Theory of trap-controlled transient photoconduction

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An analytic solution of the "conventional" multiple-trapping problem is obtained for a *small* quantity of charge moving through a spatially varying, but time-independent, electric field and an arbitrary distribution of traps. The solution is shown to apply to cases of microscopic hopping as well as free-translation through extended states. The solution for a discrete set of traps, simply characterized by their mean times for capture and release (τ_i and $\tau_{r,i}$, respectively) appears in the form of convolutions of modified Bessel functions of order unity, but for a uniform electric field and a continuum of traps satisfying the relation $\tau_i^{-1} = \tau_{r,i}^{-\alpha}$ with the $\tau_{r,i}$ uniformly spaced on a logarithmic scale, the solution reduces to a simple algebraic form which is identical to the one obtained by Scher and Montroll for their power-law waiting-time distribution function $\psi(t) \sim t^{-(1+\alpha)}$. A general equivalence between trapping and continuous-time random walk (CTRW) is further established which shows that $\psi(t)$ can always be constructed from capture and release kinetics, and vice versa. The new trapping solution (and its equivalence to CTRW) is illustrated by reinterpreting transit-time data on a-As_2Se_3. A trap density satisfying $N_i \propto \nu_i^{\alpha-1}$ for $10^{11} < \nu_i < 10^{14}$ sec^{-1} is obtained, where ν_i is the coefficient of $\tau_{r,i} = \nu_i^{-1}\exp(\epsilon_i/kT)$ and $\epsilon_i = 0.65$ eV (for all traps) is the activation energy for release. With the plausible assumption that the microscopic mobility and capture processes are similarly activated (if at all), a trap density for the half-decade interval of ν_i around 7×10^{11} sec^{-1} is found to satisfy $(N_i/N_v) = 4\times10^{-6}\mu_0$(cm^2/V sec), where N_i and N_v are concentrations of traps and transport states, respectively, and μ_0 is the prefactor in $\mu = \mu_0\exp(-\Delta_\mu/kT)$. Both hopping and extended-state motion are compatible with these results, but the most plausible tentative view is hopping with $N_i \sim 10^{13}$ cm^{-3} and $\mu_0 = 0.2$ to 0.002 cm^2/V sec. Additional photo- and dark-conduction data could significantly reduce the range of plausible values.

I. INTRODUCTION

The displacement of charge through a dielectric material plays an essential role in a wide variety of electronic or imaging devices, and a detailed understanding of the dynamics of the process can provide considerable information concerning the electronic structure of a material. Experimentally, the time rate of displacement of charge, as well as the efficiency of their generation by light or energetic electrons, has been studied using a time-of-flight technique.[1] In this technique, a sheet of charge is suddenly injected or created very close to one side of a layer of the dielectric and pushed across the sample with an appropriately directed electric field. The movement of the charge is observed by monitoring the voltage decay across the sample as a function of time. Alternatively, the induced current is often monitored while the voltage is maintained constant. This is an important distinction, because the measurement method affects the carrier motion. On the other hand, the current and voltage decay become simply related via the sample capacitance in the "small-signal" limit (i.e., when the field associated with the moving charge is small compared to the field from other sources). Because of its greater simplicity, the present theoretical formulations are restricted to this small-signal case.

Prior to the recent continuous-time random-walk (CTRW) formalism of Scher and Montrol,[2] the only published analytical solutions of the transient current induced by a moving-charge pulse have been largely restricted to the cases of very fast or no trapping,[3] and one and two traps with arbitrary capture and release times.[4-6] The solution by Teft[5] includes the time domain beyond the first carrier to transit the sample, but the formalism is difficult to extend to arbitrary trap distributions and large signals. The effect of traps on a current transient has also been studied via Monte Carlo simulation by Silver *et al.*[7] and Enck,[8] but the technique has well-known limitations.

The general CTRW problem treated by Scher and Montroll concerns the same basic phenomena, but it involves concepts which appear very different from the conventional trapping concepts. For example, the most conspicuous difference is that CTRW deals with elemental displacement events between pairs of sites, while conventional trapping deals with separate generation, displacement, and capture processes. Because of this difference, there is no place in the CTRW formalism to deal with the kinetics of capture and release explicitly. More recently, Pfister and Scher[9] have presented a phenomenological description of trapping within the framework of the CTRW theory. However, their description does not include the specific kinetics of capture and release and leads to results for a-As_2Se_3 which are incompatible with the re-

sults presented herein.

The objectives of this paper are:

(i) To provide a rigorous analytic solution of the conventional trapping problem for a small signal (negligible mobile charge) and an arbitrary distribution of traps—the results of which have been used previously[10] to explain photocurrent transients in a-As_2Se_3.

(ii) To illustrate the characteristics of the analytic solution via several numerical examples.

(iii) To show that the parameter α in CTRW theory implies a power-law relation ($\tau_i = \tau_{r,i}^{\alpha}$) between the mean trapping time (τ_i) and mean release time ($\tau_{r,i}$) for a sequence of traps whose release times are equally spaced on a logarithmic scale.

(iv) To illustrate, by application to a-As_2Se_3, how the microscopic mobility and trap concentrations can be determined in general by fitting the present trapping theory to experimental transient photocurrent data.

(v) To show that the present trapping theory and CTRW are equivalent in general.

The organization of this paper is as follows: The complete multiple-trapping problem is formulated in Sec. II in a way which shows that the basic continuity equations [Eqs. (1) and (2)] apply to any mobile entity regardless of how it moves between different or similar resting places (traps of different $\tau_{r,i}$). The equations are first formulated in the familiar context of a hole moving through valence states and trapped by localized gap states. Then, in Appendix A, a concept of a trap for a hopping carrier is quantified, and Eqs. (1) and (2) are shown to follow from the master equation for hopping on a lattice, providing the capture and release rate constants are appropriately defined.

In Sec. III, the continuity equations are solved for the case of a spatially varying, but time-independent, electric field. The solution for a uniform field is recovered in the limit of no space charge.

The characteristic features of the analytic solution are illustrated in Sec. IV by progressing from a single trap to several traps, to finally a continuum of traps. The case of a single trap is thoroughly discussed, including a criterion for the definition of a drift mobility and when it can be related to a "diffusion coefficient" via the Einstein relation. The progression from several traps to a continuum is designed to develop insights for the eventual interpretation of experimental current transients and show how the continuum limit for a power law ($\tau_i \propto \tau_{r,i}^{\alpha}$) can be extremely well approximated by a very few traps. In other words, it shows how current transients previously characterized by the parameter α in CTRW, are controlled by just three or four traps having release times ($\tau_{r,i}$) which bracket the experimental transit time. These examples also demonstrate that the experimental transit time (t_T), defined by the intersection of tangents to a log (current) vs log (time) plot,[11] is given by the free transport time (t_0) plus the total resting time in traps that are visited twice or more (i.e., $t_T = t_0 + \sum' M_i \tau_{r,i}$, where $t_0 \equiv L/\mu E$, L is the sample length, E is the electric field, μ is the microscopic mobility, $M_i \equiv L/\mu E \tau_i$ is the expected number of times a carrier visits a trap whose mean release time is $\tau_{r,i}$ and $\sum'$ means only traps for which $M_i \geq 2$ are to be included in the summation). It is shown that this fully accounts for the superlinear dependence of transit time on L/E, as suggested also by others.[12-14] And when the traps also satisfy the power law $\tau_i \propto \tau_{r,i}^{\alpha}$, both the scaling law $t_T \propto t_0^{1/\alpha}$ and "universality" of current shape (previously[2,11] considered characteristic of stochastic hopping) are obtained. But to obtain these features, it is shown that a critical trap (i.e., one for which $M_i \approx 1$ for $\tau_{r,i} \approx t_T$) must fall within the trap sequence which obeys the power law. Thus limitations to universality and scaling are identified.

In Sec. V, the results of this theory are applied to a-As_2Se_3 to show how it leads to a determination of the trap concentration. Unfortunately, this is presently incomplete because a better measure of the transient current in the limit as $t \to 0$ is required. In Sec. VI, the basic equations which define the trapping and CTRW problems are shown to be equivalent in general. Section VII presents a brief summary of the major results and conclusion.

An attempt was made throughout to discuss the physical meaning of the derived equations, and the hope is that Sec. IV in particular will provide insight for the interpretation of experimental current transients. The formal development of theory lies in Secs. II, III, and VI, and the reader who is not concerned with the use of theory to explain data or find trap densities, may find a cursory reading of the other sections adequate.

II. FORMULATION OF THE PROBLEM

The continuity equations which define the multiple-trapping problem are first formulated in the familiar context of an electronic carrier moving through extended states with localized gap states acting as traps. It is then shown that the same equations apply to any mobile entity which simply stops and starts at random from a distribution of resting places. The mean residence time in a particular trap is denoted $\tau_{r,i}$, and the mean travel time between rests of $\tau_{r,i}$ is denoted τ_i. These times, or rather their reciprocals $\omega_i = \tau_i^{-1}$ and $\gamma_i = \tau_{r,i}^{-1}$, are expressed in familiar terms for the case of free translational motion through extended

states. These parameters are broadly defined, however, and appropriate expressions for ω_i and r_i for the case of microscopic hopping are derived in Appendix A. Because of the generality of this formalism, the term trap is used for any localized state which basically immobilizes a carrier for an observable length of time. In contrast with this, the term "transport state" is used for any fundamental state which determines the microscopic mobility (μ) of a charge carrier. Stated differently, traps are states which are sufficiently isolated from each other spatially so that direct transitions between them are negligible. Transport states, on the other hand, are sufficiently interconnected spatially to sustain what appears to be a continuous drift speed (μE, where E is the local electric field). Thus the microscopic mobility is entirely determined by transitions between transport states alone, whereas (ω_i, r_i) are determined by transitions between transport states and traps. These ideas are exemplified in Fig. 1 for the case of a hole drifting through valence (transport) states, with temporary interruptions in that motion due to capture and release from gap (trap) states.

Figure 1 also illustrates a possible path of a hole which was generated near the illuminated surface at $x=0$. The probability of generation per unit volume per unit time is designated $g_v(x,t)$. Subsequent to generation, the hole drifts (under the influence of an x-directed electrostatic force qE, where q is the fundamental electronic charge) toward a substrate at $x=L$. At a point x, where the hole may be captured and released from a trap, the appropriate continuity equations may be written

$$\frac{\partial p}{\partial t} = g_v(x,t) + \sum_{i=1}^{k} p_i r_i - p \sum_{i=1}^{k} \omega_i - \frac{\partial f_p}{\partial x} , \tag{1}$$

$$\frac{\partial p_i}{\partial t} = p\omega_i - p_i r_i , \tag{2}$$

where $p(x,t)$ and $p_i(x,t)$ are the local populations of

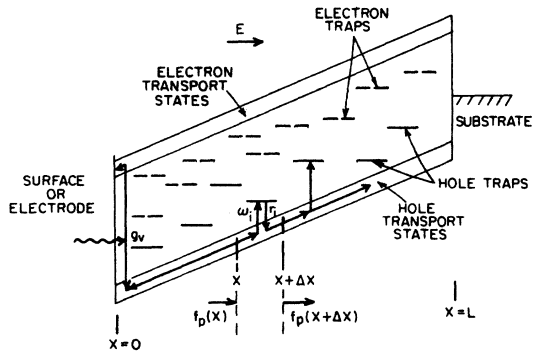

FIG. 1. Schematic of photoreceptor, illustrating continuity equations when the transport states and traps are separated energetically.

the transport states and trap i, respectively. The local flux of mobile holes f_p may be written

$$f_p = p\mu E - D\frac{\partial p}{\partial x} , \tag{3}$$

where the microscopic mobility μ, electric field E, and diffusion coefficient D can now be treated as local quantities. It should be noted that Eq. (2) implies a set of equations, one for each of k distinct traps. Equations (1) and (3) are also explicitly written for one dimension, but their extension to three dimensions is obvious. Similar equations can be written for the electrons and their solution will carry through in the same way as the solution given later for the holes. Recombination also can be included by assigning zero release from one "trap."

Except for an initial condition, such as

$$p(x,0) = p_i(x,0) = 0, \tag{4}$$

and an expression for the electric field (given later) the trapping problem is uniquely defined by Eqs. (1)–(3). It is merely necessary to know values for the set (ω_i, r_i) and μ. The diffusion coefficient is given by the Einstein relation $D = \mu k_B T/q$, where $k_B T$ is Boltzmann's constant times the absolute temperature. It should be mentioned here, however, that a result obtained later (cf. Sec. IV) is that the Einstein relation cannot be used in conjunction with the "drift mobility" (μ_d) except under very special circumstances.

