HOPPING CONDUCTION

Electrical conductivity in amorphous materials is described as a sequence of hops in which an electronic charge moves stochastically between localized states. This article discusses the nature of the disorder which leads to localization, the mechanisms which govern the microscopic hopping process, and the consequences for the electrical properties of various amorphous materials. Transient photo-induced currents are used to determine the dependence of charge carrier mobility on temperature and the applied electrical field. The results obtained through such experiments are discussed in terms of theories which account for the randomness both in the energy of the electronic states and in the transition rates between states. Finally, a summary is given of several technologies which depend on materials exhibiting hopping conduction.

Electrical conduction in crystalline solids (1), including most metals and semiconductors, can be described in terms of a gas of charged particles, electrons, moving in response to an electric field. The medium in which this gas moves is the lattice of positive ion cores consisting of the atomic nuclei plus their tightly bound remaining electrons. In classical terms, we think of the particles as moving ballistically between collisions with defects in the lattice and with ion cores which are displaced from their equilibrium positions by thermal agitation. During the time between collisions, the electrons are accelerated by the electric field, but the collisions, on average, dissipate the velocity gained; that is, the electrons are equally likely to be scattered in the direction opposite to the electric field as with it. In this picture, the concept of "mean free path" arises quite naturally as the average distance traveled between collisions.

The quantum mechanical description of the conduction process is quite analogous to the classical one. There are many subtleties which will be ignored here in order to highlight briefly the essence of the quantum physics. One describes the electrons in terms of their wavefunctions. Because of the translational symmetry of the crystalline lattice, the wavefunctions are Bloch waves; that is, they have a component which reflects the underlying symmetry of the lattice, but otherwise, they have the characteristics of plane waves propagating freely in space. The de Broglie wavelength of the wavefunction gives the momentum of the electron which is modified by the application of an electric field, and just as in the classical case, the electron waves occasionally scatter from a defect in the lattice or from a thermally excited vibrational mode of the ions, a phonon. Again, the concept of mean free path arises as the average distance between scattering events.

An additional important feature of the quantum mechanical description is the Pauli exclusion principle—only one electron can occupy any given wavefunction. Since electrons have spin 1/2, there are two distinct spin wavefunctions, and therefore, only two electrons (one spin "up," the other "down") can have the same Bloch state. If one thinks of adding the conduction electrons to the solid, the lowest energy Bloch states are filled first; one keeps adding until the crystal is electrically neutral. Thus, states of all energies up to a certain level, the Fermi energy, are filled. To understand the conductivity (and many other properties), one really only needs to consider the electrons near the Fermi energy because well below that level for every electron moving in a given direction, there is another moving with equal and opposite momentum. These lower energy electrons, therefore, contribute no net current.

We now focus on what happens if the lattice becomes disordered. As more and more defects are introduced (impurity atoms, vacancies in the lattice, atoms "out of place" from the regular lattice structure), the mean

free path gets shorter and shorter until it becomes comparable to the interatomic spacing itself. At this point, the nature of the conduction process changes qualitatively. Instead of ballistic particles colliding with defects (or freely propagating waves scattering from them), the particles (or the wavefunctions which describe their position and momentum) become localized in space (2). Electrical conduction is now better described as a hopping process—each charge carrier spends more time in one localized state and then, as a result of thermal fluctuations and the effect of the electric field, hops to another nearby state. The time spent in each state is relatively long compared with the time that it takes to make the transitions between them.

Hopping conduction is observed in several distinct classes of materials (3). Much early work focused on impurity states (donors or acceptors) randomly distributed in crystalline semiconductors. At sufficiently low temperatures, the donors' electrons (or holes from the acceptors) are localized by Coulombic attraction to the impurity atoms and move by hopping from impurity to impurity. As another example, the localization of *intrinsic* charge carriers is observed in amorphous semiconductors such as selenium (a-Se), arsenic triselenide (As_2Se_3) or hydrogenated amorphous silicon (a-Si:H). Also, the motion of injected charge in glassy insulators (for example, fused quartz—SiO_2) is a hopping process. Much recent work has involved amorphous organic materials (4), such as molecular glasses and molecularly doped polymers where the charges are either injected from a metallic electrical contacts or created by photo-excitation. In this case, the localized states are molecular orbitals, and the hopping rates are determined by the (typically small) overlap between adjacent states.

The Hopping Mechanism

In order to understand the process of hopping conduction, one must consider the nature of the localized states and the interaction between them that determines the hopping rate. In addition, since it is currently impossible to observe experimentally a single hopping event in bulk materials of the type described previously, it is necessary to account for the stochastic nature of the hopping process in order to obtain the average behavior which *is* measured in a macroscopic sample. The difficulty of the problem (and the fact that it continues to be of interest after more than 30 years of research) lies in the fact that it is impossible to separate the effects of the microscopic hopping mechanism from the statistics inherent in the macroscopic observables.

Nevertheless, considerable progress has been made toward obtaining a theoretical understanding of the vast amount of experimental data which has been accumulated.

In doped semiconductors, the impurity states are hydrogenlike orbitals (5). For example, phosphorus acts as an electron donor in silicon. At low temperature, the extra electron is bound in a spherical 1s state to the P atom which has a positive charge because of its extra proton. The binding energy is reduced relative to that of an isolated hydrogen atom by the (square of the) dielectric constant of the Si host, and the radius of the first Bohr orbit is correspondingly increased to many times the lattice spacing. In order to observe experimentally the conductivity associated with hopping from one donor state to another, several conditions must be met (6). First, the concentration of donor states (i.e., P atoms) must be low enough that any one overlaps with only a small number of other states. Thus, the hopping from one state to another will be relatively unperturbed by additional interactions. Second, the majority of donor states must be empty so that an electron in one of the few occupied states will find the majority of nearby states unoccupied and, therefore, available as a target to which to hop. This condition implies that the concentration of donors be very nearly compensated by a slightly lower number of acceptors such as boron or aluminum. Finally, the temperature must be sufficiently low such that few acceptors are ionized to create free holes in the valence band, and few donors contribute free electrons to the conduction band. Then, conventional conduction mechanisms are unimportant, and hopping among the impurity states can be observed.

