Stochastic Transport in a Disordered Solid. I. Theory

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A general theory of stochastic transport in disordered systems has been developed. The theory is based on a generalization of the Montroll–Weiss continuous-time random walk (CTRW) on a lattice. Starting from a general mobility formalism, specialized to hopping conduction, an exact expression for the conductivity $\sigma(\omega)$ for the CTRW process is derived. The frequency dependence of $\sigma(\omega)$ is determined by the Fourier transform of the zeroth and second spatial moments of the function $\psi(\vec{s}, t)$, which is equal to the probability per unit time that the displacement and time between hops is $\vec{s}$, t. The conductivity corresponding to characteristically different types of hopping distributions is discussed, as well as the basic approximation in adopting a CTRW on a lattice to transport in disordered solids.

I. INTRODUCTION

Charge conduction entirely by "free-carrier" band transport is the biggest casualty in going from an ordered to a disordered solid. At present there is a great deal of interest in a wide range of nonbandlike means of transport of both charge and excitation in disordered or amorphous solids.[1] Besides having important applications to areas such as xerography[2] and optical-memory devices,[3] amorphous systems are a basic and natural extension of the physicist's study of solids.

The lack of long-range structural order is the central essence of the problem; this lack of order causes a random potential to exist in the solid. The random potential can give rise to a distribution of localized electronic states[4] as well as the extended bandlike states.[5] Therefore, the nature of electronic transport can either[6] be the more familiar band type (free-carrier motion with occasional scattering from potential fluctuations), with the localized states acting as traps, or there can be transport among the localized states.[7]

Carriers can move from one localized center to another by hopping.[8,9] To describe hopping quantitatively, one must first know how the electron on one center communicates with another center. For this part of the problem one must know the electronic wave functions and from them calculate the transition probabilities between typical centers. The transition rate, in addition to depending on the parameters describing the wave functions, must depend on the spatial separation between the centers and on the energy difference between the initial and final state.

The second part of the problem involves the task of describing the site-to-site motion of the electron among the statistically distributed centers against the background of the random potential, which causes fluctuations in the local energy levels. Since the transition rate is a sensitive function of both the local separation and local energy fluctuation, the hopping transport will depend critically on the details of the statistical distribution of these parameters. Therefore, even given a knowledge of the nature of the localized centers and their distribution, one has to deal with the difficulties associated with the stochastic aspects of the site-to-site transport. This must be solved in order to describe, quantitatively, time-dependent transport in amorphous materials, which is the main aim of the present formalism.

We offer a new approach to this problem: it is to study in detail a stochastic process that contains the essential elements of hopping transport and yet is entirely tractable to analysis.

The process considered is a generalization of the Montroll–Weiss[10] model of continuous-time random walk (CTRW) on a discrete lattice.[11] The central approximation we make in adopting this process to hopping conduction is justified by an analysis of the structure of an arbitrary "path" in the CTRW and comparing this to an analogous quantity in a configuration-averaged random walk (RW) on a random medium. In a system with a large number of hopping sites the difference in the two processes can be shown to be small.

The simplifications inherent in the structure of the CTRW model allow one to focus on the basic fluctuating quantity in hopping motion, that is, the transition rate between centers. The basic quantity that determines the conductivity is the characteristic function of a sum of transition rates, each treated as a random variable.

In Sec. II the relation between the frequency-dependent conductivity $\sigma(\omega)$ and a RW is established.

The formalism of this section is based on a generalized theory of mobility,[12] which is specialized to hopping conduction. In Sec. III the generalization of the CTRW model of Montroll and Weiss is described. Stress is placed on the main mathematical results that are used in Sec. IV, wherein the frequency-dependent diffusion constant $D(\omega)$ of this stochastic process is calculated (exactly) and a number of representative examples are discussed [$\sigma(\omega) = (ne^2/kT)D(\omega)$, where n is the density of effective carriers]. One of the examples typifies the qualitative features for $D(\omega)$, observed in impurity conduction in semiconductors. In a following paper,[13] hereafter denoted as II, a detailed application of the present theory is made to conduction among the impurity states in a semiconductor, which is the prototype of a disordered solid.

It must be *emphasized* at the outset that the transport theory developed in Secs. II–IV, as applied to impurity condition in II, represents a dramatic departure from previous considerations of this problem (cf. references in II). Specifically, there are two basic parts to this new approach: (i) The key quantity to determine, in a calculation of the conductivity $\sigma(\omega)$, is a probability function $P(\vec{s}, t)$. The function $P(\vec{s}, t)$ is the probability of finding a carrier at a point $\vec{s}$ at time t if it was at the origin $\vec{s}_0 = 0$ at $t = 0$. Starting with general linear response theory,[12] it is shown (Sec. II) that $\sigma(\omega)$ is proportional to the product of ω^2 with a weighted space average of the Laplace transform, $\tilde{P}(\vec{s}, i\omega)$ of $P(\vec{s}, t)$. In general, in calculating a quantity such as $P(\vec{s}, t)$ one has to consider *all the possible paths* from $\vec{s}_0 (= 0)$ to $\vec{s}$ that the carrier can traverse in a time τ with $\tau \leq t$. One must consider $\tau < t$ because the carrier can arrive "earlier" than t and "wait" there until, at least, t before hopping away. Each of the paths must be "assigned" a "weighting" factor, i.e., a *measure* of its relative contribution in determining $P(\vec{s}, t)$. This *measure* naturally reflects the probabilities for the hopping time for the displacement along each intersite "link" of the path. For a fixed path or *fixed configuration of sites* the hopping times vary over a wide range from site to site. It is important to reiterate that in order to contribute to $P(\vec{s}, t)$ the sum of all the hopping times over each path must be t. With these constraints *each local configuration must be considered in the context of a total path.* Now, in addition, one must not only take into account all the paths (with their proper weighting) on a *fixed* array of sites, i.e., a total set of impurities with a given location $\{\vec{s}_i\}$, but one must average over all possible distributions of impurity locations. In other words, the probability of finding the carrier at $\vec{s}$ at time t for a fixed array of sites at $\{\vec{s}_i\}$ is $P(\vec{s}, t; \{\vec{s}_i\})$. Since it is impossible to experimentally measure $\{\vec{s}_i\}$ for a given system (sample) one must study the properties, in any theory, of an ensemble of these systems. Even for a given system, carriers initially at widely different locations experience different parts of the same fixed impurity site distribution. Thus, for a system with macroscopic spatial homogeneity (as considered in I and II), an average over the initial carrier locations is also contained in the ensemble average. Hence, the key quantity $P(\vec{s}, t)$ is equivalent to $\langle P(s, t; \{\vec{s}_i\})\rangle$, where the average is taken over an ensemble of all the site locations $\{\vec{s}_i\}$ weighted according to some assumed distribution law. The site-distribution law is almost always assumed to be a random distribution with the neglect of spatial correlations.

As the final step in calculating the conductivity $\sigma(\omega)$ one must take the Laplace transform of $P(\vec{s}, t)$. Further insight into the dynamics of hopping transport can be obtained simply from the well-known properties of a Laplace transform. For an impressed frequency ω, the main contribution to the Laplace transform $\tilde{P}(\vec{s}, i\omega)$ comes from $P(\vec{s}, t)$ with $t \lesssim \omega^{-1}$. Moderately high ω (ω is usually referred to some maximum transition rate of the system) implies, therefore, short times. At short times, $P(\vec{s}, t)$ falls off rapidly for large $\vec{s}$. Thus, moderately high ω implies hopping among *all* the sites (with total hopping times less than ω^{-1}) within some effective radius $\bar{s}(\omega)$, i.e., only *localized* hopping. For $\omega \to 0$, the pertinent time domain of $P(\vec{s}, t)$ increases and thus $\bar{s}(\omega)$ increases. However, because $\sigma(\omega) \propto \omega^2 \langle \tilde{P}(\vec{s}, i\omega)\rangle$ (where the angular brackets indicate a weighted space average), it is shown *rigorously* (Sec. IV) that for $\omega \to 0$, hopping transport confined to any localized region does not contribute to $\sigma(\omega)$. To reiterate, in the limit $\omega \to 0$, only *nonlocalized* hopping is significant.

(ii) A model stochastic process is used to calculate the hopping transport along all the paths contributing to $P(\vec{s}, t)$. In the model (Sec. III) the probability that the time between hops is in the interval $(t, t + \Delta t)$ and the displacement is $\vec{s}$, is equal to $\psi(\vec{s}, t)\Delta t$. The model process is a generalization of the Montroll–Weiss[10] CTRW. The hopping is from any point on a lattice to any other with the displacement and time at each hop governed by $\psi(\vec{s}, t)$. In applying this process to impurity conduction one must consider hopping only between positions of the impurities which occupy a random selection of a finite (large) number of lattice points in some volume V. In II the function $\psi(\vec{s} - \vec{s}_0, t)$ is obtained by taking into account the transitions from a given site to the random array of impurity locations, in a definite configuration. The result is then averaged over all configurations holding $\vec{s}$, $\vec{s}_0$ fixed. In addition, the calculation of $\psi(\vec{s} - \vec{s}_0, t)$ includes a factor weighting the probable occupancy of the lattice point $\vec{s}$. In Appendix B it is shown

that any arbitrary n-step path of a RW through the random medium of any configuration of the impurity positions $\{\vec{s}_i\}$ has a one-to-one correspondence with a path in the CTRW. Further, it is shown that the essential difference between impurity hopping conduction, where the function corresponding to $\psi(\vec{s}-\vec{s}_0, t)$, varies from site to site, and the CTRW lies in the procedure for performing the configuration average. For a system with a large number of hopping sites it is argued that this difference in the averaging procedures is small.