Since the problem defined by Eqs. (1)–(4) (for any assumed electric field) depends only on the set of mean residence times in traps ($\tau_{r,i} = r_i^{-1}$), the mean travel times between type i traps ($\tau_i = \omega_i^{-1}$) and the microscopic mobility (μ), it can be seen that the formalism presented herein is broadly applicable to a wide variety of transport problems. It is simply necessary that the parameters (ω_i, r_i) and μ be appropriately defined.

For the special case of an electronic carrier moving through valence or conduction states, the trapping parameters can be written

$$\omega_i = N_i \sigma_i \bar{v}, \tag{5}$$

$$r_i = \nu_i e^{-\epsilon_i/kT}, \tag{6}$$

where N_i is the number of type i traps per unit volume; σ_i is their capture cross section; $\bar{v}$ is the average speed of a mobile carrier; ν_i is an attempt-to-escape frequency, and ϵ_i is the activation energy for release. Of course, there is a well-known connection between ν_i and $\sigma_i \bar{v}$ provided by detailed balancing, as discussed later. But for the purpose of defining the trapping problem uniquely, one may treat the ω_i and r_i as given independent parameters. Once these are found to fit a particular

current transient, detailed balancing can be later invoked to determine the trap density N_t.

The appropriate parameters (ω_t, r_t) and μ for the case of microscopic hopping on a lattice are derived in Appendix A. The r_t and ω_t are given by Eqs. (A2) and (A3), respectively, and μ is given by Eq. (A7).

In anticipation of the problem of interpreting the trapping parameters once they are determined by fitting the theory to experimental current transients, additional comments are in order concerning temperature and field dependence of the trapping parameters. Indeed, changes in current transients with changes in temperature and field directly reflect the temperature and field dependence of the controlling parameters (ω_t, r_t) and μ, and their expected theoretical dependence on these quantities can be extremely useful.

It is customary to treat release from a trap as requiring an activation energy ϵ_t as indicated explicitly in Eq. (6). It is less common, however, to take into account explicitly a possible activation for capture. But with microscopic hopping this is expected, and one is led to write

$$\omega_t = N_t C_t e^{-\Delta_t/kT}, \tag{7}$$

$$\mu = \mu_0 e^{-\Delta_\mu kT}, \tag{8}$$

where Δ_t and Δ_μ are possible activation energies for a capture event and microscopic mobility, respectively. The form of these equations, which define the coefficients C_t and μ_0, is clearly general and independent of the nature of the microscopic motion. In fact, an interesting case where all three activation energies $(\epsilon_t, \Delta_t$, and $\Delta_\mu)$ are equal is hopping between impurities in a crystal. A trap in this case would be an impurity near the center of a local rarefaction in the impurity concentration. Direct transitions to corresponding impurities in similar rarefactions elsewhere in the crystal would be unlikely. Hence such impurities would qualify as traps. The activation energies for all hopping events, however, would be identical. Incidentally, the capture and release processes in this case would simply be the reverse of each other. In contrast with this, a case in which all three activation energies are different is the capture of a translational carrier from extended states by a repulsive center. The microscopic mobility is then unactivated, of course, and the trapped state could be at any energy. In fact, it could even be an unstable state inside the center lying above the lowest extended states. An illustration of the general case in which Δ_t and ϵ_t are different is shown in Fig. 2. This shows the expected situation for microscopic hopping, particularly for capture from localized "band tail" states in an amorphous material; but for capture from extended states one expects $\Delta_t = 0$ unless the center is repulsive.

It is clear that one can learn a great deal about the nature of trapping centers via determination of the activation energies for the different parameters. Experimentally, this can be done by simultaneously fitting a family of current transients at different temperatures. A similar study of the field dependence of the parameters can also be carried out.

Once the temperature and field dependence of the trapping parameters is known, one can appeal to the steady-state and equilibrium limits for a connection between the capture and release processes, and thereby determine the density of traps. In fact, the steady-state limit of Eq. (2) immediately gives

$$\frac{\omega_t}{r_t} = \frac{N_t C_t}{\nu_t} e^{(\epsilon_t - \Delta_t)/kT} = \frac{p_t}{p} = \frac{N_t}{N_v} e^{\epsilon_t'/kT} f_t(E,T). \tag{9}$$

Here N_v denotes the concentration of transport states, in general, (i.e., N_h in the case of hopping); $\epsilon_t' = E_p - E_v$ is the difference between the trap and transport eigenenergies, respectively; p_t and p are the steady-state population of the traps and transport states; and $f_t(E,T)$ is an appropriate function of the electric field E and temperature T as needed to distinguish the steady-state population from the thermal equilibrium populations. Note that Eq. (9) differs from the usual one obtained from the principle of detailed balance, which implies $f_t(E,T) = 1$. But in general, detailed balance may be invoked only at very low fields where the difference between steady-state and thermal equilibrium becomes negligible.

An example of f_t is the Poole-Frenkel-like expression, $f_t = \exp[-\alpha_t(E)/kT]$, where α_t characterizes the barrier lowering due to the interaction of the applied electric field and the local potential. For a local Coulomb potential, $\alpha_t = (q^3E/\pi\epsilon)^{1/2}$, where ϵ is the permittivity of the dielectric. An alternative formulation of f_t has been given by Onsager.[15]

It is possible that the entire effect of the electric field on capture and release may be due to barrier modification (as in the Poole-Frenkel example above). In this case, one obtains $C_t = \nu_t/N_v$, which

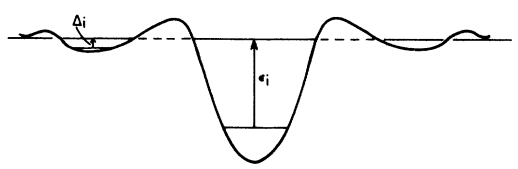

FIG. 2. Energy diagram illustrating different zero-field activation energies for the capture event (Δ_t) and the release event (ϵ_t). In general, the energy separating the two eigenstates, $\epsilon_t' = \epsilon_t - \Delta_t$, may be anything.

is the usual result obtained from detailed balancing. Actually, a sufficient condition for invoking this relation between C_i and ν_i is that the experimentally determinable quantities $N_i C_i$ and ν_i have a common field dependence. Since this can be established experimentally, one has a direct empirical test for establishing whether or not the electric field is effectively low enough to invoke detailed balancing. This is clearly an important result because it unambiguously establishes when one can invert Eq. (9) and solve for the ratio N_i/N_v as a function of trap depth ϵ_i, or attempt-to-escape frequency ν_i.

The foregoing procedure for determining trap densities is probably the most useful result of this trapping theory. It is illustrated by example in Sec. V and is believed to be the most direct and sensitive way available for determining very low trap densities. It should be stressed, however, that the procedure depends on the determination of *both* trapping parameters (ω_i, r_i) for each trap. Consequently the procedure is not available to the alternative CTRW formalism[2,11] unless $\psi(t)$ is specifically determined from the trapping parameters (cf. Sec. VI).

Before leaving this discussion of the trapping parameters, a point should be made concerning the inadequacy of the familiar energy diagram (cf. Fig. 1) to illustrate traps. The point is that a given r_i can be produced by different combinations of ν_i and ϵ_i [see Eq. (6)]. Thus the energy diagram does not uniquely relate to a particular set of trapping parameters and current transient. It is proposed that this problem be avoided by replacing the energy scale in Fig. 1 by a log$r$ scale. To illustrate the specific dependence of a particular r_i on ν_i and ϵ_i, one can extend logr_i into a two-dimensional $(\epsilon_i, \log\nu_i)$ space.

It remains yet to formulate expressions for the electric field and current. If the bulk of the dielectric is assumed space-charge neutral in the absence of any stimulated charge displacements, the local space-charge density may be written

$$\rho = \sigma_0 \delta(x-0) + q\left(p + \sum_{i=1}^{k} p_i - n - \sum_{j=1}^{k'} n_j\right), \tag{10}$$

where σ_0 is the surface charge on the "ungrounded" electrode at $x=0$; and n and n_j are the local concentrations of electrons populating their transport states and k' distinct traps, respectively. The electron distributions must be determined by solving the corresponding continuity equations which are identical in form to Eqs. (1)–(3), though the electron flux f_n drifts in the opposite direction. Thus f_n is negative. The grounded electrode (zero potential) is at $x=L$ (the sample thickness). The surface charge σ_0 depends on the measurement mode. In the open circuit (xerographic) mode,

$$\sigma_0 = \sigma_c - \int_0^t J_c(x=0)\, dt\,, \tag{11}$$

where σ_c is the initial corona charge, and

$$J_c(x) = q(f_p - f_n) \tag{12}$$

is the conduction current at any x. In the closed circuit (constant voltage) mode, σ_0 is continuously determined so that the voltage across the sample remains constant. Since the xerographic mode eliminates this step, it is somewhat easier to analyze.

In either case, the electric field is given by

$$E(x) = \int_0^x \frac{\rho}{\epsilon}\, dx\,. \tag{13}$$

In the xerographic mode, the instantaneous voltage decay rate is given by

$$\frac{dV}{dt} = -\frac{1}{\epsilon}\int_0^L J_c(x)\, dx\,, \tag{14}$$

and in the constant voltage mode, the instantaneous induced current is given by

$$I(t) = \frac{1}{L}\int_0^L J_c(x)\, dx\,. \tag{15}$$

The latter supplies the additional charge to σ_0 that is required to keep V constant. Both of these expressions follow directly from Gauss's law and charge conservation. The important thing to keep in mind is that they are not equivalent, in general, because the electric field which drives J_c is different in the two cases. For the small signal case, on the other hand, they are equivalent because E is essentially constant as mentioned earlier.

III. GENERAL SOLUTION FOR A SMALL SIGNAL FLASH

Very often, experimental test cells contain a nearly fixed space charge due to the accumulation of carriers left over from previous exposures. This is due to the slow escape of carriers from weakly populated slow traps. In fact, it is shown later from the rigorous solution for a constant E field that the post-transit current is due to release from slow traps which also have a low probability of capture. The residual population of these traps produces an electric field in accordance with Eq. (10). To derive a solution which includes this effect, we first present a formal solution of the problem assuming an arbitrary space-varying field $E(x)$, which is constant in time. We then specialize to space-charge-free case by taking the constant E limit. To justify neglect of the time-dependent part of the electric field due to charge created in a given light flash (as opposed to residual charge from previous flashes), it is necessary to restrict attention to small signals.

To accomplish the above in the simplest manner, diffusion is also neglected. Whence $f_p = p(x,t)\mu E(x)$. This is nonessential for the constant E limit; but by comparing the effect of traps on the transit-time dispersion with diffusion neglected to the effect of diffusion with traps neglected, it is shown in Appendix B that the effect of diffusion is typically negligible. Furthermore, its principle effect can even be reincorporated in the results. It should be pointed out, however, that for strongly absorbed light, diffusion may drive carriers to the upstream boundary (against the field), and this may result in surface recombination and/or surface trapping. But it can be shown that these effects can be taken into account by an apparent photogeneration efficiency and/or delayed generation, respectively. The consequences of the latter have been demonstrated by Silver *et al.*[7] using a Monte Carlo simulation of the problem.

A general solution of Eqs. (1) and (2) is now obtained for a δ-function exposure; i.e., for

$$g_\nu(x,t) = g_\nu(x)\delta(t-0). \tag{16}$$

This provides the Green's function, which is also a good approximation to the current transient induced by an actual flash exposure.

Equations (1) and (2) are now solved using the Laplace transform. The Laplace transform of each quantity is denoted by a tilde (~) over the corresponding variable. For example,

$$\tilde{p}(s,x) = \int_0^\infty p(x,t)\exp(-st)\,dt, \tag{17}$$

$$\tilde{p}_i(s,t) = \int_0^\infty p_i(x,t)\exp(-st)\,dt. \tag{18}$$

Whence Eqs. (1) and (2) become

$$(s+\omega_0)\tilde{p} + \frac{\partial}{\partial x}(\mu E\tilde{p}) = g_\nu(x) + \sum_i r_i\tilde{p}_i, \tag{19}$$

$$s\tilde{p}_i = \omega_i\tilde{p} - r_i\tilde{p}_i, \tag{20}$$

where $\omega_0 = \sum_i \omega_i$, and the initial condition given by Eq. (4) is assumed. (It may be noted here that this choice of initial conditions naturally excludes any thermally stimulated carriers, but since the equations are linear, the effect of the latter can always be superposed.) Solving (19) and (20) for $\tilde{p}_i$ and $\tilde{p}$, we obtain

$$\tilde{p} = \frac{1}{\mu E(x)}\int_0^x g_\nu(x')\tilde{K}_a(x-x')\,dx', \tag{21}$$

and

$$\tilde{p}_i = [\omega_i/(s+r_i)]\tilde{p}, \tag{22}$$

where

$$\tilde{K}_a(x-x') \equiv \exp\left[-a\int_{x'}^x \frac{dy}{\mu E(y)}\right], \tag{23}$$

and

$$a(s) \equiv s + \omega_0 - \sum_i \frac{r_i\omega_i}{s+r_i} = s\left(1 + \sum_i \frac{\omega_i}{s+r_i}\right). \tag{24}$$

The second form follows from the definition of $\omega_0 = \sum \omega_i$. The quantity $\tilde{K}_a(x'-x)$ may be recognized as a propagator which represents the probability that a carrier will arrive at x given that it was created at x'. It is assumed for Eq. (23) that the traps are distributed uniformly in space. Otherwise $a(s)$ must be placed under the integral.