Under these circumstances Miller and Abrahams (6) showed that the phonon assisted transition probability from one donor state, i with energy, ε_i, to a nearby vacant state, j energy ε_j, has the form

$$
\begin{aligned}
W_{ij} &= W_0 \exp -(r_{ij}/2r_0) \exp -(\epsilon_j - \epsilon_i)/kT && \epsilon_j > \epsilon_i \\
&= W_0 \exp -(r_{ij}/2r_0) && \epsilon_j < \epsilon_i
\end{aligned} \quad (1)
$$

where W_0 and r_0 are constants, and r_{ij} is the distance between the two sites. The energy differences between localized states are due not only to the applied electric field but also to a random internal local field which arises because of the random distribution of occupied (negatively charged) acceptors and unoccupied (positive) donors. These equations imply that an "uphill" transition (i.e., to a state of higher energy) occurs with a thermally activated rate, where the activation energy is proportional to the energy difference between the states. The hop requires that phonons of energy $(\varepsilon_j - \varepsilon_i)$ are available to be absorbed in the process so that energy is conserved. (For this reason the mechanism is frequently termed *phonon assisted hopping.*) Conversely, the downhill hop emits a phonon, and it is irrelevant how many phonons of that energy are already present so that the rate is independent of temperature. These equations apply when there are few phonons available to provide the energy for an uphill hop, that is, at low temperature.

The distance dependence is readily understood in terms of the overlap between the spherical hydrogenic orbitals of the localized states. The probability of a hop between two states is proportional to the interaction between them, that is, to the overlap of their wavefunctions. The wavefunctions decrease exponentially with distance from the impurity atom, with characteristics decay length, r_0, and hence, the overlap integral decays exponentially with $2r_0$.

In their paper, Miller and Abrahams (6) then proceeded to analyze the conductivity of such a system in terms of a random resistor network where the resistances are inversely proportional to these transition rates. They were able to obtain fairly good agreement with the temperature and donor concentration dependence in experimental data obtained in nearly compensated silicon.

Amorphous Semiconductors

The nature of the localized states in amorphous semiconductors such as a-Se, and As_2Se_3 is rather different (3). Whereas in doped tetrahedral semiconductors, there are just a few localized impurity levels in a relatively narrow band of energies; in amorphous semiconductors, the disorder introduces a broad distribution of states extending above the valence band and below the conduction band into the energy gap. (See Fig. 1.) These are called the *band tails.* The concept of the band edges (the top of the valence band and the bottom of the conduction band) must now be replaced since there are available states over a broad distribution of energies. The relevant demarcation energy is the mobility edge, following an idea and analysis due to Mott (7). Conduction band states above the electron mobility edge are delocalized, and electrons therein propagate freely. Electron states below the mobility edge are localized, and transport of electrons in those states occurs either by hopping or by thermal excitation to the mobility edge. A similar picture holds for holes in the valence band below and above the hole mobility edge.

The two mechanisms of charge transport in amorphous semiconductors were compared by Noolandi (8), who showed that there is no essential difference in the kinetics of charge propagation between hopping from one site to another and the sequence consisting of excitation out of a localized state to above the mobility edge, motion in extended states, and relaxation into another localized state. The characteristics of charge transport, particularly of photo-excited carriers, in such materials have been studied extensively by many workers and have been reported in several books and review articles (3,4,9,10). These studies involve the time dependence of the transient current following a short light pulse. The experimentalist varies the applied electric field and
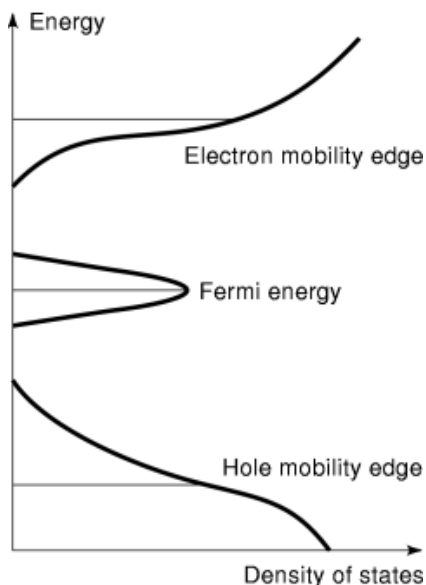
Fig. 1.   Schematic density-of-states of an amorphous semiconductor, illustrating the concepts of band tailing and mobility edges. Holes in states above the mobility edge in the valance band are localized, as are electrons below the mobility edge in the conduction band. At zero temperature, states below the Fermi energy are filled. In many amorphous semiconductors, there is also a band of localized states near the middle of the gap. In such materials at low temperature, variable range hopping [see Eq. (2)] can be observed.

the temperature and may add impurities to the sample in order to understand the effects of trapping the mobile charge. By these means, it is possible to distinguish between hopping conduction and the transport of charges which have been thermally excited above the mobility edge. In general, the data are satisfactorily analyzed in terms of the theory of dispersive transport, described below.