The basic result is in Sec. IV where it is shown that $D(\omega)$ is equal to a simple function of the zeroth and second spatial moment of the Laplace transform $\tilde{\psi}(\vec{s}, i\omega)$ of $\psi(\vec{s}, t)$.

II. GENERALIZED THEORY OF MOBILITY

The starting point for our study of hopping conduction is a generalized theory of mobility, [12] which in essence is the Nyquist formula[14] relating admittance (mobility) and noise. This is a generalization of the Einstein relation between mobility and diffusion constant to nonzero frequency[12,15] and can be given in the form

$$\mu(\omega) = (e/\kappa T) D(\omega) \ , \tag{1}$$

where

$$4\,\mathrm{Re}\,D(\omega) = 4\int_0^\infty \cos\omega t \langle v(t)v(0)\rangle\, dt \tag{2}$$

is the noise (velocity-fluctuation) spectrum at frequency $\nu = \omega/2\pi$ expressed by the Weiner–Khinchin theorem as the Fourier transform of the velocity autocorrelation. [14] The conductivity is given by the usual relation

$$\sigma(\omega) = n e \mu(\omega) \ , \tag{3}$$

where n is the density of effective carriers. The importance of (2) is that a knowledge of the fluctuations of the equilibrium ensemble in the *absence of the electric field* permits a calculation of the *linear response* of the system (mobility). The result is quite general and depends mainly on the tacit assumption of an average spatially homogeneous system.

The relation as it stands is inconvenient to use in a hopping model since it refers to velocities rather than positions. However, as shown in Appendix A, the relation can be rewritten in the form[16]

$$D(\omega) = -\tfrac{1}{6}\omega^2 \int_0^\infty e^{-i\omega t}\, dt \langle [\vec{r}(t) - \vec{r}(0)]^2\rangle \ , \tag{4}$$

where ω is understood to contain a small negative imaginary component, which can be interpreted as a weak coupling of the system and the universe. [12] The complex ac diffusion constant is now determined by the spectrum of the time-dependent mean-squared displacement and Eq. (4) therefore is a suitable basis for a study of hopping motion.

The limitation of the system to hopping conduction comes in with the specification of the ensemble average in (4). A system of sufficiently low density of centers (e.g., donors), between which hops take place, is considered such that the carriers can be considered localized. It is therefore reasonable to choose a set of orthonormalized local basis functions $\phi_s = \phi(\vec{r} - \vec{s})$, where $\vec{s}$ is used both as a position vector, and as a name for a localized site, and for this low-density system it is reasonable to take

$$\langle \phi_s | \vec{r} | \phi_{s'}\rangle \simeq \vec{s}\, \delta(\vec{s}, \vec{s}') \ . \tag{5}$$

The approximate equality in (5) can almost be taken as the definition of localization for our system. Correspondingly the equilibrium density matrix is

$$\rho_{s,s'} \simeq f(\vec{s})\, \delta(\vec{s}, \vec{s}') \ , \tag{6}$$

where $f(s)$ is the equilibrium distribution function for the initial "carrier" position.

The density matrix in (6) now determines the ensemble average in (4) and one obtains

$$\langle [\vec{r}(t) - \vec{r}(0)]^2\rangle = \mathrm{Tr}[(e^{iHt}\vec{r}e^{-iHt} - \vec{r})^2 \rho]$$

$$= \sum_{s, s_0} (\vec{s} - \vec{s}_0)^2 P(\vec{s}, t | \vec{s}_0, 0) f(\vec{s}_0) \ , \tag{7}$$

where

$$P(\vec{s}, t | \vec{s}_0, 0) = |\langle s | e^{-iHt} | s_0\rangle|^2 \tag{8}$$

is the probability of finding a particle at site s at time t if it started at site $\vec{s}_0$ at time $t=0$, H is the Hamiltonian (divided by $\hbar$) describing its motion. The main purpose for introducing the local basis (5) can be seen in (7)—it breaks up continuous space into discrete denumerable "regions." The final form in (7) has a meaning which is intuitively obvious—the mean-squared displacement is simply a sum over all the "regions" of a product of the square of the distance between them, the probability for the carrier to be at $\vec{s}$ at time t if it started at $\vec{s}_0$ at $t=0$, and the probability of being at $\vec{s}_0$ at $t=0$ $[f(\vec{s})]$.

If (7) is now inserted into (4) we have our basic relation for the frequency-dependent diffusion constant

$$D(\omega) = -\tfrac{1}{6}\omega^2 \sum_{s, s_0} (\vec{s} - \vec{s}_0)^2 \tilde{P}(\vec{s}, \omega; \vec{s}_0) f(\vec{s}_0) \ , \tag{9}$$

where

$$\tilde{P}(\vec{s}, \omega; \vec{s}_0) = \int_0^\infty e^{-i\omega t} P(\vec{s}, t | \vec{s}_0, 0)\, dt \tag{10}$$

is the Laplace or causal Fourier[17] transform (FT) of P.

At this junction in the formal theory [(9) and (10)], one approach to take is to develop a transport equation for $P(\vec{s}, t | \vec{s}_0, 0)$ and attempt an approximate (self-consistent) solution[18] that would incorporate certain features of the low-density

system. Instead, an exact calculation of $P(\vec{s}, t|\vec{s}_0,0)$ [hence, $\tilde{P}(\vec{s}, \omega; \vec{s}_0)$] is considered directly (without a transport equation) for a stochastic process that contains essential elements of the hopping problem but yet is entirely tractable. The importance of (9) and (10) is that a relation between conductivity and a stochastic process is established and one can then calculate $P(\vec{s}, t|\vec{s}_0, 0)$ for a suitable process without reference to its formal definition in (8).

III. CONTINUOUS-TIME RANDOM WALK

The stochastic process we wish to consider in detail is CTRW on a discrete lattice. Montroll[11] and Montroll and Weiss[10] (MW) in a series of papers have developed the theory of RW on lattices with the use of generating function techniques. In particular, MW have introduced an ingenious way of incorporating lattice walks with a continuous time variable into the basic theory.

We refer the interested reader to this excellent series of papers[10,11] for the necessary background in RW on discrete lattices.

In this section, a generalization[19] of the work of MW is presented. Let $R_n(\vec{s}, t)\Delta t$ be the probability for a walker to just arrive at $\vec{s}$ between time t and $t+\Delta t$ in n steps, if it started at $t=0^+$ and $\vec{s}_0=0$, where

$$\vec{s} = s_1\hat{a}_1 + s_2\hat{a}_2 + s_3\hat{a}_3 \ , \tag{11}$$

with the component s_i equal to an integer and the vectors $\hat{a}_i$, the unit primitive translation vectors of the lattice. The walks are restricted to be on infinite lattices or on finite lattices (N^3 distinct points) with periodic boundary conditions.[11] The set of functions satisfy the generalized recursion formula

$$R_{n+1}(\vec{s}, t) = \sum_{\vec{s}'} \int_0^t d\tau\, \psi(\vec{s}-\vec{s}', t-\tau)\, R_n(\vec{s}', \tau) \tag{12}$$

if $\psi(\vec{s}, t)\Delta t$ represents the probability the time between steps occurs in the interval $(t, t+\Delta t)$ resulting in a vector displacement $\vec{s}$. A generating function is now introduced to solve the difference equation in (12):

$$R(\vec{s}, t; z) = \sum_{n=0}^{\infty} z^n R_n(\vec{s}, t) \ . \tag{13}$$

Many of the results of immediate interest in the present paper can be obtained directly from $R(\vec{s}, t; z)$, i.e.,

$$R(\vec{s}, t;\ 1) = \sum_{n=0}^{\infty} R_n(\vec{s}, t) \equiv R(\vec{s}, t) \tag{14}$$

is the probability per unit time for a walker to just reach $\vec{s}$ at time t and

$$\langle n(\vec{s}, t)\rangle = \frac{\partial R}{\partial z}(\vec{s}, t; z)\Big|_{z=1} = \sum_{n=0}^{\infty} nR_n(\vec{s}, t) \tag{15}$$

is the mean number of steps per unit time to just reach $\vec{s}$ at time t, etc.