From Eq. (15), the Laplace transform for the current is

$$\tilde{I}(s) = \frac{q}{L}\int_0^L \mu E\tilde{p}\,dx. \tag{25}$$

Substituting Eq. (21) into Eq. (25), we obtain

$$\tilde{I}(s) = \frac{q}{L}\int_0^L\int_0^x g_\nu(x')\tilde{K}_a(x-x')\,dx'\,dx. \tag{26}$$

But by interchanging the order of integration, Eq. (26) may also be written

$$\tilde{I}(s) = \frac{q}{L}\int_0^L g_\nu(x')\tilde{D}(x')\,dx', \tag{27}$$

where

$$\tilde{D}(x') = \int_{x'}^L \tilde{K}_a(x-x')\,dx. \tag{28}$$

The inverse transform of these quantities may be written

$$I(t) = \frac{q}{L}\int_0^L g_\nu(x')\dot{D}(x')\,dx', \tag{29}$$

and

$$\dot{D}(x') = \int_{x'}^L K_a(t, x-x')\,dx, \tag{30}$$

where

$$K_a(t,x-x') \equiv \mathcal{L}^{-1}(\tilde{K}_a) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}\tilde{K}_a(x-x')e^{st}\,ds \tag{31}$$

is the inverse transform of $\tilde{K}_a$ by definition.

Now the inverse transform of $\tilde{K}_a$ may be expressed in terms of known functions by first factoring $\tilde{K}_a$ in the following way: from Eq. (23), and the first form for $a(s)$ in Eq. (24), $\ln\tilde{K}_a$ may be written

$$\ln\tilde{K}_a = -st_f - \omega_0 t_f + \sum_i \frac{K_i}{s+r_i}, \tag{32}$$

where

$$t_f(x-x') \equiv \int_{x'}^x \frac{dy}{\mu E(y)} \tag{33}$$

is the free (untrapped) travel time from x' to x,

and

$$K_i \equiv r_i \omega_i t_f . \tag{34}$$

The quantity K_i is an "amplified" release rate, where the amplification factor

$$m_i(x-x') \equiv \omega_i t_f = t_f/\tau_i , \tag{35}$$

represents the number of times a carrier is trapped in the ith kind of trap while traveling from x' to x. Now the inverse transform of the first factor in $\tilde{K}_a$, namely, $\exp(-st_f)$, is just $\delta(t-t_f)$. The second factor is a constant, and

$$\mathcal{L}^{-1}(\exp[K_i/(s+r_i)]) \equiv Y_i(t) = F_i(t \mid K_i, r_i) + \delta(t-0) , \tag{36}$$

where

$$F_i(t \mid K_i, r_i) \equiv (K_i/t)^{1/2} I_1(2(K_i t)^{1/2}) e^{-r_i t} , \tag{37}$$

and I_1 is the modified Bessel function of the first kind of order one. The convolution theorem thus gives

$$K_a(t, x-x') = e^{-\omega_0 t_f} \delta(t-t_f) * Y_1(t) * \cdots * Y_k(t) , \tag{38}$$

where

$$Y_1(t) * Y_2(t) \equiv \int_0^t Y_1(t-\tau) Y_2(\tau)\, d\tau . \tag{39}$$

Substitution of Eq. (38) into Eqs. (30) and (29) supplies the complete solution to the problem for rigid space charge. But unfortunately it is tedious to carry out, because the K_i are a function of $x-x'$. Thus the convolutions must be carried out for each pair of points in space, and the result inserted into Eqs. (30) and (29). The physical meaning of the quantities involved, however, will be preserved when the constant E limit is later taken. The significance of $K_a(t, x-x')$ is that it represents the distribution of travel times to x given that a carrier started in a transport state at x' at $t=0$. The $\delta(t-t_f)$ means the carriers travel $x-x'$ in exactly t_f if the carrier is not trapped at all—a consequence of neglecting diffusion; and F_i represents the distribution of times by which the travel time is extended if the carrier is trapped m_i times. The δ function in Y_i quantifies the effect of those carriers not trapped at all, and therefore, their transit time is not extended. To elaborate further on the importance of the δ function, it is of interest to consider

$$Y_1(t) * Y_2(t) = F_1 * F_2 + F_1 + F_2 + \delta(t-0) . \tag{40}$$

Thus $Y_1 * Y_2$ represents the distribution of extensions in the travel times for a carrier which is trapped m_1 times in trap 1 *and* m_2 times in trap 2, *or* m_1 times in trap 1 alone, *or* m_2 times in trap 2 alone, *or* not captured by either trap. The factor $\exp(-\omega_0 t_f)$ is needed for proper normalization.

Since the above meaning of $K_a(t, x-x')$ will be strictly preserved in the constant E limit, it can be seen that the effect of space charge is to alter the travel time between x' and x. (It can also be shown that t_f is a minimum between fixed x' and x when E is constant.)

The general solution above makes it possible to understand (and predict) the effect of residual charge trapped from previous exposures, or injected from a contact. Since such charge is the same polarity as the moving charge, the field increases monotonically with x. Hence the mobile carriers will move the fastest as $x \to L$. If enough of them do this simultaneously (i.e., if the dispersion is not too great), the current will rise to a cusp at the transit time, much like the Many-Rakavy cusp.[3] But the direct effect of the traps is to cause the pretransit current to decay, as shown later, and the two effects tend to compensate each other. Nevertheless, it can be seen that a built-in space charge will always make it easier to identify the transit time if it can be seen at all. This effect accounts for the inherent advantage of actually using large pulses and a slightly injecting contact, as found by Scharfe[16] in his studies on As_2Se_3. To avoid excessive disturbance of the transit time, however, the photoinjected charge should always be large compared to the contact-injected charge or residual space charge left from previous exposures.

An informative way of specializing to a uniform electric field is to first integrate Eq. (28) by parts. Whence,

$$\dot{D}(x') = \frac{\mu E(x')}{a} - \frac{\mu E(L)}{a} \tilde{K}_a(L-x') + \int_{x'}^{L} \frac{\tilde{K}_a(x-x')}{a} \mu \frac{dE}{dx} dx . \tag{41}$$

Now, for a uniform electric field ($dE/dx = 0$) the last term vanishes; and the first two terms become

$$\dot{D}(x') = \frac{\mu E}{a}[1 - \tilde{K}_a(L-x')] = \frac{\mu E}{a}(1 - e^{-at_f(L-x')}) . \tag{42}$$

Incidentally, this expression may be derived also from Eqs. (26) and (27). But the above approach shows that one can build solutions for an arbitrary space charge from solutions for constant E and different sample lengths. The inverse transform of $\tilde{K}_a/a$ becomes the kernel for the transformation of dE/dx into a modified displacement rate. Equation (41) may also prove useful in future studies to analyze the effect of a gradual accumulation of space charge captured by slow traps when a sample is pulsed repeatedly.

It can be seen from the above that the price of

eliminating one space integration is the need to find the inverse transform of two new quantities, a^{-1} and $\tilde{K}_a/a$. This is done in detail later; but first several remarks may be already made concerning their significance. The quantity $\tilde{K}_a(L-x')$ by itself is already familiar—it represents the probability that the carrier has arrived at the downstream boundary ($x=L$) at a time $t\sim a^{-1}$. And from the discussion to follow, it will become evident that the role of $\tilde{K}_a$ in Eq. (42) is to limit the maximum displacement of a carrier created at x' to $L-x'$. It is obvious that this feature must exist in the mathematics, because once a carrier drifts into the downstream electrode and recombines with its own image, it can no longer contribute to the current. But what may be more surprising is that this feature is a derived aspect of the formalism and is not the consequence of a previously imposed boundary condition. In fact, by neglecting the diffusion contribution to f_p, Eq. (1) automatically reduced to a first-order equation, and the only available integration constant is used implicitly to make p unity at x' where the carrier is first created. If this fact should prove disturbing, it may be comforting to know that one can show, via a rigorous solution with diffusion and all boundary conditions included, that the downstream boundary condition has no observable consequences unless the electric field in the bulk of the sample tends toward zero (i.e., unless the voltage across the possible accumulation region in front of the downstream boundary becomes comparable to the applied voltage).

Insight into the meaning of a^{-1} may be gained via consideration of an infinite sample. In this case $\tilde{K}_a \to 0$ until an infinite time also passes. Correspondingly, Eq. (42) reduces to

$$\tilde{D}(x') \to \mu E/a = l\omega_0/a\,, \tag{43}$$

where $\omega_0 \equiv \sum \omega_i = 1/\tau$ is the reciprocal lifetime for capture by any of the traps, and $l \equiv \mu\tau E$ (known as the Schubweg) is the expected distance a carrier moves between the time it is injected into the transport states and it is captured by any of the traps. Since l is an "elemental displacement" resulting from a single generation event, ω_0/a becomes the Laplace transform of the repeated generation from traps. In other words, a^{-1} is the Laplace transform of a dynamical (or time-dependent) θ factor.

After substituting Eq. (42) into Eq. (27) and replacing μE by $\omega_0 l$, $\tilde{I}(s)$ becomes

$$\tilde{I}(s) = \frac{ql}{L}\frac{\omega_0}{a}\int_0^L g_\nu(x')\left[1-e^{-at_f(L-x')}\right]dx'\,. \tag{44}$$

The inverse transform of $\tilde{I}(s)$ can now be written in the form

$$I(t) = (q/L)l\left[G(t)-\chi(t)\right], \tag{45}$$

where

$$G(t) \equiv \omega_0 \mathcal{L}^{-1}\frac{1}{a}\int_0^L g_\nu(x')\,dx'\,, \tag{46}$$

and

$$\chi(t) \equiv \omega_0 \int_0^L g_\nu(x')\mathcal{L}^{-1}\left(\frac{\tilde{K}_a(L-x')}{a}\right)dx'\,. \tag{47}$$

From the above meaning of ω_0/a, it can be seen that $G(t)$ represents the net time rate at which carriers are repeatedly released into transport states from traps, given the occurrence of an initial photogeneration event. It is also interesting that the release events may occur anywhere in the sample (except near the downstream contact), and is independent of how g_ν is distributed. The function $\chi(t)$ represents the time rate at which the photogenerated carriers finally drift out of the sample at the downstream electrode. In view of the above meaning of G and χ, they are referred to as the "generation" and "exit" functions, respectively.

To finally complete the solution for a discrete set of traps, we next find the inverse transform of a^{-1}. This is accomplished, by expanding a^{-1} in partial fractions,

$$\frac{1}{a} = \left[s\left(1+\sum_{i=1}^{k}\frac{\omega_i}{s+r_i}\right)\right]^{-1} = \sum_{j=0}^{k}\frac{A_j}{s-\alpha_j}\,. \tag{48}$$

The constants α_j are determined by the zero's of $a(s)$. Thus one $\alpha_j = 0$ and the others occur where

$$f(s) \equiv \sum_{i=1}^{k}\frac{\omega_i}{r_i+s} = -1\,. \tag{49}$$

By ordering the r_i so that $r_1 < r_2 < \cdots < r_k$, it can be seen from a sketch of $f(s)$ that Eq. (49) is satisfied by a sequence of α_j which fall between the successive negatives of the r_i; i.e., $-r_{i+1} < +\alpha_j < -r_i$. Another exception is the final α_j which is more negative than $-r_k$, where r_k is the largest r_i. Alternatively, one may define a set of positive numbers s_j with $s_j \equiv -\alpha_j$. These may then be ordered in the same way as the r_j, with each s_j being slightly larger than the corresponding r_j. Each s_j, except the largest, is also smaller than r_{j+1}. Of course, the smallest s_j is $s_0 = 0$. It may be noted that if a trap (or recombination center) were included, from which there is no release ($r_i = 0$), then the pole at $s = 0$ would no longer exist. All recombination centers with different capture probabilities may be grouped together and treated as the first trap ($r_1 = 0$). The trivial case of a single trap turning into a permanent trap or recombination center ($r \to 0$) is briefly discussed in Appendix B.