Variable Range Hopping

In amorphous semiconductors and related systems, the disorder manifests itself in two distinct ways (2), First is that the available states for the charge carriers are distributed in energy as, for example, the band tails discussed in the previous section. This aspect is frequently called energetic disorder or diagonal disorder, the latter term arising because the diagonal element of the Hamiltonian matrix are random. The second effect of disorder is that the transition (or overlap) matrix elements between one state (or site) and another are also random: hence the term "off-diagonal disorder." The transition matrix elements dictate the hopping rates from one state to another, as given by the distance dependent term in Eq. (1). In order to arrive at a microscopic description of charge transport in amorphous conductors, both features of the disorder must be taken into account. The phenomenon of variable range hopping (3,11) occurs because of a competition between the two aspects of disorder.

Consider a charge carrier in a localized state. It may hop to another nearby state which has a strong overlap with the first. However, the closest states may be higher in energy than the first state, and therefore, the activation energy for these transitions is higher than that for a longer range hop, having a less favorable transition matrix element. Thus, the most probable hop at each site is dictated by the combination of the energies of the available states and the matrix elements coupling them to the original site. This situation was

analyzed by Mott and Davis (3), who showed that it results in a temperature dependent conductivity of the form

$$\sigma = \sigma_0 \exp{-(T/T_0)^{1/(d+1)}} \qquad (2)$$

where d is the dimensionality of the system.

Variable range hopping is most easily observed in amorphous materials where the valence and conduction band tails overlap in the middle of the gap. This implies that the Fermi level lies within the band tails so that even at low temperature, there are empty states immediately above the Fermi level available, and a carrier may hop with minimal cost in energy. In such systems at sufficiently low temperatures, the experimentally measured conductivity is found to have the form of Eq. (2) (3).

Polarons

The electron-phonon interaction leads to important consequences for charge transport in both crystalline and amorphous materials. In the latter particularly, the carriers are resident for relatively extended times in localized states, and the nearby nuclei have time to respond to the presence of the electronic charge, relaxing in the Coulomb potential. This, in turn, alters the characteristics of the electronic wavefunction, tending to localize it further. Thus, there is a self-consistent redistribution of the electronic charge and the nuclear positions. The composite object of the electron and the distorted lattice is termed a polaron (12,13).

The motion of polarons is considerably different from that of an electron alone. It must involve also displacement of the nuclei. The nuclear distortion at the starting site for a hop is removed and replaced by a distortion around the target site. The mechanism of this process depends on the random, thermally excited motion of the nuclei, themselves. Random thermal fluctuations of the nuclear positions occasionally bring the electronic state into a situation where there is higher probability, both energetically and via more favorable transition matrix elements, of hopping to a nearby state. This problem was analyzed in considerable detail by Holstein and Emin (12,14). The resulting transition rates, for high temperatures when many phonons are involved, and for strong coupling of the electron to the lattice, are given by

$$W_{ij} = W_0^{(Pol)} \exp{-(r_{ij}/2r_0)} \exp{-(\epsilon_j - \epsilon_i + 2E_p)^2/8E_p kT} \quad (3)$$

where E_p is the polaron binding enegy, that is, the change in electronic energy that results from the nuclear distortion. The form of this equation is identical to that which arises in charge transfer in chemical and biological systems where it takes the names of Marcus (15) and Levich (16) who first analyzed the process for these cases. The theory of Holstein and Emin also includes the low temperature, weak coupling limit for phonon assisted hopping. In this limit, the Miller–Abrahams form [Eq. (1)] is recovered.

Experimental Methods

Charge transport phenomena are most directly studied by applying an electric field to a sample and measuring the current which flows as a result. This is one of the simplest experimental techniques imaginable, and yet, since it is readily done as a function of temperature and perhaps electric field, it can provide a wealth of information. In its simplest form, it yields a determination of the (linear) electrical conductivity of the material.
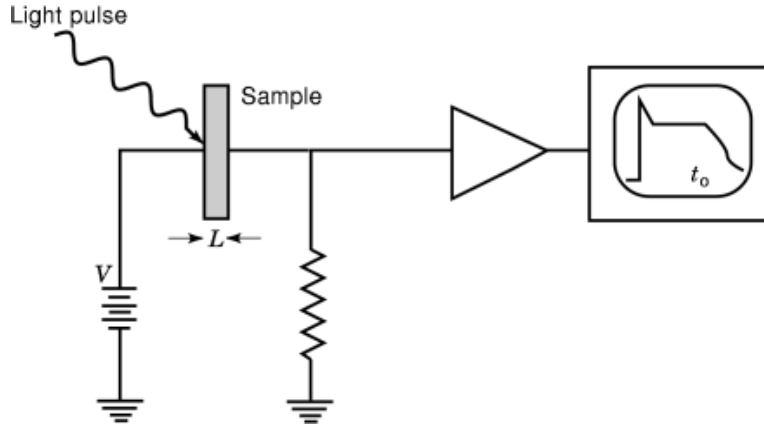
Fig. 2.   Schematic of the time-of-flight transient experimental arrangement. Following a short light pulse, a photo-induced current transient flows in the circuit containing the sample causing a voltage to appear across the series resistor. The voltage is amplified and captured by a transient digitizer.

However, two independent variables enter the expression for the conductivity

$$\sigma = ne\mu \qquad\qquad (4)$$

namely n, the density of charge carriers, and μ, their mobility. In a semiconductor, the number of mobile carriers is usually a strong function of temperature, and so one needs additional information, for example from a Hall effect measurement, to separate it from the temperature dependent mobility which contains information about the hopping rates of the carriers.