The restriction to the initial condition

$$R_0(\vec{s}, t) = \delta_{\vec{s},0}\,\delta(t-0^+) \tag{16}$$

is assumed and (12) is multiplied by z^n and summed over n to obtain

$$R(\vec{s}, t; z) - z\sum_{\vec{s}'}\int_0^t d\tau\, \psi(\vec{s}-\vec{s}', t-\tau)\, R(\vec{s}', \tau; z) = \delta_{\vec{s},0}\,\delta(t-0^+) \ . \tag{17}$$

One now takes the Laplace transform of (17) to obtain

$$\tilde{R}(\vec{s}, u;\ z) - z\sum_{\vec{s}'}\tilde{\psi}(\vec{s}-\vec{s}', u)\,\tilde{R}(\vec{s}', u; z) = \delta_{\vec{s},0}\,, \tag{18}$$

where

$$\tilde{\psi}(\vec{s}, u) = \int_0^{\infty} dt\, e^{-ut}\,\psi(\vec{s}, t) \ .$$

Equation (18) is easily solved with the use of Fourier transforms ($\vec{k} \equiv 2\pi\vec{r}/N$, r_i = integer)

$$U(\vec{k},\ u; z) = \sum_{\vec{s}} \tilde{R}(\vec{s}, u;\ z)\, e^{-i\vec{k}\cdot\vec{s}} \ , \tag{19}$$

with the result

$$\tilde{R}(\vec{s}, u;\ z) = N^{-3}\sum_{r} \frac{e^{i\vec{k}\cdot\vec{s}}}{1 - z\Lambda(\vec{k}, u)} \ , \tag{20}$$

where

$$\Lambda(\vec{k}, u) = \sum_{\vec{s}} \tilde{\psi}(\vec{s}, u)\, e^{-i\vec{k}\cdot\vec{s}} \ , \tag{21}$$

which can be called the generalized structure function of the CTRW.

We now introduce the function $P(\vec{s}, t)$, which is equivalent to $P(\vec{s}, t|0, 0)$ in Sec. II, the probability of being (found) at $\vec{s}$ at time t if initially at $\vec{s}=0$. It is evident that in determining $P(\vec{s}, t)$ one must include the possibility that the walker arrived at $\vec{s}$ earlier than t and simply waited there at least until t, i.e.,

$$P(\vec{s}, t) = \int_0^t R(\vec{s}, \tau)\,\Phi(t-\tau)\, d\tau \ , \tag{22}$$

where $R(\vec{s}, t)$ is defined in (14) and $\Phi(t)$ is the probability that the walker remains fixed in the time interval $[0, t]$,

$$\Phi(t) = 1 - \int_0^t \psi(\tau)\, d\tau \ , \tag{23}$$

with

$$\psi(t) \equiv \sum_{\vec{s}} \psi(\vec{s}, t) \ . \tag{24}$$

Taking the Laplace transform of (22) we obtain a simple final expression:

$$\tilde{P}(\vec{s}, u) = \tilde{R}(\vec{s}, u)[1 - \tilde{\psi}(u)]/u \ , \tag{25}$$

where $\tilde{R}(\vec{s}, u)$ is equal to the right-hand side of (20), with $z=1$. The physical interpretation of the Laplace variable u [and hence $\tilde{P}(\vec{s}, u)$] is completed in Sec. IV when we calculate the diffusion constant

for this CTRW process.

An analysis of the structure of the n-step walk contribution to $\tilde{P}(\vec{s}, t)$ is carried out in Appendix B and compared to the analogous quantity obtained in a configuration average of a RW on a random medium. The latter comparison is necessary in order to establish the validity of applying the CTRW process, considered here, to impurity conduction in II.

IV. DIFFUSION CONSTANT $D(\omega)$ FOR RANDOM WALK

One can now connect the discussion of Secs. II and III with the relation

$$\tilde{P}(\vec{s}, \omega; \vec{s}_0)|_{\vec{s}_0=0} = \tilde{P}(\vec{s}, u)|_{u=i\omega+\epsilon} \equiv \tilde{P}(\vec{s}, i\omega). \tag{26}$$

Thus, specifying the initial condition $f(\vec{s}_0) = \delta_{\vec{s}_0, 0}$ in (9), one can directly calculate $D(\omega)$ for the stochastic process outlined in Sec. III. Inserting (25) into (9),

$$D(\omega) = \frac{(i\omega)^2}{6} \frac{1-\tilde{\psi}(i\omega)}{i\omega} \sum_{\vec{s}} s^2 \tilde{R}(\vec{s}, i\omega) \ . \tag{27}$$

The sum over $\vec{s}$ in (27) can be accomplished easily by recognizing

$$\sum_{\vec{s}} s^2 \tilde{R}(\vec{s}, i\omega) = -\frac{\partial^2 U}{\partial k^2}(\vec{k}, i\omega; 1)|_{k=0} \ , \tag{28}$$

where $U(\vec{k}, u; z)$ is defined in (19) and $\vec{k} \equiv 2\pi\vec{r}/N$. From (20),

$$-\frac{\partial^2 U}{\partial k^2}(\vec{k}, i\omega; 1)|_{k=0} = \frac{-\partial^2}{\partial k^2}[1-\Lambda(\vec{k}, i\omega)]^{-1}|_{k=0}$$

$$= +\frac{\partial^2 \Lambda}{\partial k^2}(\vec{k}, i\omega)|_{k=0}[1-\Lambda(0, i\omega)]^{-2}$$

$$-2\left(\frac{\partial \Lambda(\vec{k}, i\omega)}{\partial \vec{k}}\right)^2|_{k=0}[1-\Lambda(0, i\omega)]^{-3} \ . \tag{29}$$

Using the definitions in (21) and (24),

$$\Lambda(0, i\omega) = \tilde{\psi}(i\omega), \tag{30}$$

$$\frac{\partial \Lambda(\vec{k}, i\omega)}{\partial \vec{k}}|_{k=0} = \sum_{\vec{s}} \vec{s}\, \tilde{\psi}(\vec{s}, i\omega) \ , \tag{31}$$

$$-\frac{\partial^2 \Lambda}{\partial k^2}(\vec{k}, i\omega)|_{k=0} = \sum_{\vec{s}} s^2 \tilde{\psi}(\vec{s}, i\omega) \ . \tag{32}$$

As the average fluctuations in (4) are those of a field-free equilibrium ensemble and the system under consideration is assumed to lack any intrinsic asymmetry, the first moment of the generalized structure factor $\Lambda(\vec{k}, i\omega)$ vanishes. Thus, substituting (29), (30), and (32) into (27), one finally has

$$D(\omega) = \tfrac{1}{6}\sigma^2_{\rm rms}(\omega)\, i\omega\, \tilde{\psi}(i\omega)/[1-\tilde{\psi}(i\omega)] \ , \tag{33}$$

$$\sigma^2_{\rm rms}(\omega) \equiv \sum_{\vec{s}} s^2 \tilde{\psi}(\vec{s}, i\omega)/\tilde{\psi}(i\omega) \ . \tag{34}$$

The diffusion constant for the CTRW in (33) is a simple function of the zeroth and second spatial moment of the FT of the basic hopping distribution function $\psi(\vec{s}, t)$. The reason $\tilde{\psi}(i\omega)$ occurs in the denominator of (33) is a reflection of the fact that we are considering a sum over many different paths to each point and we also sum over all the points of the lattice.

The expression for $D(\omega)$ in (33) has been put in a form to resemble a formula previously derived by the authors.[20] In the latter work the spatial and temporal distribution at each hop were considered independent of each other. In the present formalism the previous result can be obtained by setting

$$\psi(\vec{s}, t) = p(\vec{s})\,\psi(t) \ , \tag{35}$$

with

$$\sum_{\vec{s}} p(\vec{s}) = 1 \ . \tag{36}$$

Inserting (35) into (34), the only change in (33) is $\sigma^2_{\rm rms}(\omega) \to \sigma^2_{\rm rms}$, where $\sigma^2_{\rm rms} = \sum s^2 p(\vec{s})$. Thus, the main effect in a conductivity calculation of a space-time correlation at each hop is to include a frequency dependence in the rms displacement. This simple consequence results from the fact that $D(\omega)$ is just the second spatial moment of $\frac{1}{6}(-)\omega^2\tilde{P}(\vec{s}, i\omega)$. It should be stressed, that (35) is a sufficient but *not* a *necessary* condition to have $\sigma^2_{\rm rms}(\omega) \simeq \sigma^2_{\rm rms}$.

Characteristic of hopping among the random sites in an amorphous system is the dominant fact that the hopping time is exponentially dependent on the hopping displacement. That is, a small variation in displacement leads to a change of orders of magnitude in hopping time. A clear experimental demonstration of this fact is shown in Fig. 2 of Ref. 21, which is a study by Colbow on the radiative recombination of donor-acceptor pairs in GaP. The time of light emission is plotted against the pair separation responsible for this light. The plot shows that a variation in spatial separation of almost a factor of 3 leads to a change in emission time of five orders of magnitude. The emission time in the radiative recombination process is a direct measure of hopping time between sites. In II, in fact, we establish an intimate relation between the present formulation of hopping transport and the FT of time-dependent pair luminescence.