The corresponding A_j may be found by the method of residues. Thus

$$A_j = \left(s_j \sum_{i=1}^{k} \frac{\omega_i}{(r_i - s_j)^2} \right)^{-1}, \quad j \geq 1, \tag{50}$$

and

$$A_0 = \left(1 + \sum_{i=1}^{k} \frac{\omega_i}{r_i} \right)^{-1}. \tag{51}$$

Alternatively,

$$A_0 = \prod_{i=1}^{k} r_i \Big/ \prod_{i=1}^{k} s_j,$$

and

$$A_j = -\prod_{i=1}^{k} (r_i - s_j) \Big/ s_j \prod_{i \neq j} (s_i - s_j), \quad j \geq 1. \tag{52}$$

Taking the inverse transform of Eq. (48), we obtain

$$\mathcal{L}^{-1}(1/a) = \sum_j A_j e^{-s_j t} \tag{53}$$

and $G(t)$, according to Eq. (46) is

$$G(t) = \omega_0 \left(\int_0^L g_\nu(x')\, dx' \right) \sum_j A_j e^{-s_j t}. \tag{54}$$

It may be helpful to think of the above partial fraction expansion as a "normal coordinate" transformation. The s_j then become the rate constants for release from a set of characteristic traps which are "located" intermediate between the real traps. The corresponding A_j are then the free-carrier components due to release from each of the characteristic traps independently. This is consistent with the fact that A_0, given by Eq. (51), is just the familiar θ factor used to define the drift mobility for the steady-state limit.

The characteristic traps have the useful property, at least conceptually, that they are truly uncoupled from each other. That is, once a carrier is released from one "characteristic" trap it is never captured again by a different characteristic trap. This may be contrasted with the real situation in which a carrier has a probability of ω_i/ω_0 of being captured by the ith trap, independently of the specific trap from which it was previously released. The important role of the characteristic traps is that they simply supply carriers to the transport states at the net rate of $\omega_0 A_j \exp(-s_j t)$. Thus an interesting consequence is that all the characteristic traps except the one corresponding to $s_0 = 0$ eventually become exhausted. A further consequence for sufficiently thick samples is that a steady-state current must obtain after t approaches several times s_1^{-1}.

Another interesting fact, which can be shown from Eq. (48), is that $\sum_j A_j = 1$. This means each photogenerated carrier is initially distributed among the characteristic traps in proportion to A_j. Thus charge is properly conserved even though all the characteristic traps except s_0 eventually become exhausted.

The partial fraction expansion of a^{-1} may now be used to compute the exit function. Since

$$\frac{1}{a} \tilde{K}_a(L - x') = \sum_j A_j \frac{\tilde{K}_a(L - x')}{s + s_j}, \tag{55}$$

we can use the convolution theorem once more to find the inverse transform of each term on the right-hand side of Eq. (55). It thus follows from Eq. (47) that

$$\chi(t) = \omega_0 \sum_{j=0}^{k} A_j \int_0^L g_\nu(x') \int_0^t e^{-s_j(t-\tau)} \times K_a(\tau, L - x')\, dx'\, d\tau, \tag{56}$$

where $K_a(\tau, L - x')$ is given by Eq. (38). When Eqs. (54) and (56), for $G(t)$ and $\chi(t)$, respectively, are inserted into Eq. (45), the final expression for the transient current is obtained.

Unfortunately, the above solution is still rather cumbersome because it requires $K_a(\tau, L - x')$ for arbitrary $L - x$. To alleviate this final complexity, we now restrict attention to the case of strongly absorbed light. In this case,

$$g_\nu(x') = N_0 \alpha \eta(x') e^{-\alpha x'} \xrightarrow[\alpha \to \infty]{} N_0 \eta(0) \delta(x' - 0), \tag{57}$$

may be approximated by a δ function. N_0 is the total number of nonreflected photons in a flash exposure. α is the absorption coefficient and $\eta(x')$ is the local effective conversion efficiency of an absorbed photon into a mobile carrier. The case of strong absorption is frequently studied experimentally and is essential for studying the motion of the electrons and holes separately. A further assumption which is implicit in approximating $q_\nu(x')$ by $\delta(x' - 0)$ is that all the photographed countercharge reaches the floating electrode where it simply negates an equal amount of surface charge. To justify this, it is essential that the Schubweg of the counter charge (l_- say) be large compared to α^{-1}. Thus strong absorption means both $\alpha l_- \gg 1$ and $\alpha L \gg 1$. Incidentally, the case of $\alpha l_- < 1$ is interesting because the associated space charge leads to enhanced photogeneration at high fields and recombination at low fields. But the study of this case is beyond the scope of this paper.

For strongly absorbed light, Eqs. (54) and (56) simplify to

$$G(t) = \eta N_0 \omega_0 \sum_{j=1}^{k} A_j e^{-s_j t}, \tag{58}$$

$$\chi(t) = \eta N_0 \omega_0 \sum_j A_j \int_0^t e^{-s_j(t-\tau)} K_a(\tau, L - 0)\, d\tau, \tag{59}$$

where $K_a(\tau, L - 0)$, given by Eq. (38) with $x - x' = L - 0$, now represents the distribution of transit

times. After executing the convolution with the δ function in Eq. (38), the latter may be written

$$K_a(t, L-0) = \begin{cases} 0, & \text{for } t' \equiv t - t_0 < 0 \\ e^{-\omega_0 t_0} Y_1(t') * Y_2(t') & \\ * \cdots * Y_k(t'), & \text{for } t' > 0, \end{cases} \tag{60}$$

where $t_0 \equiv t_f(L-0)$ is the free transit time corresponding to no capture events. Substitution of Eq. (60) into Eq. (59) then gives

$$\chi(t) = \eta N_0 \omega_0 u(t-t_0) \sum_j A_j e^{-s_j(t-t_0)} \times \int_0^{t-t_0} e^{s_j t'} K_a(t', L-0)\, dt', \tag{61}$$

where

$$u(t-t_0) = \begin{cases} 0, & t < t_0 \\ 1, & t > t_0 . \end{cases} \tag{62}$$

According to Eq. (45), the resulting current can also be written

$$I(t) = \frac{q\eta N_0}{t_0} \sum_j A_j \left(e^{-s_j t} - u(t-t_0) e^{-s_j(t-t_0)} \times \int_0^{t-t_0} e^{s_j t'} K_a(t', L-0)\, dt \right). \tag{63}$$

This is the complete solution to the trap controlled transport problem for a discrete set of traps in a uniform electric field. To evaluate the current for the complete time range, one first transforms the $(\omega_i, r_i) \rightarrow (A_j, s_j)$ in accordance with the procedure described earlier, and evaluates the distribution of transit times according to Eqs. (36), (37), and (60). It should be stressed that the distribution of transit times for each trap alone, $Y_i(t)$, is dependent only on (M_i, r_i), where $M_i \equiv m_i(L-0) = \omega_i t_0$ is the expected number of times a carrier is captured in the ith kind of trap alone while traversing the sample. To elucidate the connection between the (ω_i, r_i) and the resulting characteristic features in the current $I(t)$, a detailed study of special cases is carried through in the next section.

IV. DETAILED STUDY OF SPECIAL CASES

Before embarking on the case of a discrete set of traps, it should be emphasized that any real situation can be adequately analyzed in terms of relatively few discrete traps. The reason for this is that r_i which differ from each other by less than a factor of 2 or 3 are indistinguishable. This follows by analogy from the fact that resolution of r_i finer than this would be equivalent to distinguishing energy states which differ by less than $k_B T$. Recall $r_i = \nu_i \exp(-\epsilon_i/kT)$. Thus 10 traps say, distributed equally on a logarithmic scale, would cover a factor of 10^4 in the corresponding time coordinate. The analytical simplicity and insight gained by treating any arbitrary distribution of traps as a discrete set is next illustrated by several examples.

First, the case of a single trap is examined in depth. From this simple case, the key parameters controlling the general case can be gleaned. The resulting insights are then verified by exhibiting numerical solutions for several different trap distributions. The case of a power law $(\omega_i \propto r_i^{\alpha})$ is studied for later comparison with the corresponding continuum limit.

A. Single trap

In this case it is easy to show that

$$s_0 = 0, \quad s_1 = \omega_1 + r_1, \qquad A_0 = r_1/(\omega_1 + r_1), \quad A_1 = \omega_1/(\omega_1 + r_1). \tag{64}$$

By definition, $\omega_0 = \omega_1$, $t_0 = L/\mu E$, and

$$Y_1(t') = F_1(t' | K_1, r_1) + \delta(t' - 0), \qquad F_1(t') = e^{-r_1 t'} \left(\frac{K_1}{t'}\right)^{1/2} I_1[2(K_1 t')^{1/2}], \tag{65}$$

where $K_1 = M_1 r_1$, and $0 < t' < t - t_0$.

The corresponding current becomes

$$I(t) = \frac{q\eta N_0}{t_0} \left\{ A_0 + A_1 e^{-s_1 t} - u(t-t_0) e^{-M_1} \left[A_0 \left(1 + \int_0^{t-t_0} F_1(t')\, dt' \right) + A_1 \left(1 + e^{-s_1(t-t_0)} \int_0^{t-t_0} e^{s_1 t'} F_1(t') dt' \right) \right] \right\} \tag{66}$$

as obtained by direct substitution of Eq. (60) for a single trap into Eq. (63). Now it may be noted in general from the definition of $M_i = \omega_i t_0$, that $\omega_0 t_0 = \sum_i M_i$. Thus M_1 appears in Eq. (66) as the replacement of $\omega_1 t_0$. This exemplifies the fact that the magnitude of the exit function is always $\exp(-\sum M_i)$ at $t = t_0$. Physically, this is just the probability that a carrier crosses the sample without capture in any of the traps. Such is the significance of the exponential prefactor in Eq. (60). It also follows from this, that the exit function does not grow substantially until some time beyond t_0, and the growth must come from the integral of $F_1(t')$.

To identify the characteristic time for the growth of the exit function, it is of interest to examine the asymptotic forms of $F_i(t)$. From the known properties of $I_1(2(K_i t)^{1/2})$, one finds

$$F_i(t) = e^{-r_i t} M_i r_i (1 + \tfrac{1}{2} M_i r_i t) \quad \text{as } t \to 0, \tag{67}$$

and

$$F_i(t) = e^{-r_i t} \frac{K_i^{1/4}}{2\sqrt{\pi} t^{3/4}} \exp[2(M_i r_i t)^{1/2}] \quad \text{as } t \to \infty. \tag{68}$$

Thus F_i decays monotonically with time if $M_i < 2$, but it starts increasing at $t = 0$ and builds to some peak value for $M_i > 2$ (cf. Fig. 3). For large M_i, the argument of the combined exponential in Eq. (68) may be expanded in a Taylor series about the maximum at $t_i = M_i/r_i$. Whence

$$F_i(t) \approx \frac{\exp(r_i t_i)}{(2\pi)^{1/2}\sigma_i} \exp -\frac{(t - t_i)^2}{2\sigma_i^2} \tag{69}$$

reduces to a Gaussian, with the variance

$$\sigma_i^2 = 2M_i r_i^{-2}. \tag{70}$$

Since $r_i t_i = M_i = \omega_i t_0$, the exponential prefactor in Eq. (60) may now be combined with the $Y_i(t)$ to give

$$e^{-\omega_i t_0} Y_i(t) \approx \frac{1}{\sqrt{2\pi}\sigma_i} \exp \frac{(t - t_i)^2}{2\sigma_i^2} + e^{-M_i}\delta(t - 0). \tag{71}$$

This vividly shows that the carriers which are not trapped at all are weighted by $\exp(-M_i)$ compared to those which are trapped at least once. Since

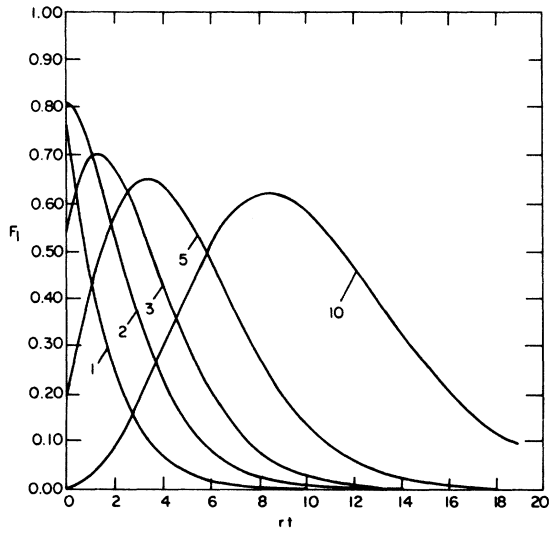

FIG. 3. Illustration of the distribution function $F_1(t)$, and its approach to a Gaussion (the central limit theorem) as the expected number of capture events M_1 increases from 1 to 10.