A technique which determines the carrier mobility more directly is the photo-induced time-of-flight transient method (17) (Fig. 2), which can be employed with most nonmetallic materials. Here, the sample to be measured is placed, usually in a thin film geometry, between two electrodes, one of which is semitransparent, and a voltage is applied. The electrodes are arranged to be "blocking" by coating them with a thin layer of insulator so that there is minimal current flow in the dark. A light pulse is incident through the semitransparent electrode and is absorbed within a thin layer of the semiconductor adjacent to the electrode, exciting charge carriers (electron-hole pairs). Depending on the sign of the applied voltage, one or other of the carriers moves across the layer of semiconductor, resulting in a current flow which is detected in the electric circuit attached to the electrodes. The duration of this current transient is a measure of the time it takes the charge carriers to cross the thickness of the sample (the transit time)

$$t_0 = L/\mu E = L^2/\mu V \qquad\qquad (5)$$

where L is the thickness of the film, V is the applied voltage, and E is the (assumed uniform) electric field in the sample. Ideally, the experiment is carried out with a minimal number of excited charge carriers so that the electric field that they create (the space charge field) is small compared to the field applied at the electrodes.

Other methods can be used to determine the transport characteristics of charges injected into materials of interest (17). For example, a high voltage pulse may be used to inject carriers of a given sign, which then drift in the electric field given by a much smaller steady voltage. In other techniques, electrons are injected in a pulse from an distant electron gun similar to that used in an electron microscope. Then, the current in the sample is monitored as a function of time. In another method, using a geometry similar to the time-of-flight

method, but with (at least one) electrode selected so that it readily injects charge in the dark, the space charge limited current (18) can be used to determine mobility. However, the photo-induced current transient method has become by far the most popular experimental method of determining carrier mobility.

The mobility (and indeed the entire shape of the current transient, which will be discussed in more detail below) depend on several experimental parameters. First is the applied electric field, itself. In many cases (4,19,20), the electric field dependence is well described by the form

$$\mu = \mu_0 \exp{-\beta\sqrt{E}} \qquad (6)$$

The so-called *zero-field mobility,* μ_0, and β are parameters determined by experiment, and both are generally temperature dependent. In some cases, the zero-field mobility is thermally activated with an Arrhenius dependence—$\mu_0 \sim \exp(-\Delta/kT)$, while in other cases, especially for molecular glasses and molecularly doped solids, the data are better described by the form

$$\mu_0 = \mu_0' \exp{-(2\sigma/3kT)^2} \qquad (7)$$

As will be discussed in more detail in the section on the Gaussian Disorder Model (*GDM*) below, the parameter σ (not to be confused with the conductivity above) is a measure of the degree of energetic disorder. The factor of 2/3 also arises in the GDM.

The form of Eq. (6) is reminiscent of the Poole–Frenkel (*PF*) (21) mechanism which describes the field assisted escape of carriers from charged traps, and for this reason, β is frequently called the *Poole–Frenkel parameter*. However, it is now generally recognized that the PF mechanism is not active in most materials which show hopping transport. Rather, the electric field dependence arises, at least in part, because energetic disorder is not totally random. A theoretical account of this phenomenon is given below.

Another parameter of experimental interest is the concentration of localized states, which in turn, affects the mean hopping distance. In molecular solids, it is frequently possible to span the range of concentration from 100% (i.e, the pure molecular glass) to less than 10% of the active molecule doped into a passive host polymer. It is then found that mobility depends on the mean intersite distance r in the form $\mu \sim \exp{-r/2r_0}$. As discussed above in connection with Eq. (1), such a distance dependence is easily understood in tems of the distance dependence of the overlap integral of localized wave functions. This is one aspect of the microscopic mechanism which persists in experiments on macroscopic samples.

Dispersive Transport

In this section, the concept of dispersive transport, commonly observed in materials with hopping conduction, is introduced by contrasting the normal band transport seen in crystalline materials.

There are several different uses of the term *dispersive* in the literature, not all of which are precisely defined. We will try to indicate these various uses and provide some clearer definitions.

In a single crystal of semiconductor, charge transport (1,5) is well described by a picture in which the carriers drift under the influence of an applied electric field, all the carriers having a velocity close to some mean value. If a packet of carriers is injected into such a crystal, the small fluctuations in velocity lead to diffusional spreading of the charge packet. The situation is well described by Gaussian statistics: while the mean displacement of the packet increases linearly with time ($x_0 = \mu Et$), its (root mean square) width increases with the square root of time

$$\langle(x - x_0)^2\rangle^{1/2} = (2Dt)^{1/2} \qquad (8)$$

where the diffusion coefficient, D, is related to the mobility by the Einstein relation

$$D = \mu k T / e \qquad (9)$$

Thus, in a transient time-of-flight experiment, at the end of the transit time, the width of the carrier packet relative to its displacement is given by

$$w = \frac{\langle (x - x_0)^2 \rangle^{1/2}}{x_0} = \left(\frac{2kT}{eV} \right)^{1/2} \qquad (10)$$

Note that this depends only on temperature and the applied voltage, not the thickness of the sample or the carrier mobility. In a typical experiment at room temperature and with an applied voltage of order 100 V, $w \sim 10^{-2}$. One would therefore expect the current to be constant to a time within about 1% of the transit time, then fall to zero rapidly as all the carriers reach the collecting electrode. Such an ideal current transient [Fig. 3(a)] is never observed in materials which show hopping conductivity. Rather, in [Fig. 3(b)] the current rises sharply after the light pulse, then starts falling immediately. The rate of fall may slow noticeably giving a "plateau" before accelerating again near the transit time as the carries reach the electrode and no longer contribute to the current. The width of the carrier packet, which is given by the length of the tail in the transient, is often comparable to the transit time itself—that is, $w \sim 1$. The large spread is intimately related to the disorder inherent in hopping conduction. Although the term "dispersive" has been applied to the excessive and non-Gaussian broadening of the carrier packet, a better term to use in this context is "anomalous diffusion."