Thus, the frequency dependence of $\sigma^2_{\rm rms}(\omega)$ is expected to be very slow (changing by a factor of 3 over many decades of ω). The dominant ω dependence is in $\tilde{\psi}(i\omega)$. The quantitative aspects of a detailed calculation of the expression in (34) will be contained in the forthcoming paper mentioned in Ref. 19. In the present paper we shall neglect the ω dependence of $\sigma^2_{\rm rms}$. However, the importance of retaining the general form of $\psi(\vec{s}, t)$ for a discussion of the connection between the CTRW and a RW among the random impurity

sites can be seen in Appendix B. In that discussion a simplification in the enumeration of the random configurations of hopping sites obtains in impurity conduction as the impurities actually lie on lattice points.[22]

In taking the dc limit ($\omega \to 0$) in (33), a familiar form is recovered:

$$D(0) = \sigma_{\rm rms}^2(0)/6\bar{t} \ , \tag{37}$$

with

$$\bar{t} \equiv \int_0^\infty t\psi(t)\,dt \ , \tag{38}$$

the mean time for a hop (anywhere) or mean waiting time. It is assumed that the carrier does make a hop at some time (no permanent traps) and therefore $\psi(t)$ is normalized to unity [$\tilde{\psi}(i\omega) \to 1$ as $\omega \to 0$]. The existence of a finite dc conductivity for the CTRW process can be traced to the divergence of the sum over $\vec{s}$ in (27). By explicit calculation in (28)–(30) and (32), one observes $\sum_{\vec{s}} \sim \omega^{-2}$ for $\omega \to 0$. If the $\vec{s}$ sum is restricted, e.g., $|\vec{s}| < r_{\max}$ then

$$\omega^2 \sum_{\vec{s}}^{r_{\max}} s^2 \tilde{R}(\vec{s}, 0) \xrightarrow[\omega \to 0]{} 0 \tag{39}$$

and $D(0) \to 0$. In other words, any restriction of the hopping motion to a localized spatial region results in a vanishing contribution to the dc conductivity. Transport in the dc limit is obviously related to unrestricted carrier range or current flow.

A. Example

To gain some insight about the results obtainable with the use of (33) and (37) before going into an extensive first-principles calculation of $\psi(\vec{s}, t)$ and $\psi(t)$ (in II) we shall consider some representative examples assuming the form (35) for $\psi(\vec{s}, t)$. In particular, a versatile functional form for $\psi(t)$ (normalized) is

$$\psi(t) = \lambda(\lambda t)^\nu e^{-\lambda t}/\Gamma(\nu+1) \ , \tag{40}$$

where ν and λ are two arbitrary parameters (λ can be considered the minimum transition rate in the system). The FT of (40) is

$$\tilde{\psi}(i\omega) = (1 + i\omega/\lambda)^{-\nu-1} \ , \tag{41}$$

from which one can obtain

$$\bar{t} = \frac{d\tilde{\psi}(i\omega)}{d(i\omega)}\Big|_{\omega=0} = \frac{\nu+1}{\lambda} \ , \tag{42}$$

where $\bar{t}$ is the mean waiting time [cf. (38)]. Alternatively, $\bar{t}$, λ can be chosen as the independent parameters, and substituting (41) into (33) one can write

$$D(\omega) = \frac{\sigma_{\rm rms}^2}{6} \frac{i\omega}{(1 + i\omega/\lambda)^{\bar{t}\lambda - 1}} \ . \tag{43}$$

A range of values of the two parameters $\bar{t}$, λ will be considered, that produce distinctive *types* of random-time distributions. A particular choice is a sequence of values for $\bar{t}\lambda$: (i) $\bar{t}\lambda \to \infty$, (ii) $\bar{t}\lambda = 1$, (iii) $\bar{t}\lambda \sim 0$. The first corresponds to the limit of a highly peaked distribution. For a fixed $\bar{t}$, let $\lambda \to \infty$:

$$\tilde{\psi}(i\omega) = (1 + i\omega\bar{t}/\bar{t}\lambda)^{-\bar{t}\lambda} \to e^{-i\omega\bar{t}} \tag{44}$$

and therefore

$$\psi(t) \to \delta(t - \bar{t}) \ ,$$

which, when substituted in (43), yields

$$D(\omega) = \tfrac{1}{6}\sigma_{\rm rms}^2[\tfrac{1}{2}\omega \cot(\tfrac{1}{2}\omega\bar{t}) - \tfrac{1}{2}i\omega] \ . \tag{45}$$

In this limit the RW is, in fact, the one discussed initially in Ref. 11. That is, the steps occur at fixed regular intervals, $t = n\bar{t}$. It is interesting to note that Re$D(\omega)$ in (45) exhibits resonance behavior for $\omega = 2\pi n/\bar{t}$ or when the time to hop coincides with an integer multiple of the period of the ac signal. This should not be surprising.

In the second case, $\bar{t}\lambda = 1$, and one obtains the simple exponential decay $\psi(t) = \lambda e^{-\lambda t}$, and for this distribution

$$D(\omega) = \tfrac{1}{6}\sigma_{\rm rms}^2\lambda \ , \tag{46}$$

a result which is completely independent of frequency. The parameter λ^{-1} simply plays the role of of a time scaling factor. With the exponential form for $\psi(t)$ there is only one transition rate in the system, so the frequency response of a system is connected with the possibility of more than one or a range of transition rates.

The case $\bar{t}\lambda \sim 0$ is an example of a spread of transition rates. This type of distribution is necessary to describe impurity hopping (cf. II). In the well-known results of Pollak and Geballe[23] (PG) the real part of the conductivity Re$\sigma(\omega)$ varies as ω^s, where $s \sim 0.7$–0.9, in the frequency range 10^2–10^5 Hz.

For the high-frequency limit $|i\omega/\lambda| \gg 1$ in (43),

$$D(\omega) \sim \sigma_{\rm rms}^2\lambda(\omega/\lambda)^{1-\bar{t}\lambda}\, e^{i(\pi/2)(1-\bar{t}\lambda)} \ . \tag{47}$$

If the identification $1 - \bar{t}\lambda = s$ is made in (47), $\sigma(\omega) \propto \omega^s$ and Im$\sigma(\omega)$/Re$\sigma(\omega) = \tan\frac{1}{2}\pi s$. Therefore, the parameter $\bar{t}\lambda$ must be small in order to describe the basic ac hopping results. One determining relation for the parameters is $\bar{t}\lambda \simeq 0.1$–$0.3$. The other relation that fixes the values of $\bar{t}$, λ can be obtained from the dc diffusion constant in (37), which is independent of λ. In PG, Fig. 5, the measurements [Re(σ) vs $10/T$] on a heavily doped sample, donor concentration $N_D = 2.7\times10^{17}$ cm^{-3}, acceptor concentration $N_A = 0.8\times10^{15}$ cm^{-3}, exhibit *both* ac and dc impurity conductivity (the only example of such measurements reported in their paper). Using (1) and (3) for $n = N_A$,

$$D(\omega)\,(\text{cm}^2/\text{sec}) = 0.6723\,T[\sigma(\omega)\,(\Omega^{-1}\,\text{cm}^{-1})] \tag{48}$$

and evaluating $\sigma(0)$ at $T=3\,^{\circ}\mathrm{K}$, $D(0)=5\times10^{-14}$ cm^2/sec. For the rms displacement in (37), $\sigma_{\rm rms}\sim r_D = 10^{-6}$ cm; thus $\bar{t}=\sigma^2_{\rm rms}/6D(0)\simeq 3.3$ sec and, with $\bar{t}\lambda=0.1$, $\lambda=0.03$ sec^{-1}. The distribution (40) with $\nu=-0.9$ and $\lambda=0.03$ is a very *wide one* (long tail for $t>\bar{t}$). PG needed a distribution of pair lifetimes $G(\tau)$ varying as $\tau^{-1.9}$ (for $s=0.9$).

As an independent estimate of λ, note that λ sets the frequency scale. For $\omega<\lambda$, $D(\omega)$ exhibits essentially dc behavior and for $\omega>\lambda$, $D(\omega)\sim\omega^s$. More precisely, if the absolute value of the denominator in (43) is taken, one finds that $D(\omega)\propto\omega^s$ when $(\omega/\lambda)^{2(1-s)}\gg1$. The minimum value of ω satisfying the latter condition for $\lambda\sim0.03$ is $\omega\sim10$. Although PG did not make measurements for $0<\omega<10^2$, an estimate of $\omega\sim10$ for the "turnover frequency" is certainly reasonable (at 3 °K).

As a final consideration involving the last hopping distribution, we would like to point out there is something disturbingly unphysical about $D(\omega)\propto\omega^s$ for arbitrarily large ω or the singular nature of $\psi(t)\propto t^{-0.9}$ for $t\to0$. This behavior simply denotes the fact that a maximum transition rate has not been put into the system. Such a maximum rate would correspond to the smallest effective impurity separation. A physically more realistic (normalized) distribution leading to a finite value for small t would be

$$\psi(t)=\frac{\lambda[\lambda(t+\alpha)]^{-s}\,e^{-\lambda(t+\alpha)}}{\Gamma(1-s,\,\alpha\lambda)}\ , \tag{49}$$

where now α is an additional parameter and $\Gamma(u,v)$ is the incomplete Γ function.[24]

The results for $D(\omega)$ using (49) are similar to the ones obtained using (43) for the case when $\alpha\omega<1$. However, for $\alpha\omega\gg1$, the leading term of $D(\omega)$ is independent of ω and $D(\omega)\to\sigma^2_{\rm rms}\lambda(\alpha\lambda)^{-s}e^{-\alpha\lambda}/6\times\Gamma(1-s,\,\alpha\lambda)$. With a value $\alpha\sim10^{-11}$ sec, which corresponds to a high-frequency "turndown" of $\omega\sim10^{11}$ rad/sec one obtains $D(\omega)\sim10^{-5}$ cm^2/sec. This value of the high-frequency diffusion constant agrees well with the values obtained by Tanaka and Fan[25] at $\omega/2\pi=9\times10^9$ Hz.

