mortality", with survivors having ever less chance per unit time of failing. On the other hand, for $k > 1$ there is an aging distribution, the failure probability increasing with time. What makes this relevant for the current discussion is that the integral of the failure rate — or in other words the survival fraction — with a Weibull distribution gives the stretched exponential. (Note that these statistics are for finite systems.) The Weibull statistics idea can be mapped onto the organic conduction system. Trapping of charges from the conductive band to localized trap states can be seen as failure (to conduct). Even without knowledge of the underlying mechanism of trapping, the "empirical" Weibull statistics then results in a stretched exponential.

A final remark on transients. If we assume that the transients are the result of convolutions of simple exponentials, we can reverse the convolution, in what is called an inverse Laplace or Fourier transform, and find the distribution of time constants, and inverse-Laplace-transform again (assuming the time constant depends exponentially on the energy depth) and find the associated density of states (DoS). (Which sounds easier than it is, it being an ill-conditioned problem.[37]) The interesting thing is that such distributions and such forward and inverse transforms, when expanded and approximated, will result in equations containing tell-tale "unphysical" sine terms,[38] often encountered in the literature, see for example the work of Shur and Hack (specifically Equation 8 of that reference).[14] Unphysical in the sense that it falsely suggests "periodicity", by having terms like $\sin(\pi T/T_2)$. Remember that these theoretical works are only approximations (for instance $T \ll T_2$) resulting from applying mathematical tools to the physical problems.

We abandon here the transients and present another argument. Recently we reported in this journal on a puzzling device with intriguing behavior. Upon retrospect, this is very relevant for the discussion on the conduction mechanism. It consists of a TFT in which the active layer was formed by a metal, namely gold.[23] This was the direct result of extrapolating the theory of representing the TFT as a two-dimensional device, a basic ingredient of our description of organic accumulation TFTs.[25] As such, we were not surprised to find that the device indeed works as a transistor, with a drain–source conductance programmed by the gate bias. Apparently, the material does not even have to have semiconductor properties to behave as a (typical) semiconductor device. In fact, the behavior of the metal transistor is very similar to any run-of-the-mill organic transistor. Similar modeling is thus justified. What is puzzling, then, is the fact that the device can conduct even without a continuous path from source to drain. Currents in the microamp range were observed for devices in which the coverage by gold consisted of clearly isolated islands. While we are still puzzled by the exact results, this aspect is incompatible with percolation theories.

To explain this we have to take a closer look at percolation theory; see for instance the section "Phase transitions and critical phenomena" of the paper by Newman for a good introduction.[29] If we divide the two-dimensional surface of our TFT device into squares (the number and the size of these squares are irrelevant; percolation theory and power laws in general

have the property of being scale-free[29]), then, in the framework of percolation theory, a square can be either conductive or not. Clusters of continuously connected adjacent conductive squares will be formed. Obviously these clusters will be bigger the more squares are conductive. For 0% conductive squares, there will be no cluster whatsoever, while for all squares being conductive a single cluster exists that is made up of the entire surface. There is now a critical value for the percentage of conductive squares that make a cluster marginally span from one end of the device to the other, that is, an infinite conducting cluster size. This critical percentage is well known and can be calculated to be 59.27462…%. Note the accuracy. In percolation theory this is the critical limit. We expect the current to shoot up from that moment on.

Our TFTs with various levels of coverage (0%, 30%, 50%, 65%, 75%, and 90%) are then an excellent testbed for percolation theory. We assume that gold is a good conductor and a square with gold is conductive, whereas uncovered silicon oxide is assumed to be made of insulating squares. The doubt about percolation theory is: How can there be substantial current well below the critical coverage of 59%? The current from 50% coverage to 75% coverage only increased by a factor of three; in fact, in the entire range of devices the current rises continuously and gradually. No form of criticality is observed.

A device *visibly* without a continuous path is obviously below the percolation threshold. In the conventional percolation analysis, it consists of a network of disconnected resistances; no current should be possible. One of the strong points of percolation theory is that one can visualize what goes on in the device. Apparently not. If this is lost, the support for the theory is lost. The (visible) absence of a physical path while the currents continue in a "business as usual" way, without any signs of criticality, strongly undermines percolation theory. For band theory there is no problem. The bands are the result of interacting energy levels. These interacting entities apparently do not necessarily have to touch each other, as long as they have overlapping wave functions. (There remains only the puzzlingly large distance at which it apparently still works.) We thus consider the result of the metal transistor as an indication that band theory is more likely to be correct than percolation theory, while obviously still a great deal of research has to be done before a final conclusion can be reached.

As an example, it is puzzling how in band theory the conductivity and the transient time can depend on the sample thickness, often reported in the literature.[30] A reason might be that for thin devices the MTR approach used in band theory is no longer valid. In reality the device may be better described by few-trap-and-release,[19] and this might manifest itself in a sample-thickness dependence.

Of course, everything may be a matter of mere semantics. Hopping theory and band theory might blend into the same thing, some kind of Grand Unification Theory for electronic conduction. As Tessler writes in his summary on electronic conduction in organic materials: "The conceptual leap in understanding transport in disordered media is realizing that current can also be the result of charge transport through localized states."[9] This might be true, but then it amounts to a contradiction in terms; current being by definition delocalization,

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the above statement is equal to saying "delocalization takes place through localized states". The truth is that when hopping occurs frequently and mobility is large, the localized states (traps) form a band and we are back to band theory. This is in fact what happens to conductive disordered materials, in our opinion.

In summary, in our opinion, if current is not a perturbation but a significant feature, as in electronic devices, band theory should be used. There is no need for new theories. If it conducts, band theory is good. In other cases, when only minute currents are present, in non-electronic materials or doped crystalline materials at extremely low temperatures, percolation/hopping theory might be a better description. Since electronic materials for modern electronic devices – the focus of this journal – fall necessarily in the conductive range of the materials spectrum, they are more adequately described by band theories. We do not consider this a closing argument to end the discussion, but this Essay rather points out that there exists an alternative explanation besides the more often used percolation theory for the behavior of organic electronic materials.

Acknowledgements

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