In many materials (4,9,19), and especially at low temperatures it is not possible to observe the plateau in a linear plot of current (i) versus time (t). The current just appears to fall smoothly towards zero [Fig. 3(c)]. This makes it difficult to identify the transit time. In such cases, it is common to plot the current-time behavior on a log-log scale. The transit time can then be identified as a change in slope [Fig. 3(d)]. In experiments on many materials, it is observed that the log(i) versus log(t) plot, both before and after the transit time, is linear over a significant range of time; that is

$$\begin{aligned} i &\sim t^{-(1-\alpha)} & t &< t_0 \\ i &\sim t^{-(1+\alpha)} & t &> t_0 \end{aligned} \qquad (11)$$

(The meaning of the parameter α is given in the next paragraph.) The absences of a plateau and a clear transit time in a linear i-t plot has been used in the literature as indicative of dispersive transport, but this is really a matter of degree, since it ultimately depends on the signal-to-noise ratio in the experiment.

The form of Eq. (11) was explained in a classic series of papers culminating with that by Scher and Montroll (22). They considered statistics of residence (or waiting) times, that is, the mean length of time that a carrier stays on a given site before hopping. (The theory is commonly called *continuous time random walk*.) Many sites which have strong interactions with one or more neighbors will have short residence times, while other, more isolated sites or those having particularly low energy, will have very long residence times. They argued that, in amorphous materials, the distribution of residence times would be extremely wide, perhaps as wide as the time scale (the transit time) of the experiment itself. Thus a few carriers' paths across the sample might take them to sites with very long residence times where they remain until the majority of the carriers have already reached the collecting electrode. Eventually, they leave the long time sites and contribute again to the current until they, too, reach the other side, thus explaining the wide tail in the current transient. The wide waiting time distribution also explains the early time decay of the current transient. Initially, the carriers occupy sites at random, so most of them are in the numerous ones with short waiting times. However, their path
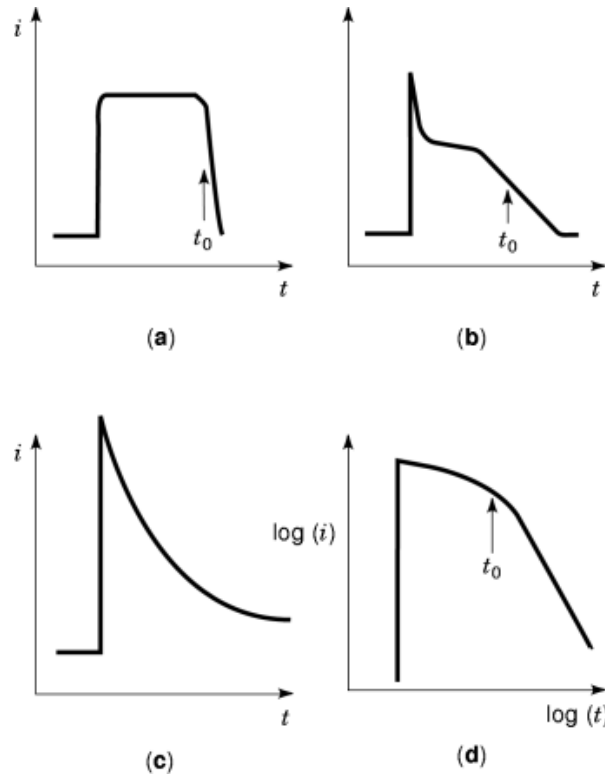
Fig. 3.   Current transients obtained in time-of-flight mobility experiments. Current, i, is plotted against time, t. (a) Ideal current transient expected for nondispersive transport and Gaussian diffusion. The current decays in a very small time range around the transit time, t_0. (b) Typical transient observed in disordered materials showing a rapid drop in current after the light pulse, a plateau region before the transient time, and a "tail" comparable in length to the transit time. (c) A highly dispersive current transient plotted linearly as current vs. time. (d) The data of curve c plotted on a double logarithmic scale. Note the power law behavior below and above the transit time.

explores more and more sites, and so as time goes by, there is an increasing probability that some of the carriers will land in longtime sites where they stay for a while. Thus, the occupation of long wait sites increases with time, and because these stationary carriers no longer contribute, the current decreases, Scher and Montroll analyzed the statistics in the case where the probability of residence times (τ) is given by a power-law behavior (Fig. 4)