$M_i \gg 1$ is required for the Gaussian limit, it is consistent to drop the δ-function contribution to Y_i. The remaining distribution of transit times then becomes properly normalized automatically. In terms of the exit function, this means the integral of F_1 in Eq. (66) grows to the order of $\exp(M_1)$ at $t - t_0 \sim t_1$ and the additional unity (which originated from the δ function) should be dropped.

The above transition of F_1 from a monotonically decreasing function to a Gaussian is illustrated in Fig. 3 by a family of curves for $M_1 = 1$–10. Note that a maximum in F_1 appears for $M_1 > 2$ and that the Gaussian character is becoming apparent for $M_1 = 10$. The decay is still slower than the rise, however, which illustrates the difficulty with which F_i yields to the central limit theorem. It should be stressed that the above change in the shape of F_1 with increasing M_1 is dependent only on M_1. The magnitude of r_1 merely determines the time scale. This fact can be seen directly from the definition of F_1 and its asymptotic forms given by Eqs. (67) and (68).

The current traces corresponding to the above family of M_1 are shown in a linear plot in Fig. 4(a) and a logarithmic plot in Fig. 4(b). To facilitate comparison of the shapes of the current traces, they are normalized to unity at $t = t_0$, and time is normalized in units of t_0. Correspondingly, the normalized release rate becomes $R_1 \equiv r_1 t_0$, and M_1 is invariant. The main point to note in these current traces is that the fastest transit time is clearly marked by a discontinuity at t_0 for small M_1, and it reappears again in the neighborhood of

$$t_m = t_0 + M_1/r_1 = t_0 + M_1 \tau_{r,1} \tag{72}$$

for large M. This is the mean transit time t_m and its identification is clearly facilitated by the logarithmic plot. The rounded fall off in the neighborhood of t_m follows the approximate normal probability function with a variance

$$t_\sigma^2 = 2M_1 \tau_{r,1}^2 = 2\omega_1 \tau_{r,1}^2 \frac{L}{\mu E}, \tag{73}$$

as shown earlier by the Gaussian approximation to F_1.

The discontinuity at t_0 is simply an artifact of having left out diffusion. If diffusion were included, as shown in Appendix B, the discontinuity at t_0 would become slightly rounded due to the diffusive dispersion

$$t_{\sigma,D}^2 = 2Dt_0/(\mu E)^2 = 2kTL/\mu^2 E^3. \tag{74}$$

This is clearly very much smaller than the dispersion due to the trapping and it has a different field dependence. Use of the latter to distinguish between diffusion and trapping was pointed out by Teft.[5] It has also been utilized experimentally by

Juska *et al.*[17] A simpler quantitative way to distinguish whether the dispersion in a single current trace is due to trapping or diffusion is to evaluate the magnitude of the dispersion relative to the mean; i.e.,

$$\frac{t_{\sigma_D}^2}{t_0^2} = \frac{2kT}{qEL} = \frac{2kT}{qV} \tag{75}$$

for diffusion,

$$\frac{t_\sigma^2}{t_m^2} = \frac{2M_1\tau_{r,1}^2}{(t_0 + M_1\tau_{r,1})^2} \rightarrow \frac{2}{M_1}, \quad \text{for } M_1\tau_{r_1} \gg t_0 \tag{76}$$

for trapping. For typical sample voltages ($V \sim 500$ V), it is obvious that the trapping dispersion will remain the larger for $M_1 < 10^4$. It should be emphasized that it can also be shown from the above that trapping can produce a broader relative dispersion (t_σ/t_m) than diffusion whenever $\tau_r > t_0\, kT/qV$—even when $M_1\tau_{r,1} < t_0$. In other words, trapping can be identified via its effect on the dispersion even when it does not affect the average transit time. This is clearly a very useful result because it shows that traps can be studied via dispersion, even when they do not extend the transit time beyond the expected trap free limit. A good example may be a-Se at high temperature. It has been claimed by Grunwald and Blakney[1] and Juska *et al.*[17] that the drift mobility approaches the trap-free limit slightly above room temperature. This is supported by fitting the temperature dependence of the measured average carrier speed with a single-trap θ factor. However, an alternative fit (and possibly a better one) can also be obtained by admitting a second trap with a much smaller activation energy. In fact, this appears more consistent with the available data, though additional measurements should be made to clarify this question.

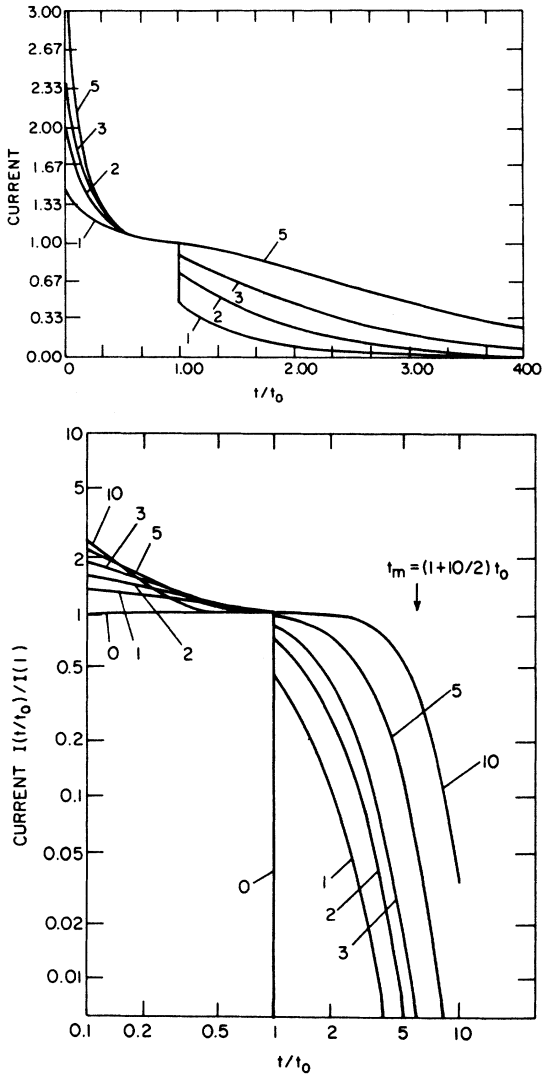

FIG. 4. Family of transient-current traces on linear (a) and logarithmic (b) scales for an increasing number of capture events ($M_i = 1$ to 10) and constant $R_i \equiv r_i t_0 = 2$.

The physical difference between trapping and diffusive dispersion also warrants emphasis. The trapping dispersion (for large M_1) is due to statistical fluctuations in M_1, the number of times a carrier is trapped while crossing the sample. Indeed, this is the reason for the $(M_1)^{1/2}$ law that relates t_m and t_σ. In other words, any carrier which is trapped from a drifting diffusive pulse falls behind by an amount determined by the mean release time. It tends to catch up again when the other carriers become trapped. The only reason they do not stay together on the average is that some carriers stop and "rest" more often than others. This is a very different thing from diffusion and the two phenomena should not be confused, even though both are described by Gaussians in the limit of large M_1. It is significant that there is still a way to tell them apart in the Gaussian limit via a physical measurement.

A still more fundamental point that should be made concerning the difference between trapping and diffusive dispersion is that the Einstein relation ($D = "\mu" kT/q$) cannot be used to relate the diffusion coefficient D to a "drift mobility" $\theta\mu$ whenever the trapping dispersion remains dominant. Thus the usual way to justify the use of the drift mobility (or θ factor) via the "steady-state" solution of the trapping equations overlooks the fact that quasi-steady-state (which is sufficient to characterize the average effect of the traps) can be profoundly different from thermal equilibrium (or detailed balancing) on a *local* level. This is basically what it means when the trapping dispersion is greater than the diffusive dispersion. If a trapped carrier drops behind a diffusing packet

it can no longer participate locally in detailed balancing. A more general criterion then for invoking the Einstein relation (in connection with transient conduction) is to require $t_\sigma < t_{\sigma,D}$. In other problems, of course, where thermal equilibrium prevails uniformly over a sample, the Einstein relation can be used in conjunction with the drift mobility. Indeed, this assumption and the requirement of no net current ($f_p = 0$) is known to be sufficient to derive the Einstein relation for any kind of mobility. On the other hand, it seems that the Einstein relation is invoked more frequently than is justifiable. Hence, the criterion suggested above may be found useful in this regard.

Returning to the artifical discontinuity at t_0 in Fig. 4, it can now be viewed as a convenience. It helps to keep track of t_0 as the mean transit time shifts from t_0 to $t_0 + M_1/r_1$, while M_1 changes from 1 to about 5. For large M_1, the current transient approaches a "rectangular" shape again, though a discontinuity would no longer appear at $t_0' \equiv t_0 + M_1/r_1$. It can be seen that a similar cycle would result from the addition of a second much slower trap. This time, however, the transit time would start shifting smoothly once M_2 exceeded approximately two. And for M_2 of the order of unity or less, the effect of trap 2 would only affect the dispersion.

It can also be seen from the above that the rate at which the mean transit time shifts as M_1 increases from 1 to 5 is modulated by $r_1^{-1} = \tau_{r,1}$. Therefore, it can clearly be very large if $\tau_{r,1} \gg t_0$. To follow it experimentally then, may require a great deal of care in adjustment of the time scale. This alone would be a good reason for studying current transients on a log time scale, if it had not already been found efficacious for other reasons.[2,11]

A second consequence of trapping, which is illustrated in Fig. 4 by the family of curves for increasing M_1, is the initial disappearance of the "plateau" (quasi-steady-state current) for small M_1 and its reappearance for large M_1. The intermediate region, where the plateau just prior to the fastest transit is absent, is a very useful earmark. It implies $M_1 \sim 1$ for $\tau_{r,1} = r_1^{-1} \gtrsim t_0$, as follows from inspection of the condition

$$s_1 t_m = (\omega_1 + r_1)(t_0 + M_1/r_1) \sim 1 . \tag{77}$$

This rule prevails throughout and is made even stronger in Sec. IV B. It is the basis of the critical trap criterion for broad dispersion stated in the Introduction.

Another manifestation of trapping is the early current decay prior to the plateau. This is due to the relaxation of free carriers into traps; and as the general solution shows, it contains all the information about all the traps. Note, in particular, from Eq. (64), that (A_1, s_1) determines (ω_1, r_1) uniquely. This exemplifies the general case in which any set of characteristic parameters (A_j, s_j) can be transformed to a corresponding set of (ω_i, r_i) uniquely. For a single trap, the same information lies in the dispersion; but this is not true in general, as shown in Sec. IV B. Because of this, the current decay in the pretransit region is of great interest; but unfortunately, much of it will often disappear too quickly to measure accurately.

Finally, it should be noted that the magnitude of the quasi-steady-state current is given by

$$I = q\eta N_0 \frac{A_0}{t_0} = q\eta N_0 \frac{\mu E}{L} \frac{r_1}{\omega_1 + r_1} = q\eta N_0 \frac{\theta \mu E}{L} . \tag{78}$$

The initial current, on the other hand, is $I(t \to 0) = q\eta N_0/t_0 = q\eta N_0 \mu E/L$. This shows that the quasi-steady-state current in the plateau region is quantified by the "drift mobility" $\theta\mu$, while the initial current is quantified by the microscopic mobility. Since the mean transit time subsequent to a plateau provides a direct measure of the drift mobility,

$$t_m = t_0(1 + \omega_1/r_1) = L/\theta\mu E , \tag{79}$$

the magnitude of the plateau current then provides a measure of ηN_0. Any higher current prior to the plateau is therefore of great interest, because it provides a measure of some mobility which is larger than the drift mobility corresponding to the plateau region. Although it would be difficult to claim that one has obtained a measure of the microscopic mobility this way, one can at least obtain a lower bound for the microscopic mobility.

Incidentally, the reason the average motion of the carriers can be characterized by a drift mobility when the dispersion cannot is that a quasi-steady-state population of all the traps in the entire sample can obtain even though it does not occur on a local level. Recall that only the total population (as the local population averaged over the entire sample) is manifest in the magnitude of the measured current.

Many of the foregoing results can now be readily extended to the case of a distribution of different kinds of traps.

B. Several traps (with different r_i)

Consider first the case in which all $M_i > 5$, say. The distribution of transit times (Y_i) for each one alone can then be approximated by a Gaussian, and the convolution of all such Gaussians produce another Gaussian (an even better one) whose mean and variance are given by

$$t_m - t_0 = \sum_{i=1}^{k} M_i \tau_{r,i}, \qquad (80)$$

$$t_o^2 = 2 \sum_{i=1}^{k} M_i \tau_{r,i}^2 .$$

Recalling from the solution of Eq. (49) that the smallest characteristic time constant s_j (designated s_1) satisfies the condition $r_1 < s_1 < r_2$, it follows that

$$s_1 t_m > r_1 t_m = M_1 + r_1 (t_0 + \sum_{i=2}^{k} M_i \tau_{r,i}) \gg 1, \qquad (81)$$

if $M_1 > 5$, independently of how small the other $\tau_{r,1}$ may be compared to $\tau_{r,1}$. Therefore, a well-established current plateau must precede a normal probability tail off, just as it did in the single trap case for large M_1.