V. CONCLUSION

A general theory of stochastic transport in a disordered system has been developed. It is based on a generalization of a model process: the Montroll–Weiss (MW) CTRW on lattice.[10]

The theory is considered to have wide applicability as the main assumption in adopting the CTRW to transport in an amorphous system is a difference in the procedure for taking configuration averages of products of transition probabilities. This difference is small in a system of a large number of hopping sites and an exponential dependence of the intersite hopping rate on distance (cf. Appendix B). In particular, the theory leads to a simple expression for the frequency-dependent conductivity in which the frequency dependence is determined by the Fourier spectrum of the spatial moments of the function $\psi(\vec{s},t)$. The function $\psi(\vec{s},t)$ is calculated, in detail, for the case of impurity conduction in II. In general, the spectrum of transition rates of the system is used in an explicit determination of $\psi(\vec{s},t)$.

The CTRW process, as described in this paper, can be generalized to include a number of different $\psi(\vec{s},t)$. One can associate a basis of inequivalent points with each lattice point. Montroll has considered this generalization for the familiar RW (steps taken at regular time intervals) in Sec. IV of the second paper of Ref. 11. In the case of two points per unit cell the function $p(\vec{s})$ of Sec. IV is replaced by 2×2 matrices, e.g.,

$$p(\vec{s})\equiv\begin{pmatrix} p_{11}(\vec{s}) & p_{12}(\vec{s}) \\ p_{21}(\vec{s}) & p_{22}(\vec{s}) \end{pmatrix}\ , \tag{50}$$

where $p_{ij}(\vec{s})$ is the probability that a carrier on the jth lattice point in an arbitrary cell makes a transition, in one step, to the ith lattice point of a unit cell which is displaced by $\vec{s}$ from the originally occupied one. The inclusion of the continuous time variable would be a straightforward extension of MW and Montroll.[11] Basically, $\psi(\vec{s},t)$ would be replaced by matrix of dimension $m\times m$ for m points per unit cell. In general, the main necessity for the use of different $\psi(\vec{s},t)$ is that there may be inequivalent sites in the actual system (microscopic inhomogeneity) such that the transition rates from one of these sites is not included in the total *class* of transition rates from another site. An example of this type of situation can be found in impurity hopping in low-compensated semiconductors (cf. Sec. II of II). The inequivalent sites refer to different positions in the vicinity of the ionized acceptor (i.e., the *local* potential). Some aspects of this problem are discussed in II; however, the replacement of $\psi(\vec{s},t)$ by a matrix will be the subject of another paper.[19]

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APPENDIX A: DISPLACEMENT FORMULA FOR DIFFUSION CONSTANT

First, (2) is inverted and use is made of the evenness of $\mathrm{Re}D(\omega)$ and stationicity $\langle v(t)v(t')\rangle = \langle v(t-t')v(0)\rangle$ to rewrite the result in the form

$$\langle v(t)v(t')\rangle=\frac{1}{\pi}\int_{-\infty}^{\infty}\mathrm{Re}D(\omega)e^{i\omega(t-t')}\,d\omega\ . \tag{A1}$$

Displacement (x component) can now be obtained by integration:

$$\langle [x(t)-x(0)]^2\rangle = \int_0^t dt' \int_0^t dt'' \langle v(t')\, v(t'')\rangle = \frac{4}{\pi}\int_0^\infty \mathrm{Re}D(\omega) d\omega \frac{1-\cos\omega t}{\omega^2} \quad . \tag{A2}$$

Now

$$\frac{d}{dt}\langle [x(t)-x(0)]^2\rangle = \frac{4}{\pi}\int_0^\infty d\omega \sin\omega t\, \mathrm{Re}D(\omega)/\omega \quad . \tag{A3}$$

Inverting, again,

$$\mathrm{Re}D(\omega) = \tfrac{1}{2}\omega \int_0^\infty dt \sin\omega t \frac{d}{dt}\langle [x(t)-x(0)]^2\rangle, \tag{A4}$$

and integrating by parts (assuming an $e^{-\epsilon t}$ convergence factor),

$$\mathrm{Re}D(\omega) = -\tfrac{1}{2}\omega^2 \int_0^\infty \cos\omega t\, dt \langle [x(t)-x(0)]^2\rangle \quad . \tag{A5}$$

The Kramers–Kronig relationship requires that

$$-\mathrm{Im}D(\omega) = \frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty} \frac{\mathrm{Re}D(\omega')}{\omega'-\omega} d\omega' \quad , \tag{A6}$$

providing

$$|D(\omega)| \leq A/|\omega| \text{ as } |\omega| \to \infty.$$

But

$$\frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty} \frac{\sin\omega t}{\omega'-\omega} d\omega' = \cos\omega t. \tag{A7}$$

Thus, using (A5) and (A7) in (A6) and then adding the result to (A5), we obtain

$$D(\omega) = \tfrac{1}{2}\omega^2 \int_0^\infty dt\, e^{-i\omega t} \tfrac{1}{3}\langle [\vec{r}(t)-\vec{r}(0)]^2\rangle \quad . \tag{A8}$$

APPENDIX B: STRUCTURE OF n-STEP WALK IN CONTINUOUS-TIME RANDOM WALK AND RELATION TO RANDOM WALK ON RANDOM MEDIUM

To analyze the structure of the n-step walk in the CTRW we examine the basic recursion relation (12):

$$R_n(\vec{s}, \vec{s}_0, t) = \sum_{\vec{s}'} \int_0^t d\tau \psi(\vec{s}-\vec{s}', t-\tau) R_{n-1}(\vec{s}', \vec{s}_0, \tau), \tag{B1}$$

where $R_n(\vec{s}, \vec{s}_0, t)\Delta t$ is the probability for a walker to just arrive at $\vec{s}$ between time t and $t+\Delta t$, in n steps, if it started out at $t=0^+$ from $\vec{s}_0$, and $\psi(\vec{s}, \tau)\Delta\tau$ represents the probability that the time between steps occurs in the interval $(\tau, \tau+\Delta\tau)$ resulting in a vector displacement $\vec{s}$. As evident from the form of (B1), a determination of the probability (density) function $R_n(\vec{s}, \vec{s}_0, t)$ at time t requires a knowledge of the entire time history of the carrier motion ($t \geq \tau \geq 0$). The process is non-Markovian.[26] To simplify the discussion we shall work mainly in Laplace space, i.e.,

$$\tilde{R}_n(\vec{s}, \vec{s}_0, u) = \sum_{\vec{s}'} \tilde{\psi}(\vec{s}-\vec{s}', u) \tilde{R}_{n-1}(\vec{s}', \vec{s}_0, u). \tag{B2}$$

Thus, in Laplace space (B2) has the form of a more familiar RW[10] on a lattice. We now iterate (B2) and derive

$$\tilde{R}_n(\vec{s}, \vec{s}_0, u) = \sum_{\vec{s}^{(n-1)}, \ldots, \vec{s}^{(1)}} \tilde{\psi}(\vec{s}-\vec{s}^{(n-1)}, u) \times \tilde{\psi}(\vec{s}^{(n-1)}-\vec{s}^{(n-2)}, u)\cdots \times \psi(\vec{s}^{(2)}-\vec{s}^{(1)}, u)\tilde{\psi}(\vec{s}^{(1)}-\vec{s}_0, u) \quad . \tag{B3}$$

The total contribution to $\tilde{R}_n(\vec{s}, s_0, u)$ is a sum of products of n factors of $\tilde{\psi}(\vec{s}^{(i)}-\vec{s}^{(i-1)}, u)$, $i=1, \ldots, n(\vec{s}^{(n)} \equiv \vec{s}, \vec{s}^{(0)} \equiv \vec{s}_0)$. A specific set of $\vec{s}^{(i)}$ $(i=1, \ldots, n-1)$ "labels" a "path" and the product of the corresponding n factors of $\tilde{\psi}$ "weights" the relative measure of the path in a determination of $\tilde{R}_n(\vec{s}, \vec{s}_0, u)$.

If we iterate directly from (B1) and take each range of integration as an integral number of intervals of width Δt and sum over this discrete set of time intervals, e.g., $t=L\Delta t$, $\tau=l\Delta t$, $l=0, \ldots, L$, we generate for each set of $\vec{s}^{(i)}$ a sum of products of n $\psi(\vec{s}^{(i)}-\vec{s}^{(i-1)}, l^{(k)}\Delta t)\Delta t$ factors. The sum is over all combinations of integers $l^{(k)}$ such that

$$\Delta t \sum_{k=1}^{n} l^{(k)} = L\Delta t \equiv t. \tag{B4}$$

However, for our present purpose the simpler characterization of the n-step walk in Laplace space (B3) will be considered. Using (25) and (14) we can write

$$\tilde{P}_n(\vec{s}, \vec{s}_0, u) = \tilde{R}_n(\vec{s}, \vec{s}_0, u)[1-\tilde{\psi}(u)]/u \quad , \tag{B5}$$

where $\tilde{P}_n(\vec{s}, \vec{s}_0, u)$ is the Laplace transform of $P_n(\vec{s}, \vec{s}_0, t)$ the probability of being (found) at $\vec{s}$ at time t after n steps if initially at $\vec{s}_0$. The second factor on the right-hand side of (B5) is the Laplace transform of $\Phi(t)$, defined in (23), the probability that the walker remains fixed in time interval $[0, t]$. The properties of $\Phi(t)$ can be obtained from (23) and the fact that $\tilde{\psi}(0)=1$,

$$\Phi(0)=1, \quad \Phi(\infty)=0, \quad -\frac{d\Phi(t)}{dt} = \psi(t). \tag{B6}$$

In II we use the notation $\langle Q(t)\rangle \equiv \Phi(t)$ and discuss this probability function and its Laplace transform in considerable detail.