$$P(\tau) \sim \tau^{-(1+\alpha)} \tag{12}$$

where the "dispersion parameter" is $0 < \alpha \leq 1$. Such a form for the distribution has the very important properties that it approaches zero very slowly as $\tau \to \infty$, and that the mean waiting time is infinite. Thus, there is some (small) probability of sites with $\tau > t_0$, but because there are few of them, the carriers take a long time to encounter them. Within the time scale of the experiment, the full width of the distribution function is not sampled by the population of carriers. This feature of the continuous time random walk theory then gives perhaps the most precise definition of dispersive transport; the carriers never come fully into equilibrium with the distribution of site residence times.
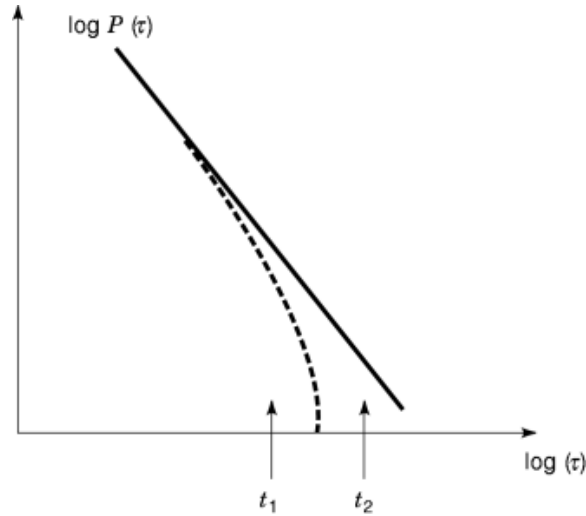
Fig. 4. Waiting time distributions plotted on log-log scales. The solid line shows the Scher–Montroll distribution; no matter how long the transit time, there are always some sites with longer residence times, resulting in dispersive transport. The dashed line shows a waiting time distribution with a cutoff at long times. If the transit time is in the region of t_1, the carriers will not fully equilibrate with the distribution, and the transport is dispersive. If the transmit time is in the region of t_2, nondispersive transport may be observed, although the carrier packet will still be anomalously broadened.

The Scher–Montroll waiting time distribution has several important consequences which can be observed in experiments (9). First is the troublesome result that the transit time, and hence the mobility, depends on the thickness of the sample. The mean displacement of the carrier packet is $x_0 \sim t^\alpha$. (Since the current is proportional to the mean carrier velocity, the time derivative of this expression gives the early time current in Eq. (11).) Thus, the transit time and mobility are given by $t_0 \sim L^{1/\alpha}$ and $\mu \sim L^{1-1/\alpha}$. Second is the concept of "universality:" for a given value of α, all current transients have the same time dependence. That is, if one plots $\log(i/i_0)$ versus $\log(t/t_0)$ (here, i_0 is the value of the current at the transit time t_0), then all the transients will lie on top of each other. In amorphous semiconductors, for example, α does not depend on electric field, and so transients taken at various electric fields (but at the same temperature) show universal behavior. Universality is a consequence of dispersive transport which arises in the particular case of a power law distribution of waiting times.

In summary, the most general definition of "dispersive transport" implies a distribution of waiting times which is wider than the experimental time scale. The packet of carriers does not reach equilibrium with the waiting time distribution.

Gaussian Disorder Model

The statistical theory of Scher and Montroll starts from a distribution of residence times. It says little about the microscopic mechanism of hopping which determines the mean residence time on each site, and hence, the temperature and electric field dependences of the distribution. Indeed, since the only parameter in the theory is the dispersion parameter, α, the only way in which temperature and field can affect the transport properties is through their effect on α. Moreover, the crossover between dispersive and nondispersive transport is contained only in the limiting behavior at $\alpha = 1$, where the mean waiting time becomes finite. To proceed beyond the statistical theory, as useful as it is, to microscopic mechanisms requires a different approach.

We have seen in the preceding sections that each individual hop between two nearby sites (i, j) is dependent on the (random) energy difference between them

$$\Delta \epsilon = \epsilon_i - \epsilon_j - eEr_{ij} \cos \vartheta_{ij} \qquad (13)$$

where the electrostatic energy is now explicitly included as the last term. Here, r_{ij} is the distance between the two sites, and θ_{ij} is the angle between the vector joining them and the applied field, E. The transition rate also depends on the overlap integral between the two sites which falls off exponentially with the distance r_{ij}. However, in asymmetric systems such as nonspherical molecules, the rate of falloff depends on the relative orientation of the two molecules. Thus, the overlap integral is not just a function of r_{ij}, in the following, we write it as exp γ_{ij}. The complexity of the problem is now evident, there are three random variables to be considered: the on-site energies (ε_i), which describe the diagonal disorder, the overlap parameters, γ_{ij}, which describe the off-diagonal disorder, and the combination of distance and angle between site positions $(r_{ij} \cos \theta_{ij})$, which is necessary to account for the electric field dependence of the hopping. It should, therefore, come as no surprise that there is no completely analytic mathematical solution of this problem. Considerable progress has been made, however, using computer methods to treat the problem numerically.

The computational technique which was developed explicitly to deal with random distributions of the type encountered here for the case of transport in amorphous systems is the Monte Carlo method. One uses a random number generator to assign to the properties of each site and site-pair a specific value of the variables from within an appropriate distribution function. (The choices of distribution functions are inputs to the model.) Then, a charge carrier is put on a starting site, and the computer "decides" which sequence of sites it hops to, in accordance with the probabilities inferred from the hopping rates from the occupied site to all its neighbors. The process is repeated many times, for many realizations of the distributions and for many carriers, and the resulting averages are tabulated for comparison with experimental data. One of the major proponents of this method in the field of hopping conduction has been the group of Bässler at Phillips University, Marburg (23).

The core of Bässler's approach is the choice of distribution function for the site energies, ε_i. It is taken to be a Gaussian, a form which is commonly observed in the spectroscopy of systems with inhomogeneous broadening, and hence, the name given to this model and its many extensions is the Gaussian Disorder Model (*GDM*). The center of the Gaussian is taken to be the zero of energy, and its width is σ. The hopping rates are assumed to have the Miller–Abrahams form [Eq. (1)], where the energy difference between sites includes the electrostatic energy.