The current decay prior to the plateau, however, contains much more structure. In fact, it contains all the information necessary to determine the complete set of (ω_i, r_i). From this, the subsequent current tail off could even be predicted, in principle. The measured mean and variance in the transit times, however, provides only two numbers. Hence the tail off of the current for a collection of frequently visited traps cannot be distinguished from the effect of a single trap. The magnitude of the plateau current is also quantified again by $A_0 = \theta$. Therefore, apart from the interesting pretransit decay, which may be too fast to measure, the entire effect of frequently visited traps can be characterized by a θ factor and a Gaussian dispersion.

It is of interest to compare the above result with the solution of Eq. (1) when steady state is assumed for Eqs. (2). It is easy to show, in this case, that Eq. (1) reduces to the trap-free limit with a shift in the time scale by θ. Hence, one would find the correct magnitude of the current and correct transit time at $t_0' = t_0/\theta$. The missing features, however, are the early pretransit current decay and the dispersion, which looks like an exaggerated diffusion. Of these, the dispersion is the most accessible experimentally for showing that the transport is really trap controlled.

Let us now add one infrequently visited trap to the set considered above. We assume the added trap is the slowest one. This is a nonessential assumption, but it turns out that the added trap must be the slowest to produce significant consequences—we designate this added trap by (ω_1, r_1) and advance all the previous indices one unit. This is in accordance with the assumed trap ordering procedure, which requires $r_1 < r_2$. The previous mean and variance in the transit time may be designated t_0' and $t_o'^2$ respectively.

By comparing $Y_1(t)$ to the resultant Gaussian distribution of transit times for all the frequently visited traps, it is easy to predict what happens when the two are convoluted. Recall that $F_1(t)$ monotonically decreases with time for $M_1 < 2$, and its characteristic half width is of the order of $\tau_{r,1}$. It follows that the result of the convolution will not appreciably disturb the Gaussian if $\tau_{r,1} \ll t_o'$, but the result will appear more like F_1 if $\tau_{r,1} \gtrsim t_o'$. This shows that $\tau_{r,1} \sim t_o' > \tau_{r,2}$ is necessary for the added trap to have significant consequences. It is also a result which is clearly in agreement with the central limit theorem.

Now it can also be shown from the characteristic equation [Eq. (48)] that $s_1 \simeq r_1 + \theta\omega_1$ for small ω_1. Therefore, for $t \sim t_0'$, $s_1 t_0' \sim r_1 t_0' + M_1$. Barring $M_1 \ll 1$ (which means no capture and no affect), we obtain $M_1 \sim 1$ for $\tau_{r,1} \gtrsim t_0'$ is necessary to avoid a plateau prior to the fastest transit (t_0'). It is evident from this that one relatively slow trap superposed on the effect of many frequently visited traps must appear much like the single-trap case discussed earlier, but with no discontinuity at t_0'. This demonstrates the critical trap criterion for broad dispersion under the most general conditions. It is also shown later that t_0' is identifiable as the empirical transit time t_T.

We are finally left with the case in which more than one trap satisfies the condition that $M_1 \sim 1$ for $\tau_{r,1} \gtrsim t_0$, but with the $\tau_{r,i}$ separated by at least a factor of 2, only a very few traps can fall in this category at one time. As a result, this case acquires a great interest. It not only encompasses all the practical cases in which the current transient exhibits an interesting structure (broadly identified by no plateau), it means the particular structure observed is sensitive to only a few traps.

To develop further insight for the eventual decomposition of current transients, into a set of trapping parameters, the forward synthesis process is illustrated in Fig. 5 for the case of three traps. The release times for the three traps are separated by a factor of 5, and the corresponding capture frequencies are chosen in accordance with the power law $M_i = R_i^{0.6}$. This is to facilitate later comparison with the continuum limit. The center trap (trap 2) is placed at $(M, R) = (1, 1)$.

All frequently visited traps and diffusion are neglected. Hence the discontinuity at t_0 remains pronounced until the effect of the fastest of the three traps (trap 3) is included. Notice that trap 3 also speeds up the initial decay rate. Trap 1, on the other hand, speeds up the pretransit decay close to the transit time and slows down the long term post-transit decay.

The effect of choosing the R's closer together or farther apart is illustrated in Fig. 6. When they are placed a factor of 10 apart (3a), the post-tran-

sit decay begins to exhibit some structure, and when they are placed a factor of $(10)^{1/2}$ apart (3c), the long-term decay is increased. It can also be shown that when the R's are chosen still closer together (less than a factor of 2 apart), the combination rapidly becomes indistinguishable from ($M=3$, $R=1$) for a single trap, as expected.

Finally, it is informative to compare the above 3-trap sequence to a 7-trap sequence which obeys the same power law. The trapping parameters are listed in Fig. 7 and the corresponding current trace (labeled $t_0 \times 1$) is reproduced in Fig. 6 to facilitate the comparison. The previous 3 traps placed $(10)^{1/2}$ apart (3c) are identical to traps 4, 5, and 6 in the 7-trap sequence. It is evident that the tangents to the pre- and post-transit regions, which define the empirical transit time t_T, are parallel to each other for the 3- and 7-trap sequences. Therefore, trap 7 simply pushes out the transit time and finishes submerging the discontinuity. Trap 3 straightens out the long-term tail off, and traps 1 and 2 in the 7-trap sequence are too infrequently visited to affect anything.

The slower traps in the above sequence become manifest when $t_0 = L/\mu E$ is increased. This physically corresponds to an increase in sample length

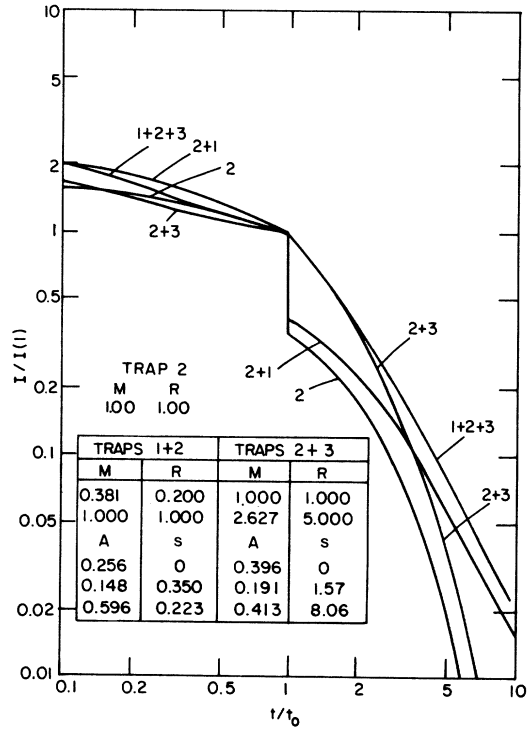

FIG. 5. Comparison of current traces for one, two, and three traps. See text for discussion of how the three-trap case may be viewed as synthesized from its individual members.

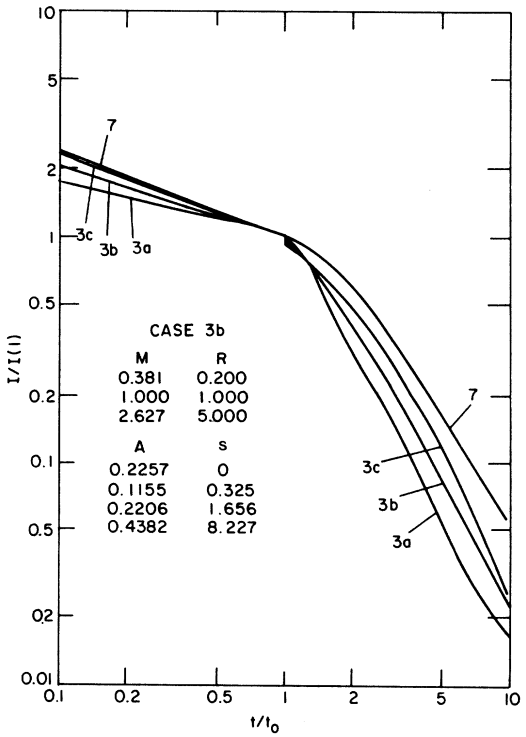

FIG. 6. Comparison of 3- and 7-trap sequences obeying $M_i = R_i^{0.6}$ with $M_i = 1$ at $R_i = 1$. The R_i in the 7-trap sequence are spaced a factor of $(10)^{1/2}$ apart. In the 3-trap sequence, the R_i are spaced apart by factors of 10 (3a), 5 (3b), or $(10)^{1/2}$ (3c). In all cases the center member is $R_2 = 1$.

L or a decrease in electric field E. The effect of increasing t_0 by a factor is illustrated in Fig. 7 by the family of curves labeled $t_0 \times$ multiplier. The corresponding trapping parameters for these curves may be obtained from the table by increasing the indicated (M, R) by the same factor. Note that the "fastest transit time," defined by the intersecting tangents (t_T) increases with t_0. It can be readily verified that the empirical transit time is well approximated by

$$t_T = t_0 + \sum_{i=k^*}^{k} M_i \tau_{r,i} \quad \text{(in real time)}, \tag{82}$$

or

$$\left(\frac{t_T}{t_0}\right) = 1 + \sum_{i=k^*}^{k} M_i/R_i$$

$$= 1 + \sum_{i=k^*}^{k} \frac{\omega_i}{\gamma_i} \quad \text{(in normalized time)},$$

where k^* corresponds to the slowest trap for which $M_i \approx 2$. Therefore, t_T represents the fastest transit as determined by the "frequently" visited traps

(meaning $M_i \geq 2$) alone. It is apparent from this that t_T may be used to define an effective θ factor or "effective drift mobility", providing it is understood that it characterizes only the average speed of those carriers which successfully avoid the infrequently visited traps. With this understanding one can attach real meaning to the previously unacceptable idea that the "drift mobility" depends upon sample thickness. It is simply a consequence of the fact that more traps qualify as being frequently visited as the sample size increases. This is manifest in the above example by the fact that k^* reduces from 6 to 3 as t_0 is expanded by a factor of 10. It can also be seen that the general requirement of $M_i \gtrsim 2$ for a trap to be included among the frequently visited traps quantitatively accounts for the superlinear dependence of the empirical transit time t_T on sample thickness. More generally, however, the scaling of t_T is a function of $t_0 = L/\mu E$ alone. Superlinear effects therefore result from the fact that more and more terms must be included in the sum in Eq. (82). The basic idea that this is responsible for the observed scaling of t_T with L/E has been proposed by others[12-14] also, but this is apparently

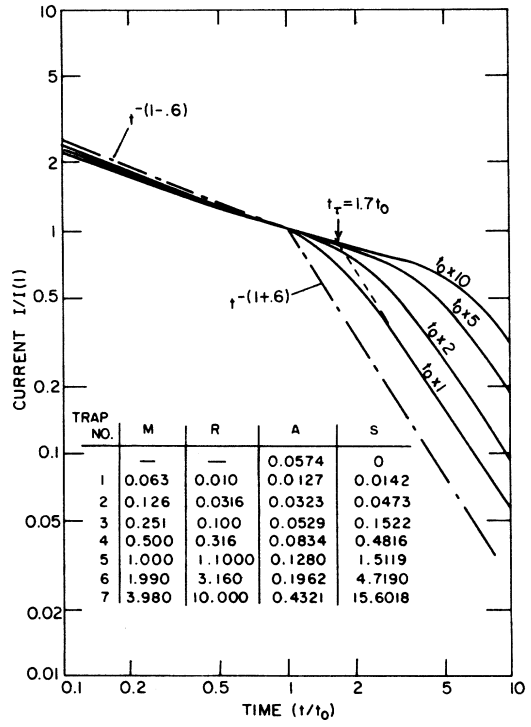

FIG. 7. Comparison of discrete 7-trap sequence with continuum obeying the same power law, $M_i = R_i^{0.6}$. The family of traces for increasing $t_0 = L/\mu E$ illustrates a departure from "universality" as the critical trap (see text) approached the end of a finite sequence.

the first analytical quantification of the concept. Connection between the fastest transit t_T and an average drift mobility is supported by the analysis herein, it is inappropriate to attribute the dispersion in transit times to a "distribution of mobilities," as has been suggested.[16] The dispersion is predominantly controlled by the infrequently visited traps which must be excluded from the set of traps which control the drift mobility. In fact, it is more meaningful to view the dispersion as simply the generation limited discharge[20] due to the release of carriers which happen to be trapped just once in "slow" (meaning $\tau_{r,i} \gtrsim t_T$) traps.