We shall now examine an n-step random walk on a random medium (RWRM). The random medium is a set of $N+1$ impurities (or hopping sites) located randomly on lattice points in a volume V. Both N and V can be considered as arbitrarily large with the constraint $N/V=N_D$, a fixed density. A given configuration of N sites is designated as $\{\vec{s}_i\}$. The initial position of the carrier at $\vec{s}_0$ is always fixed. The analog to (B1) in the random medium is

$$R_n(\vec{s}, \vec{s}_0, t\,|\,\{\vec{s}_i\}) = \sum_{\vec{s}' \in \{\vec{s}_i\}} \int_0^t d\tau\, W(\vec{s}-\vec{s}', t-\tau\,|\,\{\vec{s}_i\})$$

$$\times \mathcal{R}_{n-1}(\vec{s}', \vec{s}_0, \tau \mid \{\vec{s}_i\}), \quad \text{(B7)}$$

where $\mathcal{R}_n(\vec{s}, \vec{s}_0, t \mid \{\vec{s}_i\})$ and $W(\vec{s}, t \mid \{\vec{s}_i\})$ are defined in the same manner as $R_n(\vec{s}, t)$ and $\psi(\vec{s}, t)$, respectively. There are two essential differences between (B1) and (B7): (i) In the former case (CTRW) the position vectors $\vec{s}$, $\vec{s}'$, etc., could correspond to any lattice point. All knowledge of the fact that there are N hopping sites must be included in a calculation of $\psi(\vec{s}, t)$. In the RWRM all the position vectors $\vec{s}$, $\vec{s}'$ correspond to the net $\{\vec{s}_i\}$ of hopping sites, i.e., the sum over $\vec{s}'$ in (B7) is only over $\{\vec{s}_i\}$ [the point $\vec{s}$ is included in the sum if we assume $W(0, t \mid \{\vec{s}_i\}) = 0$]. (ii) In contrast to the CTRW, in the RWRM the $\mathcal{R}_n(\vec{s}, \vec{s}_0, t \mid \{\vec{s}_i\})$ is a function of the positions of all the hopping sites $\{\vec{s}_i\}$ in addition to $\vec{s}$, $\vec{s}_0$; also, the transition probabilities $W(\vec{s} - \vec{s}', t \mid \{\vec{s}_i\})$ vary from site to site; i.e., in addition to a dependence on $\vec{s} - \vec{s}'$; the W function depends on the relative positions of all the $\{\vec{s}_i\}$ to $\vec{s}'$.

The site dependence of $W(\vec{s} - \vec{s}', t \mid \{\vec{s}_i\})$ needs to be clarified. In II, Eq. (14), we determine

$$W(\vec{s} - \vec{s}', t \mid \{\vec{s}_i\}) = W(\vec{s} - \vec{s}')Q(t; \vec{s}'), \quad \text{(B8)}$$

$$Q(t; \vec{s}') = \exp\left(-t \sum_{i=1}^{N} W(\vec{s}_i - \vec{s}')\right), \quad \text{(B9)}$$

where $W(\vec{s} - \vec{s}')$ is the (quantum mechanical) two-body transition rate[8] between an impurity at $\vec{s}'$ to an impurity at $\vec{s}$, and $Q(t, \vec{s}')$ is the probability that the carrier remains on site $\vec{s}'$ for at least a time t since it hopped there. The transition rate $W(\vec{s} - \vec{s}')$ between any two sites always has the same form, it depends only on the vector displacement $\vec{s} - \vec{s}'$ (three-body transition rates are not considered). The explicit site dependence of (B8) is in the $Q(t; \vec{s}')$ function in the sense of (B9). One can easily see from (B8) and (B9) that

$$\int_0^\infty dt \sum_{\vec{s} \in \{\vec{s}_i\}} W(\vec{s} - \vec{s}', t \mid \{\vec{s}_i\}) = -\int_0^\infty dt \frac{dQ(t; \vec{s}')}{dt} = 1. \quad \text{(B10)}$$

The sum of all possibilities for leaving a site is equal to unity, *independent of the site*. To understand this constraint consider the following situation: A site $\vec{s}_n$ has no nearer than average neighbors. Thus, to leave $\vec{s}_n$ a carrier must jump a larger than average distance. As the transition rate is exponentially dependent on displacement, the probability that the carrier leaves $\vec{s}_n$ at some time t is smaller than from a site with nearer neighbors. However, (B10) must be satisfied. Thus the jumps to far neighbors from $\vec{s}_n$ must somehow be enhanced.[27] The main point to be made now in this discussion is that the transition rates $W(\vec{s}_i - \vec{s}_n)$ between $\vec{s}_n$ and *any* site $\vec{s}_i$ are not enhanced; rather $Q(t; \vec{s}_n)$ is enhanced. From (B10) one can observe for a site with no near neighbors, the probability to *remain* on the site is larger. Thus the $Q(t; \vec{s})$ function in (B9) has the explicit site dependence (relative to the fixed configuration $\{\vec{s}_i\}$) and it "soaks up" the normalization of (B10) from site to site.

The form of the time dependence of (B7) is similar to (B1).[28] As in the CTRW we take the Laplace transform of (B7) and iterate:

$$\tilde{\mathcal{R}}_n(\vec{s}, \vec{s}_0, u \mid \{\vec{s}_i\}) = \sum_{\vec{s}^{(n-1)}, \ldots, \vec{s}^{(1)} \in \{\vec{s}_i\}} \times \tilde{W}(\vec{s} - \vec{s}^{(n-1)}, u \mid \{\vec{s}_i\}) \cdots \times \tilde{W}(\vec{s}^{(1)} - \vec{s}_0, u \mid \{\vec{s}_i\}). \quad \text{(B11)}$$

To compare (B11) with (B5) and (B3) of the CTRW we first must consider $\vec{s}$ to be an arbitrary lattice point [as it is in (B5)]. Thus, we must multiply (B11) by the probability that the $\vec{s}$ is an impurity site, $Nv/V = N_D v$, where v is the cell volume (for the simple lattice we are considering V/v is the number of lattice points in V). In both RW $\vec{s}_0$ is an impurity site by definition of the initial condition. In addition, we must multiply (B11) by the function $\tilde{Q}(u; \vec{s})$ and finally, as discussed in Sec. I, the result has to be configurationally averaged over all random distributions $\{\vec{s}_i\}$ of N impurities on V/v lattice points. Hence

$$\tilde{\mathcal{P}}_n(\vec{s}, \vec{s}_0, u) \equiv \langle N_D v \tilde{\mathcal{R}}_n(\vec{s}, \vec{s}_0, u \mid \{\vec{s}_i\}) \tilde{Q}(u; \vec{s}) \rangle_{\{\vec{s}_i\}} \quad \text{(B12)}$$

is to be compared to

$$\tilde{P}_n(\vec{s}, \vec{s}_0, u) = \tilde{R}_n(\vec{s}, \vec{s}_0, u)\tilde{\Phi}(u), \quad \text{(B13)}$$

with (B3) for $\tilde{R}_n(\vec{s}, \vec{s}_0, u)$.