The first result of GDM is the temperature dependence of the mobility. Rather than being simply activated with an Arrhenius form, it is found to depend on the square of temperature in agreement with many experimental results as expressed by Eq. (7). This may be understood by means of a straightforward calculation, realizing that the carriers tend to occupy the lowest states in the distribution, according to a Boltzmann thermal occupation factor. The mean energy is given by

$$\begin{aligned}
\langle \epsilon \rangle &= \int \epsilon (\exp -\epsilon^2/2\sigma^2)(\exp -\epsilon/kT) \, d\epsilon \\
&= -\sigma^2/kT
\end{aligned} \qquad (14)$$

which is below the peak in the density of states distribution. Thus, the rate limiting hops are thermally activated with a cost in energy proportional to $-\langle \varepsilon \rangle$, that is, the mobility $\mu \sim \exp -(\sigma/kT)^2$. The factor of 2/3 in Eq. (7) is given by a more detailed analysis.

Off-diagonal disorder is included in the GDM by assuming that the pair-wise overlap parameters, γ_{ij}, are given by a simple sum $\gamma_{ij} = \gamma_i + \gamma_j$, where each γ is again drawn from a Gaussian distribution of width Σ. The

results of many computer "experiments" can be expressed in the form

$$\mu = \mu_0 \exp{-(2\sigma/3kT)^2} \exp{-C\left[\left(\frac{\sigma}{kT}\right)^2 - \Sigma^2\right]E^{1/2}} \qquad (15)$$

Although one may wonder whether the choices made for input to the computer simulation (Gaussian distributions, Miller–Abrahams hopping) are entirely in agreement with the physics applicable to real systems, the GDM provides remarkably good qualitative agreement with a large body of experimental data on molecular glasses and molecularly doped polymers. It also gives a framework with which to analyze that data so that parameters may be compared from one material to another. There is remarkably little variation in the value of σ obtained from a large number of dopant molecules and host polymers (4). One finds that σ is generally about 0.1 eV to within perhaps 20%. More recent computer simulations by others (24) have explored the effects of a polaronic form for the energetics of hopping as well as more realistic distributions for the overlap integrals (25,26). These are found to make rather small qualitative differences, although they do affect the detailed interpretation of the parameters. The reader is referred to original papers for an account of these differences.

Origins of Energetic Disorder

What are specific causes of the random site energy which has such important consequences in the temperature dependence of hopping transport? When a localized state is charged the energy depends on several different types of interactions between the electron or hole and the surroundings, and if the localized state is molecular, with the molecule itself.

First, there is the electric field due to all the other electrons and nuclei in the neighborhood. Since apart from the single mobile charge in the state in question, the solid is electrically neutral (recall that experiments are generally performed in the limit where space charge effects are negligible), this field may be thought of as the sum of fields due to a random assembly of dipoles (27). For example, in the case of a molecular solid, one might think of a dipole associated with each of the molecules surrounding the one that is charged. It might be even more accurate to assign a dipole to each chemical bond in the surrounding solid. In an amorphous solid, the dipolar field is random in both magnitude and orientation. Theoretical and experimental estimates suggest that it can be as large as 10^7 to 10^8 V/m, which is comparable to the externally applied field in many time-of-flight experiments.

Several recent experiments (28,29) have been performed using molecularly doped polymers in an effort to determine the magnitude of the energetic disorder provided by the charge-dipole interactions. In some cases, nontransporting dipolar molecules were added to the molecular glass, while other experiments studied series of charge transport molecules differing only in a substituent which altered the dipole moment of the dopant itself. For each material (and concentration), the energetic disorder, σ, is determined from the temperature dependence of the mobility. It is found that the experimental data agree quite well with the theoretical prediction (30) that the contribution to the energetic disorder due to molecular dipoles of magnitude, p, and at concentration, c_d, is

$$\sigma_d = \frac{k_0 c_d^{2/3} p}{a^2 \kappa} \qquad (16)$$

where a is the intersite distance, and κ is the dielectric constant. k_0 is a constant whose magnitude can be estimated theoretically (30) or from Monte Carlo simulations (31). Since the charge-dipole contribution is

assumed to be uncorrelated with other sources of energetic disorder (σ'), its effect is given by

$$\sigma = (\sigma_d^2 + \sigma'^2)^{1/2} \qquad\qquad (17)$$

It is found, for example (29), that when charge transport molecules with a dipole moment of about 2 Debye are put into a nonpolar polymer binder at a concentration of about 50% by weight, the charge-dipole contribution is comparable to all other sources of disorder.

A second source of energetic disorder lies in the variability of the local polarizability of the medium in the vicinity of the charge site (32). Since the environment of each site differs, so too will the dielectric response around the charge when it occupies a given site. Part of the response is due to the electronic polarizability of the medium, and in the case of molecular solids, there is also the possibility that dipolar molecules rotate to align with the electric field of the perturbing charge. The magnitude of this polarization energy is quite well known for many solids; it is typically of order 1 eV (33). It is more difficult to account for its variability from site to site in a random structure, but it is quite conceivable that it provides a major contribution to the observed σs which are typically 0.1 eV.

In molecular solids, there is the possibility of a difference in the geometry between the neutral and charged states of the molecule. This phenomenon has already been introduced above in the section on polarons. In the case of organic molecules, the polaron distortion introduces a change in the bond lengths. The freedom that a molecule has to distort in response to the presence of an electron or hole will dictate the binding energy of the polaron. Thus, randomness in polaron binding enegy is potentially an additional contribution to energetic disorder.