The importance of excluding the infrequently visited traps from the summation in Eq. (82) can also be clearly seen from the data provided in Fig. 7. Note that the slower traps contribute increasingly to the summation. Note also that trap 7 alone gives $t_T = 1.4t_0$, while the inclusion of trap 6 as well gives $t_T = 2.0t_0$. These should be compared to the graphical (empirical) result of $t_T = 1.7t_0$. Thus trap 6 marginally satisfies the criterion $M_i \gtrsim 2$. It can also be readily verified that traps 3 through 7 give $t_T = 7.1t_0$. This is in good agreement with the empirical value of $t_T = 7t_0$ for the case of "$t_0 \times 10$" (for which $M_3 = 2.51$). It should also be noted how erroneous it would be to not delete the traps for which $M_i < 2$. In fact, it is apparent that the sum would even diverge if the trap sequence were extended to $R_i \to 0$. This is evidently intimately related to the diverging moments of the waiting-time distribution function in an equivalent CTRW problem. We see here that the divergence results from the potential influence of the unvisited traps which are not actually manifest in controlling the transport.

The particular trap distribution which produces current traces identical to those predicted by CTRW for a power law $\psi(t)$ is obtained next by passing to a continuum of traps.

C. Continuum of traps

Passage to a continuum of traps is readily accomplished by treating the ordered pairs (ω_i, r_i) as a continuous function, $\omega(r)$. Motivated by the fact that $\tilde{I}(s)$ [cf. Eq. (44) with $g_\nu(x') = \delta(x' - 0)$] becomes identical to Scher and Montroll's[2] $\tilde{I}(s)$ [i.e., their Eq. (54)] if $a(s) \to s^\alpha$, we are led to try $\omega(r) \propto r^\alpha$. With this, it is natural to choose the r equally spaced on a logarithmic scale. Hence, we write

$$r_{n+1} = r_1 z^n, \quad \omega_{n+1} = \omega_1 z^{\alpha n} = \omega_1 (r_{n+1}/r_1)^\alpha,$$

from which it is easy to show that

$$\frac{a(s)}{s} = 1 + \sum_{i=1}^{\infty} \frac{\omega_i}{r_i + s} \to 1 + \frac{\omega_1}{r_1} \int_0^\infty \frac{z^{\alpha n}}{s/r_1 + z^n}\, dn. \tag{83}$$

After substituting $u = z^n r_1/s = r_{n+1}/s$,

$$\frac{a(s)}{s} = 1 + \frac{\omega_1 s^{\alpha-1}}{\ln z r_1^{\alpha}} \int_{r_1/s}^{\infty} \frac{u^{\alpha-1}}{1+u}\, du . \tag{84}$$

But for $r_1 \ll s$,

$$b(\alpha) \equiv \int_{r_1/s}^{\infty} \frac{u^{\alpha-1}}{1+u}\, du \approx \int_0^{\infty} \frac{u^{\alpha-1}}{1+u}\, du - \frac{1}{\alpha}\left(\frac{r_1}{s}\right)^{\alpha}$$
$$= \frac{\pi}{\sin\alpha\pi} - \frac{1}{\alpha}\left(\frac{r_1}{s}\right)^{\alpha}, \tag{85}$$

using formula 856.2 of Dwight.[18] Whence

$$a(s) \approx s + \frac{b(\alpha)\omega_1}{\ln z} \frac{s^{\alpha}}{r_1^{\alpha}} \sim \frac{\omega_1 s^{\alpha}}{r_1^{\alpha}} . \tag{86}$$

The last approximation follows from the facts that $b/\ln z \sim 1$, and

$$a\left(\frac{1}{t_T}\right) t_0 = \frac{t_0}{t_T} + \frac{\omega_1 t_0 t_T^{-\alpha}}{r_1^{\alpha}} \sim 1 . \tag{87}$$

We know $t_0 \ll t_T$, if the traps are controlling the transit time. By substituting ω_n/r_n^{α} for ω_1/r_1^{α} in this expression for at_0, one also readily finds $M_n = \omega_n t_0 \sim 1$ for $r_n = t_T^{-1}$—regardless of α. It may also be noted that the overwhelming contribution to $b(\alpha)$ comes from $u \sim 1$, which again means $s \approx r_n \approx t_T^{-1}$.

The above results show that the choice of $\omega(r) \propto r^{\alpha}$ not only reproduces the Scher and Montroll solution identically, but it also verifies the critical trap criterion once again; namely, that the absence of a current plateau near the transit time means that a trap exists that captures a carrier approximately once, and releases it after the order of the fastest transit time.

To show that only a very few traps actually control the power law character of the continuum limit, the asymptotic solution for the inverse transform of the current for $\alpha = 0.6$ is compared to the corresponding 7-trap sequence in Fig. 7. From the close similarity it is apparent that the three or four traps whose release time falls in the neighborhood of the transit time completely controls the slopes of the pre- and the post-transit current near the transit time.

The features of "universality" and a superlinear dependence of transit time on sample thickness [$t_T \propto t_0^{1/\alpha}$, cf. Eq. (87)], therefore carry over to the finite-trap sequence as well. It is merely necessary that the sequence extends one or two traps beyond the critical trap which satisfies the criterion of $M_i \sim 1$ for $\tau_{r,i} \sim t_T$. Indeed, this defines the range of validity for the universality and superlinearity features. The "$t_0 \times 10$" case in Fig. 7 (for which $M_1 = 0.63$) provides a good example of the change in character when the critical trap falls too close to the slow end (smallest M_i) of the sequence. The effect is most evident in the pretransit region which exhibits a slight curvature. It is significant that this behavior is often manifest in measured characteristics. It indicates that a change in character may be on the horizon with thicker samples or lower electric fields. Unfortunately, it may not be possible to explore this region experimentally, because of dark current limitations.

V. Application to a-As_2Se_3

Having established the identity between the current transient produced by a continuum of traps and that produced by the stochastic hopping case of CTRW,[2] it follows that all experimental data previously fit with the stochastic hopping theory can now be reinterpreted in terms of traps. Also, in view of the fact that the two interpretations and their material implications are different, it is clearly an important exercise to carry out. Some of the major differences between trapping and stochastic hopping are discussed in the Introduction. But a more specific difference that deserves further emphasis is that $\psi(t)$, in the case of stochastic hopping, may be envisioned to arise from hopping between a disordered array of intrinsic molecules. With a trapping interpretation, on the other hand, transport is controlled by a relatively low concentration of traps, which are most likely extrinsic. This difference is manifest analytically by the appearance of a trap concentration and a well-defined microscopic mobility in the trapping analysis, while these quantities are missing in the stochastic hopping analysis.

To illustrate the above differences, a-As_2Se_3 provides a good example. It has been thoroughly studied experimentally,[9,11,13,14,16] and apart from the excessive activation energy for t_T, it is in good agreement with stochastic hopping theory.[9] The current transients for a-As_2Se_3 have been fit with α [*in* $\psi(t) \sim t^{-(1+\alpha)}$] ranging between 0.45 and 0.65. Universality (i.e., a specific α) is well satisfied for a single sample, though significant differences arise between different samples. A dependence of current shape on the nature of the contact and process conditions (such as simultaneous exposure with weakly absorbed light) has also been noted. But these effects are most pronounced at lower fields, and it appears that they are explicable in terms of bulk space charge. They are also not a major concern because of their lack of effect on the scaling laws for the transit time at high fields ($> 2 \times 10^4$ V/cm). In all cases $t_T \propto [L/\bar{l}(E)]^{1/\alpha}$, with $\bar{l}(E) \propto E$, Scher and Montroll's expected dis-

placement per hop,[2] is well satisified; with a blocking top electrode (Al or metalized insulator), the activation energy of t_T at low fields (less than 5×10^4 V/cm is 0.65 eV for temperatures between 220 and 320° K.[9,11] With an injecting top electrode (Au), a smaller activation energy (~0.57 eV) is typical.[9]

The established scaling of t_T carries over to the trapping solution (for a continuum of traps) identically if $\bar{l}(E)$ is replaced by μE. This connection between $\bar{l}$ and μ for hopping is also the one expected according to Eq. (104) in Sec. VI.

By making use of the critical trap criterion for broad dispersion (which is actually well defined for a continuum of traps), we next determine a connection between the microscopic mobility and trap density. The critical trap criterion of $M_i \sim 1$ for $\tau_{r,i} \sim t_T$ actually provides two relations which can be used to determine ν_i (for known ϵ_i) and the relative trap concentration. For example, from Fig. 9 of Ref. 11 (Chap. III), $t_T = 100$ sec at 235 °K for 100 V across a 58-μm sample. The corresponding activation energy is 0.65 eV. Hence, $\nu_i = 7\times10^{11}$ sec^{-1}. By putting $M_i \sim 1$, for the same trap, we obtain

$$\frac{N_i}{N_v} \sim \nu_i \frac{\mu E}{L} e^{\Delta_i/kT_*} = 4\times10^{-6}\ \mu e^{\Delta_i/kT}. \tag{88}$$

This assumes a sufficiently low field to justify using $C_i = \nu_i/N_v$, and allows for a possible activation in the capture process (Δ_i).

Applying the above procedure to the critical traps for a range of E/L, and assuming the activation energy is strictly constant, one finds $10^{11} < \nu_i < 10^{14}$ sec^{-1}. Although the range of ν_i for $\epsilon_i = 0.65$ eV could be narrowed substantially if the activation energy for t_T were not strictly constant, a spread of at least a factor of 10 to 100 appears well established.

As shown in general, the concentration of any trap can be determined from the experimentally determined trapping parameters at low fields. But to illustrate the meaning of α, it is informative to use the principle of detailed balancing and the power law, $\omega_i \propto r_i^\alpha$ to obtain the corresponding relative trap concentration. Thus

$$\frac{N_i}{N_v} = \text{const}\,\nu_i^{\alpha-1} e^{-(\alpha\epsilon_i - \Delta_i)/kT} \tag{89}$$

in general, where T is the temperature at which the trapping parameters are determined. This means the power law can arise for a distribution of ν_i if ϵ_i = const, a distribution of ϵ_i if ν_i = const, a distribution of Δ_i, or a combination of all three. The most complex case arises when a distribution of ϵ_i and ν_i produce the same r_i. The corresponding ω_i in this case becomes the net summation of $N_i C_i \exp(-\Delta_i/kT)$ for all traps with a common r_i. Equation (89) imples α must be temperature dependent unless ϵ_i = const or $\Delta_i = \alpha\epsilon_i$. One of these two situations apparently prevails in a-As_2Se_3, because α is found to be insensitive to the temperature. Extreme care must be exercised to establish this, however, because the maximum possible dependence of α on temperature is simply $\alpha \propto T$. Thus the limit of accuracy depends strongly on the temperature range investigated. Incidentally, to rule out variable α (and variable ϵ_i), it is necessary that both the pre- and post-transit slopes of log current versus log time be independent of temperature. It is not enough to find that the activation energy of the experimental transit time (t_T) is independent of temperature. This will happen also when M_i for the critical trap is temperature independent.

The above results illustrate how a set of transport parameters can be obtained from current transients. But unfortunately, it is not possible to determine μ and N_i/N_v separately. This is due to the fact that neither t_0 nor μ is directly manifest in the measured time range.

In principle, one can obtain μ from $\mu = (L/t_T E)I(t \to 0)/I(t_T)$. But to date a good measure of this current ratio is unavailable. This is unfortunate because it is perhaps the most direct means of determining the microscopic mobility. Because of the information reflected in the microscopic mobility as well as the trap density, additional experiments are encouraged. Actually, further experiments on a-As_2Se_3 could be very revealing because the pretransit current decay is so slow. On the other hand, the dark current is also large in As_2Se_3, and an associated space charge accumulation can complicate the interpretation.