To explicitly compute the configuration average in (B12) we must consider sums of the form

$$\langle X \rangle_{\{\vec{s}_i\}} = \sum_{\vec{s}_{N-1}, \ldots, \vec{s}_1} X p(\vec{s}_1, \ldots, \vec{s}_{N-1}), \quad \text{(B14)}$$

with

$$\sum_{\vec{s}_{N-1}, \ldots, \vec{s}_1} p(\vec{s}_1, \ldots, \vec{s}_{N-1}) = 1, \quad \text{(B15)}$$

where each $\vec{s}_i$ sum extends over all the lattice points in V. We assume each impurity is randomly located on the lattice:

$$p(\vec{s}_1, \ldots, \vec{s}_{N-1}) = \prod_{i=1}^{N-1} p(\vec{s}_i), \quad \text{(B16)}$$

$$\sum_{\vec{s}_{N-1}, \ldots, \vec{s}_1} p(\vec{s}_1, \ldots, \vec{s}_{N-1}) = \prod_{i=1}^{N-1} \sum_{\vec{s}_i} p(\vec{s}_i) = 1. \quad \text{(B17)}$$

Thus

$$\sum_{\vec{s}_i} p(\vec{s}_i) = 1 \quad \text{(B18)}$$

and

$$p(\vec{s}_i) = v/V. \quad \text{(B19)}$$

For simplicity, we first consider

$$\tilde{\Phi}_2(\vec{s}, \vec{s}_0, u) = \sum_{\vec{s}_{N-1}, \cdots, \vec{s}_1} \prod_{i=1}^{N-1} p(\vec{s}_i)\left(N_D v \tilde{Q}(u; \vec{s}) \sum_{\vec{s}^{(1)} \in \{\vec{s}_i\}} \tilde{W}(\vec{s} - \vec{s}^{(1)}, u \mid \{\vec{s}_i\}) \tilde{W}(\vec{s}^{(1)} - \vec{s}_0, u \mid \{\vec{s}_i\})\right) \quad \text{(B20)}$$

$$= \sum_{i=1}^{N-1} \sum_{\vec{s}_i} \langle \tilde{Q}(u; \vec{s}) N_D v \tilde{W}(\vec{s} - \vec{s}_i, u \mid \{\vec{s}_i\}) \tilde{W}(\vec{s}_i - \vec{s}_0, u \mid \{\vec{s}_i\})\rangle_{\vec{s}_i} p(\vec{s}_i), \quad \text{(B21)}$$

where $\langle \cdots \rangle_{\vec{s}_i}$ is the configuration average over $\vec{s}_1 \cdots \vec{s}_{i-1}$, $\vec{s}_{i+1} \cdots \vec{s}_{N-1}$. We insert (B19) and observe that since each $\vec{s}_i$ sum is now unrestricted (extends over all lattice points),

$$\tilde{\Phi}_2(\vec{s}, \vec{s}_0, u) = \frac{(N-1)v}{V} \sum_{\vec{s}'} \langle \tilde{Q}(u; \vec{s}) N_D v \tilde{W}(\vec{s} - \vec{s}', u \mid \{\vec{s}_i\}) \tilde{W}(\vec{s}' - \vec{s}_0, u \mid \{\vec{s}_i\})\rangle_{\vec{s}'} . \quad \text{(B22)}$$

It is obvious that

$$\tilde{\Phi}_n(\vec{s}, \vec{s}_0, u) = \sum_{\vec{s}^{(n-1)}, \cdots, \vec{s}^{(1)}} \langle \tilde{Q}(u; \vec{s}) N_D v \tilde{W}(\vec{s} - \vec{s}^{(n-1)}, u \mid \{\vec{s}_i\}) \cdots N_D v \tilde{W}(\vec{s}^{(1)} - \vec{s}_0, u \mid \{\vec{s}_i\})\rangle_{\vec{s}^{(n-1)}, \cdots, \vec{s}^{(1)}} . \quad \text{(B23)}$$

In II, Eqs. (14) and (16), it is shown that

$$\langle Q(t; \vec{s})\rangle = \langle Q(t)\rangle \equiv \Phi(t) \quad \text{(B24)}$$

and

$$\langle N_D v W(\vec{s}' - \vec{s}_0, t \mid \{\vec{s}_i\})\rangle_{\vec{s}'} = \psi(\vec{s} - \vec{s}_0, t). \quad \text{(B25)}$$

Thus, the difference between $\tilde{\Phi}_n(\vec{s}, \vec{s}_0, u)$ in (B23) and $\tilde{P}_n(\vec{s}, \vec{s}_0, u)$ in (B13) with (B3) for $\tilde{R}_n(\vec{s}, \vec{s}_0, u)$ is in the procedure for taking the configuration average.

For *every* path in (B23), i.e., for every given set of $\{\vec{s}^{(i)}, i = 1, \ldots, n-1\}$, there is a one-to-one correspondence with a path in the CTRW [(B13) and (B3)]. For each of these paths (each term of the sum) in (B23) one holds the $\vec{s}^{(i)}$ fixed and then averages the product of $\tilde{Q}(u; \vec{s})$ with the n $\tilde{W}$ factors over all possible configurations of the remaining $N-n$ impurities. For the same path in the CTRW one proceeds by writing $N_D v \tilde{W}(\vec{s}^{(i)} - \vec{s}^{(i-1)}, u \mid \{\vec{s}_i\})$ for the ith step and then averages over all the N impurities except the ones at $\vec{s}^{(i)}$, $\vec{s}^{(i-1)}$. Hence, from (B25) for $\vec{s}^{(i-1)} \to \vec{s}^{(i)}$, we have a $\tilde{\psi}(\vec{s}^{(i)} - \vec{s}^{(i-1)}, u)$ factor for this ith step. Now in a system with an arbitrarily large number of impurities N, the difference in the averaging procedures should be very small. In other words, each step $\vec{s}^{(i-1)} \to \vec{s}^{(i)}$ in the averaged RWRM can be thought of as taking place against a background of all possible configurations of a very large number of impurities. The fact that a small finite number $\vec{s}^{(1)}, \ldots, \vec{s}^{(i-2)}, \vec{s}^{(i+1)}, \ldots, \vec{s}^{(n-1)}$ remain fixed in all these possible configurations should not be consequential. In any case, one can in principle compute (B23) for each n and quantitatively compare the result to (B13) with $\psi(\vec{s}, t)$ and $\Phi(t)$ determined from (B25) and (B24).

We continue now with this analysis. In performing the configuration averages in (B23) one must exercise care. Each step of a given path is defined by fixing one transition rate in (B8) and (B9) and allow all others to vary, e.g., for $\vec{s}_0 \to \vec{s}_1$,

$$W(\vec{s}_1 - \vec{s}_0, t \mid \{\vec{s}_i\}) = W(\vec{s}_1 - \vec{s}_0) e^{-W(\vec{s}_1 - \vec{s}_0)t} \times \exp\left(-t \sum_{j \neq 1} W(\vec{s}_j - \vec{s}_0)\right) . \quad \text{(B26)}$$

In order to do the configuration average one then drops the restriction on the sum in the exponent of (B26).[29] In other words, only the explicit steps of the path are fixed, all others varied. Now, for the actual computation of the average the product of terms in (B23) has to be in separable form [cf. Ref. 29 and II, Eq. (10)]. Therefore, it is necessary to consider $P_n(\vec{s}, \vec{s}_0, t)$ (the details of the following calculations are reserved for the paper in Ref. 19). For $n = 1$ and $\vec{s}_0 = 0$,

$$\Phi_1(\vec{s}, 0, t) = N_D v W(\vec{s}) \int_0^t d\tau\, e^{-W(\vec{s})\tau} \exp\left(-N_D \int d^3r \{1 - \exp[-\tau W(\vec{r}) - (t-\tau) W(\vec{r} - \vec{s})]\}\right), \quad \text{(B27)}$$

$$P_1(\vec{s}, 0, t) = N_D v W(\vec{s}) \int_0^t d\tau\, e^{-W(\vec{s})\tau} \exp\left(-N_D \int d^3r \{2 - \exp[-\tau W(\vec{r})] - \exp[-(t-\tau) W(\vec{r} - \vec{s})]\}\right). \quad \text{(B28)}$$

For $n = 2$, one obtains

$$\Phi_2(\vec{s}, 0, t) = \sum_{\vec{s}^{(1)}} (N_D v)^2 W(\vec{s} - \vec{s}^{(1)}) W(\vec{s}^{(1)}) \int_0^t d\tau \int_0^\tau d\tau' \exp[-W(\vec{s} - \vec{s}^{(1)})\tau' - W(\vec{s}^{(1)})(\tau - \tau')] \times \exp\left(-N_D \int d^3r \{1 - \exp[-(\tau - \tau') W(\vec{r}) - \tau' W(\vec{r} - \vec{s}^{(1)}) - (t-\tau) W(\vec{r} - \vec{s})]\}\right) \quad \text{(B29)}$$

and for $P_2(\vec{s}, 0, t)$ the same expression as (B29) except the $1-\exp(\cdots)$ term is replaced with

$$3-\exp[-(\tau-\tau')W(\vec{r})]-\exp[-\tau' W(\vec{r}-\vec{s}^{(1)})]-\exp[-(t-\tau)W(\vec{r}-\vec{s})]\ . \tag{B30}$$

The difference between Φ_n and P_n is simply the replacement of an average of a product of $n+1$ Q's by a product of $n+1$ $\langle Q\rangle$'s. More specifically, the replacement is of the type (B30). To evaluate the integrals in (B27)–(B29), one must now insert a definite function for $W(\vec{r})$. For $W(\vec{r}) = W_M e^{-r/R_d}$ [as in II, Eq. (18)] the integrals are very difficult to calculate. The details of such a calculation for $n=1,2$ will be contained in the paper in Ref. 19. One can, however, gain a semiquantitative understanding of the comparison of (B27) and (B28). At either end of the τ integration in (B27) the integral in the exponent is the same as the corresponding one in (B28). In particular, for small τ [$W(\vec{s})\tau < 1$] in both (B27) and (B28), $\exp\{\cdots\} \sim \langle Q(t)\rangle$. Now, in general, both $\exp\{\cdots\}$ terms can be expected to vary slowly as a function of τ [cf. Paper II, Eqs. (21), (24), (25), and (27)]. The slow variation in τ is due to the exponential form of $W(\vec{r})$ (cf. Ref. 19). Thus, a very reasonable approximation to (B27) and (B28) is

$$\Phi_1(\vec{s}, 0, t) \simeq P_1(\vec{s}, 0, t) \approx N_D v \langle Q(t)\rangle (1-e^{-W(\vec{s})t}). \tag{B31}$$

For $W_M t < 1$, $Q(t) \simeq 1$, so

$$P_1(\vec{s}, 0, t) \simeq N_D v W(\vec{s}) t, \tag{B32}$$

the probability of being at $\vec{s}$ increases with t. However, for $W_M t \gg 1$ [cf. II, Eq. (21)]

$$P_1(\vec{s}, 0, t) \approx N_D v \langle Q(t)\rangle = N_D v \exp\{-\tfrac{4}{3}\pi N_D R_D^3 [\ln(W_M t)]^3\}\ , \tag{B33}$$

the probability decreases with t and the decrease depends on the concentration of hopping sites. For large t one is not likely to find the carrier locally confined.