Electric Field Dependence of the Mobility

The experimental observation which has been among the most difficult to account for theoretically is the electric field dependence of the mobility, Eq. 6, commonly seen in amorphous molecular solids. The exponential square root form is reminiscent of the Poole–Frenkel (21) effect which applies to field-assisted ionization of charged traps but is considered not to be active in molecular solids. The PF mechanism involves a field dependent reduction of the barrier which a carrier must overcome to leave the trap and enter a conduction band. That barrier is a maximum at a calculable distance from the trap, and it can be shown that the maximum is considerably beyond the mean intersite distance in organic glasses. Moreover, the behavior persists both qualitatively and quantitative as samples are purified in an attempt to remove charged traps. Finally the traditional Poole–Frenkel parameter (the slope of log μ versus $E^{1/2}$)) is inversely proportional to temperature and does not reverse in sign above a certain temperature as observed experimentally. Thus, one must conclude that the similarity in field dependence to the Poole–Frenkel effect is coincidental.

Although the Gaussian Disorder Model yields, empirically, a log $\mu \approx E^{1/2}$ behavior, it does not explain its origin in any detail. Indeed, the empirical form was suggested by experimental data and chosen as a way to provide the most direct comparison between computer simulations and real samples. The electric field appears in the GDM mobility in the exponential which contains the spatial disorder parameter Σ. Thus, one might think that the field dependence is related to off-diagonal disorder. However, recent theoretical work suggests another origin.

An analysis of transport in amorphous media has been given (27,34,35) which goes beyond the simple distribution functions described above. The concept is that site energies are not truly random, but because of the slow spatial variation of dipolar fields, they are similar for neighboring molecules; that is, the energies are correlated. When correlations in site energy are taken into account, Dunlap et al. (34) were able to show, using Laplace transform methods applicable to random hopping, that the mobility has the form of Eq. (6) over a wide

range of electric fields. The values of parameters obtained by fitting the experimental field dependent mobility data are in accord with those from the temperature dependence of the same sample. Thus, it appears likely that the long-standing problem of the electric field dependence can be attributed to correlations in energetic disorder due to the long range nature of the charge-dipole interaction.

Applications

Many of the ideas discussed in this article are applicable to materials of technological importance. By far, the largest use of amorphous semiconductors is as photoconductors for electrophotographic (also termed xerographic) copying and printing (commonly known as laser printers) (4). This industry began with the use of amorphous selenium, and its alloys with arsenic and tellurium. These glassy materials can be coated uniformly over large areas. Amorphous silicon is also an excellent electrophotographic photoconductor, but it has found little use because of the high cost of production. As a result of environmental and other concerns in the last ten years, organic photoconductors have virtually replaced their inorganic predecessors. The role of the photoconductor is to generate an electrostatic image, which can then be developed (36) with charged toner (solid ink) particles for transfer to the paper. A surface charge is first deposited on the photoconductor from a corona. Then, the surface is selectively discharged by exposing it to light from a page image or from a scanning laser beam. The generated charges travel across the thickness of the photoconductor layer with sufficiently high mobility that the latent electrostatic image is fully formed in the time that it takes to move between the exposure and the developer. The factors affecting charge mobility and the optimization of photoconducting materials are of great importance to the electrophotographic industry.

Hopping conduction is also observed in inorganic glassy insulators, materials which are used, for example, as the gate insulators in the field-effect transistors used in today's computer logic and memory chips. As the circuitry shrinks in size and the gate insulator layer gets proportionally thinner, leakage current between the gate and the channel becomes an increasing problem. There is a growing realization in the microelectronics industry that the leakage is due to hopping conduction between localized defect states in the insulator (37). The insulator is so thin that only a few such states can significantly affect the current. Indeed, in a theory developed to deal with the phenomenon, trap assisted tunneling, only one such intermediate state is required to enable charges to hop from gate, to defect, to channel. The identification and elimination of the defects responsible for leakage will permit the continued trend to ever smaller circuit dimensions.

Finally in this section, one must mention a technology which is on the commercial horizon: organic light-emitting diodes (*OLED*s) are being developed and evaluated as light sources for possible flat panel display applications (38,39). OLEDs consist of one or more layers of organic material sandwiched between two electrodes: a cathode which injects electrons from one side of the layer(s), and an anode which injects holes from the other when a voltage is applied to the device. The electrons and holes move toward each other under the influence of the applied electric field and recombine to form molecular excitons. This excited state can, under favorable circumstances, relax to the molecular ground state by the emission of light in a process which is essentially identical to the fluorescence of the organic molecule. Several of the physical processes necessary for operation of OLED devices involve hopping conduction. Most obvious is the mobility of the electrons and holes as they travel across the organic layers, but two other aspects of device operation are closely related: charge injection from the metallic electrodes into the adjacent organic material and the recombination of electron–hole pairs. Injection can be thought of as a tunneling process (a hop) from the extended states at the Fermi energy of the electrode into the localized states of the organic molecules. Recombination involves motion of the electrons and holes in the field created by the sum of their mutual Coulomb attraction, the externally applied field, and the random field of their disordered environment.

Hopping conduction is a rich scientific problem requiring an understanding of many aspects of materials science, organic chemistry, solid state physics, experimental and computational techniques, and the statistical

mathematics of random processes. This article has attempted to summarize in a few pages the key relevant concepts which occupy volumes of the scientific literature: the disorder induced localization of electronic states, the factors which govern the distance and temperature dependence of the hopping rates, roles of diagonal and off-diagonal disorder, and the experimental, mathematical, and computational techniques which have been developed to deal with the problem of a random microscopic process observed through its effect on a measurable macroscopic property. We have discussed some of the materials which exhibit hopping conduction and some of the technologies where hopping conduction is important. The field has been driven by a combination of scientific curiosity and technological necessity, and it appears that it will continue to provide interesting challenges in the future.

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