Thus, we have shown the relation between the CTRW, using (B25) for $\psi(\vec{s}, t)$, and the RWRM. The averaging procedures in the two cases turn out to produce similar results for two reasons: (i) The number of hopping sites in the system volume V is very large; (ii) the exponential dependence of $W(r)$ on r leads to a relatively slow t variation of $\langle Q(t)\rangle$ [cf. II, Eq. (21) and Ref. 19]. The careful quantitative comparison between the two processes, based on calculating integrals of form shown in (B29), will be continued in a forthcoming paper.[19]

[1]W. E. Spear, J. Non-Crystalline Solids 1, 197 (1969); H. Fritzsche, J. Non-Crystalline Solids 6, 49 (1971); and in *Electronic Properties of Materials*, edited by R. H. Bube (McGraw-Hill, New York, 1971), Chap. 13. For additional recent articles, see J. Non-Cryst. Solids (to be published); 8–10, 1 (1972). For phonon transport in disordered solids, R. C. Zeller and R. O. Pohl, Phys. Rev. B 4, 2029 (1971).

[2]M. D. Tabak, S. W. Ing, and M. E. Scharfe, IEEE Trans. Electron. Devices ED-20, 132 (1973); I. Chen, J. Mort, and M. D. Tabak, IEEE Trans. Electron. Devices ED-19, 413 (1972).

[3]J. Feinleib, J. deNeufville, S. C. Moss, and S. R. Ovshinsky, Appl. Phys. Letters 18, 254 (1971).

[4]N. F. Mott, Phil. Mag. 17, 1259 (1968); 22, 1 (1970); B. I. Halperin and M. Lax, Phys. Rev. 148, 722 (1966).

[5]M. H. Cohen, Phys. Today 24, 26 (1971); R. Zallen and H. Scher, Phys. Rev. B4, 4471 (1971).

[6]E. A. Davis, in *Conduction in Low-Mobility Materials*, edited by N. Klein, D. S. Tannhauser, and M. Pollak (Taylor and Francis, London, 1971).

[7]P. G. LeComber and W. E. Spear, Phys. Rev. Letters 25, 509 (1970).

[8]A. Miller and E. Abrahams, Phys. Rev. 120, 745 (1960).

[9]N. F. Mott and W. D. Twose, Advan. Phys. 10, 107 (1961).

[10]E. W. Montroll and G. H. Weiss, J. Math. Phys. 6, 167 (1965).

[11]E. W. Montroll, Proc. Symp. Appl. Math., Am. Math. Soc. 16, 193 (1964); E. W. Montroll, J. Math. Phys. 10, 753 (1969); E. W. Montroll, in *Energetics in Metallurgical Phenomenon* (Gordon and Breach, New York, 1967), Vol. 3, p. 123.

[12]M. Lax, Phys. Rev. 109, 1921 (1958).

[13]H. Scher and M. Lax, following paper, 7, 4502 (1973).

[14]M. Lax, Rev. Mod. Phys. 32, 25 (1960), Sec. I.

[15]E. W. Montroll, Suppl. to Nuovo Cimento, Rendiconti della Scuola, Internazionale Fisica "Enrico Fermi," 10, 217 (1960).

[16]We have omitted in our use of the Nyquist relation a quantum correction factor [Ref. 14, Eq. (7.10)] $C(\omega) = (\hbar\omega/2kT)\coth(\hbar\omega/2kT)$, to divide the right-hand side of Eq. (4). $C(\omega)$ is close to unity for $\omega \ll kT/\hbar$, as it is in conduction problems.

[17]A. Papoulis, *The Fourier Integral and its Applications* (McGraw-Hill, New York, 1962).

[18]H. Scher and M. Lax, Bull. Am. Phys. Soc. 14, 311 (1969); and unpublished.

[19]This generalization was initiated and will be further pursued in a paper by S. C. Maitra and H. Scher (unpublished).

[20]H. Scher and M. Lax, J. Non-Crystalline Solids 8–10, 497 (1972).

[21]K. Colbow, Phys. Rev. 139, A274 (1965).

[22]Dramatic effects of the fact that impurities lie on lattice points are provided by the sharp line fluorescence of pair emission from GaP [J. J. Hopfield, D. G. Thomas, and M. Gershenzon, Phys. Rev. Letters 10, 162 (1963)].

[23]M. Pollak and T. H. Geballe, Phys. Rev. 122, 1742 (1961).
[24]*Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (National Bureau of Standards, Washington, D. C., 1964).
[25]S. Tanaka and H. Y. Fan, Phys. Rev. 132, 1516 (1963); S. Tabaka, M. Kobayashi, E. Hanamura, and K. Uchinokura, Phys. Rev. 134, A256 (1964).
[26]L. Takács, *Stochastic Process* (Methuen, London, 1960); and Ref. 14.
[27]We are indebted to Dr. S. C. Maitra for a discussion of this subtle point as well as others in this Appendix.
[28]The *W* function, however, has the Poisson form for a fixed configuration; hence the RWRM is Markovian (cf. Refs. 26 and 19).
[29]D. G. Thomas, J. J. Hopfield, and W. M. Augustyniak, Phys. Rev. 140, A202 (1965), Eqs. (17) and (18).

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Stochastic Transport in a Disordered Solid. II. Impurity Conduction

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In a previous paper, the authors have developed a general theory of stochastic transport in disordered systems. In the present paper, the theory is applied, in detail, to a prototype of transport in a disordered system – impurity conduction in semiconductors. The complete frequency dependence of the real and imaginary part of the conductivity is calculated. In particular, the calculation details the transition from an ω^s dependence to essentially dc behavior (at a finite frequency), where $s \sim 0.6$–0.8, depending on temperature and concentration. The theoretical results for frequency, temperature, and concentration dependence of the conductivity are shown to be in good agreement with the measurements of Pollak and Geballe (PG). In addition, the ac conductivity data of PG interpreted with the present theory yield experimental evidence for the existence of two-channel hopping in n-type Si.

I. INTRODUCTION

In the preceding paper[1] (hereafter referred to as I) a general theory of transport via localized states in a disordered system has been developed. The motion of the carriers in such a system has been modeled as a continuous-time random walk (CTRW) on a lattice.[2] The carrier executing such a CTRW makes a displacement $\vec{s}$ from each site in time t between steps with a distribution described by a function $\psi(\vec{s}, t)$. All the dynamics of the motion are incorporated into $\psi(\vec{s}, t)$. This simplification, inherent in the structure of the CTRW model, allows one to focus on the basic fluctuating quantity in the hopping motion—the transition rate between the sites. That is, the transition rate is treated as the random variable. For the transport in disordered systems of most interest, the transition rate is a very sensitive function of the intersite separation, so that the fluctuations in the spatial separation are quite mild compared to those, produced by them, in the transition rate. An extensive qualitative discussion of the nature of the present approach to hopping transport is included in the Introduction in I. The mathematical justification of the model is detailed in Appendix B in I.

For this CTRW model the conductivity $\sigma(\omega)$ has been determined exactly and is completely specified by the Fourier transform (FT) of the spatial moments of $\psi(\vec{s}, t)$,

$$\sigma^2_{\rm rms}(\omega) \equiv \sum_{\vec{s}} s^2 \int_0^\infty e^{-i\omega t}\psi(\vec{s}, t)\,dt \,/\, \tilde{\psi}(i\omega) \tag{1}$$

and

$$\tilde{\psi}(i\omega) \equiv \sum_{\vec{s}} \int_0^\infty e^{-i\omega t}\,\psi(\vec{s}, t)\,dt\,. \tag{2}$$

Specifically,

$$D(\omega) = \tfrac{1}{6}\sigma^2_{\rm rms}(\omega)\, i\omega\tilde{\psi}\,(i\omega)/[1 - \tilde{\psi}(i\omega)]\,, \tag{3}$$

where

$$\sigma(\omega) = (ne^2/\kappa T)D(\omega)\,, \tag{4}$$

n is the density of effective carriers (e.g., $n = N_A$, the acceptor concentration, in the case of impurity hopping in a low-compensated n-type semiconductor, to be discussed below), T is the absolute temperature, and $D(\omega)$ is the complex frequency-dependent diffusion constant.[1] In common units, e.g.,

$$D(\omega)\ (\mathrm{cm^2/sec}) = (0.6723\,T)[\sigma(\omega)\ (\Omega^{-1}\,\mathrm{cm^{-1}})] \tag{5}$$