Fortunately, for a-As_2Se_3, we can turn to dark-current data for more information concerning the trap density. The most directly applicable data in this regard is Ing and Neyhart's[19] study of the transient dark discharge of similar samples (i.e., a-As_2Se_3 with a blocking contact). By analyzing the data in terms of generation limited conduction,[20] a density of populated traps was found which increases linearly with activation energy. The total trap population for activation energies between 0.64 and 0.84 eV (at zero field) was 10^{14} cm^{-3}, and the equivalent trapped hole concentration for a half decade of release times around the $\tau_{r,i}$ corresponding to $\nu_i = 7\times10^{11}$ sec^{-1} and $\epsilon_i = 0.64$ eV is 10^{13} cm^{-3}. Although Ing and Neyhart assumed a constant ν_i with a spectrum of ϵ_i (spaced approximately $k_B T = 0.02$ eV apart), the dark decay data can probably be fit with a spectra of both ν_i and ϵ_i as well. The effective average value of $\nu = 10^{11}$ sec^{-1} was found to fit the dark discharge rate of As_2Se_3 very well,

and is in good agreement with the ν_i determined above from the transient photocurrent data. The location of the initial Fermi energy (prior to any dark decay) is not known, but a reasonable assumption is that it lies either at 0.64 or 0.84 eV above the activated complex during release. The corresponding concentration of hole traps is then found to be $N_i = 10^{13}$ or 10^{16} cm^{-3}, respectively, for $\epsilon_i = 0.64$ eV and $\nu_i = 2 \times 10^{11}$ sec^{-1}. Assuming $N_v = 10^{19}$ to 10^{21} cm^{-3}and $\mu = \mu_0 \exp(-\Delta_\mu/kT)$ with $\Delta_\mu = 0$ for free translation, and $\Delta_\mu \sim \Delta_i$ for hopping, Eq. (88) immediately gives $\mu_0 = 0.2$ to 0.002 cm^2/V-sec, if $N_i = 10^{13}$ cm^{-3}, or $\mu_0 = 2$ to 200 cm^2/V sec, if $N_i = 10^{16}$ cm^{-3}. Since the lower value is characteristic of hopping, and the larger value is characteristic of extended state transport, we are led to the interesting point where the interpretation of the microscopic motion is dependent on the assumed placement of the initial Fermi energy.

When all available information concerning the behavior of a-As_2Se_3 is taken into consideration— especially its good xerographic performance,[20] and the shift in the activation energy of t_T from 0.64 to 0.57 eV with replacement of insulated contacts by Gold[9]—the lower trap density ($N_i - 10^{13}$ cm^{-3}) is most plausible. The spectrum of ν_i can then be attributed to a spectrum of hopping transitions out of traps. The physical origin of this spectrum may indeed be due to disorder, as in "stochastic hopping."[2] But it should be remembered, that the required ν_i also appear defensible in terms of capture from extended states as well, and cannot be unambiguously ruled out at this time.

Now the notion of "trap controlled hopping" implicit in the above discussion should not be confused with a different concept of "trap controlled hopping" recently proposed by Pfister and Scher.[9] Although the two concepts are closely related, they are fundamentally different, as borne out by the different analysis and results. Pfister and Scher have pointed out the difficulty of accounting for the activation for the observed activation energy of t_T in terms of stochastic hopping alone, and have constructed a phenomenological description of trapping which is appended to the pure stochastic hopping theory. The present analysis, however, has shown that the previous CTRW analysis already fully accounts for the observed behavior of a-As_2Se_3. It was merely necessary to reinterpret the power law $\psi(t)$ in terms of traps instead of stochastic hops. The observed activation energy of t_T is then simply explained as the activation energy for release from the controlling traps. No additional analysis is involved.

VI. EQUIVALENCE BETWEEN TRAPPING AND CTRW

The most general connection between trapping and CTRW is most easily established via the corresponding master equations. A useful preliminary, however, is to show that Eqs. (1) and (2) are equivalent to the following integrodifferential equation:

$$\frac{\partial p(x,t)}{\partial t} = \int_0^t \phi(t-\tau)[g_v(x)\delta(\tau-0) - \nabla\cdot\vec{f}_p]\,d\tau, \quad (90)$$

if

$$\phi(t) = \mathcal{L}^{-1}[S/a(s)]. \quad (91)$$

This may be readily verified by equating the Laplace transform of Eq. (90) to the Laplace transform of Eqs. (1) and (2) combined. Whence,

$$\tilde{\phi}(s) = \frac{s\tilde{p}}{s\tilde{p} - \tilde{g}_e(s)} = \frac{s}{a(s)} = \left(1 + \sum_i \frac{\omega_i}{s+\gamma_i}\right)^{-1}, \quad (92)$$

where

$$\tilde{g}_e(s) \equiv \sum_{i=1}^{k} \frac{\gamma_i\omega_i}{s+\gamma_i}\tilde{p} - \omega_0\tilde{p} = s\tilde{p}\sum_{i=1}^{k}\frac{\omega_i}{s+\gamma_i} \quad (93)$$

is an effective source function [in Eq. (1)] due to capture and release from traps.

Equation (90) is now to be compared to the generalized master equation (GME) of CTRW[2,21]

$$\frac{\partial P(\bar{x}_l,t)}{\partial t} = \int_0^t \phi_w(t-\tau)[-P(\bar{x}_{l'},\tau) + \sum_{l'\neq l}\gamma_{ll'}P(\bar{x}_{l'},\tau)]\,d\tau, \quad (94)$$

with initial condition $P(\bar{x}_l, 0) = \Delta x g_v(\bar{x}_l)\delta(t-0)$. Here $P(\bar{x}_l, t)$ represents the probability that a carrier is on a site at $\bar{x}_l$ at time t, and $\gamma_{ll'}$ is the conditional probability that if a carrier moves it will transfer from $\bar{x}_{l'}$ to $\bar{x}_l$. As Kenkre *et al.*[21] have shown, Eq. (92) will yield the same expression for $P(\bar{x}_l, t)$ as CTRW if $\tilde{\phi}_w = s\tilde{\psi}/(1-\tilde{\psi})$, with $\tilde{\psi}$ being the Laplace transform of the waiting-time distribution function in CTRW. It may be noted that Eq. (94) originated from the master equation for hopping [cf. Eq. (A1) of Appendix A] by factoring the time dependence $\phi_w(t)$ out of the intersite transition probabilities and generalizing it to functions other than $\tau^{*-1}\delta(t)$. It can thus be said that CTRW and the trapping formalism are different mathematical approaches to solving Eq. (A1).

To make the comparison of the above GME for CTRW with Eq. (90) for trapping more compatible, it is appropriate to transform the difference relation in Eq. (94) into a differential relation. Obviously, the reverse procedure can be applied alternatively to Eq. (90), but it is less natural. By passing over to a continuous space variable,

$$\frac{1}{\tau^*}\left(-P(\bar{x}_{l'},\tau) + \sum\gamma_{ll'},\tau\right) \to \nabla\cdot\vec{F}_p, \quad (95)$$

where

$$F_p \equiv (\gamma_{l,l-1} - \gamma_{l,l+1}) \frac{\Delta x}{\tau^*} P(\bar{x}_l, \tau) - \tfrac{1}{2} \frac{\Delta x^2}{\tau^*} \nabla P(\bar{x}_l, \tau) \quad (96)$$

follows from an expansion of $P(x, \tau)$ in a Tayor's series. Equation (94) then becomes

$$\frac{\partial P(x, t)}{\partial t} = \int_0^t \tau^* \phi_W(t - \tau)[-\nabla \cdot \vec{F}_p] \, d\tau . \quad (97)$$

A time constant τ^* is introduced in the above to make $\phi_W \tau^*$ have the same dimensions as ϕ and F_p the dimensions of a flux. However, one should avoid thinking of qF_p as a local conduction current, which it is not, as the results below show.

It is evident now that Eqs. (90) and (97) have a similar form except for the conspicuous absence of the photogeneration source in Eq. (97). But this is a nontrivial difference which turns out to be essential.

To finally establish the equivalence between trapping and CTRW, it remains to find the trapping quantities which correspond to $P(x, t)$ and ϕ_W. Physically, $P(x, t)$ must account for the total local charge. Consequently, we must have

$$P(x, t) = p(x, t) + \sum_{i=1}^{k} p_i(x, t) , \quad (98)$$

or

$$\tilde{P}(x, s) = \tilde{p} + \sum_i \tilde{p}_i = \left(1 + \sum \frac{\omega_i}{r_i + s}\right) \tilde{p} = \frac{\tilde{p}}{\tilde{\phi}} . \quad (99)$$

The latter follows from Eq. (2). After summing Eqs. (1) and (2), one also obtains

$$s\tilde{P} - g_v = s\tilde{P} - P(x, 0) = -\nabla \cdot \vec{\tilde{f}}_p , \quad (100)$$

whereas the Laplace transform of Eq. (97) gives

$$s\tilde{P} - P(x, 0) = \tau^* \tilde{\phi}_W[-\nabla \cdot \vec{\tilde{F}}_p] . \quad (101)$$

Equations (100) and (101) together finally give

$$\tau^* \tilde{\phi}_W[-\nabla \cdot \vec{\tilde{F}}_p] = -\nabla \cdot \vec{\tilde{f}}_p , \quad (102)$$

which is consistent with the above identification of P, if

$$\tau^* \tilde{\phi}_W = \tilde{\phi} , \quad (103)$$

$$\mu E = (\gamma_{l,l-1} - \gamma_{l,l+1}) \frac{\Delta x}{\tau^*} . \quad (104)$$

These relations therefore establish the complete equivalence between trapping and CTRW. For further verification, one can use the most general expression for the Laplace transform of the current in CTRW,[2,22] expressed as a function of $\tilde{\psi}/(1 - \tilde{\psi})$ only, and show that the above correspondence relations always produce identical current expressions. In the case of stochastic hopping, it is also necessary to identify τ^* as W_M^{-1}, where W_M is the maximum jump frequency.[2]

Having established the above correspondence relations, the basic mathematical differences between trapping and CTRW, which are manifest in Eqs. (90) and (94), become readily understandable. The photogeneration source must appear in Eq. (90), while it must be absent in Eq. (94). This is necessary because P must be conserved while the free carriers relax into slower and slower traps. To directly verify this, Eqs. (90) and (94) or (97) may be integrated over the sample length. For times short compared to the first carrier transit, one obtains

$$\frac{\partial}{\partial t} \int_0^L p(x, t) = \phi(t) , \quad (105)$$

while

$$\frac{\partial}{\partial t} \int_0^L P(x, t) = 0 . \quad (106)$$

If one now identifies the traps with special sites, following a procedure given in Appendix A, then Eq. (98) becomes tantamount to the replacement of every site by an ensemble average. It should be stressed, however, that this is a different kind of ensemble average than the one used by Scher and Montroll[2] (cf. their Appendix D).

Using the equivalence between ϕ_W and ψ established by Kenkre *et al.*[21] and $\tilde{\phi} = \tau^* \phi_W^*$, one can readily verify that

$$\tilde{\psi}(s) = 1/[1 + \tau^* a(s)] , \quad (107)$$

where $a(s)$ is explicitly given by Eq. (24) in terms of the trapping parameters. This may be used in either direction to convert any trapping problem into an equivalent CTRW or vice versa.

The above results show that trapping and CTRW are mathematically equivalent in general; and in view of their different conceptual bases, this first appears as a remarkable result. The reason for this unusual occurrence, however, can now be seen by comparing the different ways in which the trapping equations and the GME of CTRW are derived from the master equation for hopping transport [Eq. (A1)]. In the trapping formalism, certain sites were identified as traps and these were separated from the spatially coupled transport states. The kinetics of capture and release between the traps and transport states were then dealt with explicitly. But in formulating the GME or CTRW, all states were treated on an equal basis (i.e., as if all were transport states). The time dependence of all transitions were made identical, though it was recognized that this was done on a statistical sense. The more important and subtle point however, is that all spatial transitions were made identical as well by effectively replacing

every site by an ensemble average site. This is why the population of the spatially connected sites in CTRW is $P(x, t)$, rather than the mobile carriers $p(x, t)$, alone. The connection between the two, however, is just the inverse relaxation function $\tilde{\phi}^{-1}$, as shown by Eq. (99). When this is inserted in Eq. (99), or rather its Laplace transform given by Eq. (102), one finds that $\tau^* \tilde{\phi}_W \tilde{\phi}^{-1}$ is just the identity operator. This means ϕ_W in the GME of CTRW basically undoes the effect of having previously treated all the sites on an equal basis. In other words, ϕ_W operates on P to take into account the fact that only the mobile component of P (namely p) plays a role in the redistribution of carriers spatially.

VII. SUMMARY AND CONCLUSION

The basic continuity equations which apply to the interrupted motion of charge moving through a dielectric material have been shown to broadly apply to any mobile entity which stops and starts at random from a distribution of resting places. The mean resting times ($\tau_{r,i}$), and the mean travel times (τ_i) between rests of $\tau_{r,i}$, have been formulated for electronic charge carriers whose microscopic mobility is controlled by either extended states or hopping states. The basic trapping equations have been solved analytically and the characteristics of the solution have been illustrated via several examples. The principal general results from this study are:

(i) The empirical transit time t_T is approximately the free transit time plus the total resting time in all traps visited at least twice ($M_i \geq 2$).

(ii) The post-transit current decay is controlled by the rate of release from the slow traps ($\tau_{r,i} \geq t_T$), which capture a carrier once or less (on the average).

(iii) To obtain a broad dispersion of transit times (or featureless[11] current trace) a carrier must be captured approximately once in a trap whose mean release time $\tau_{r,i}$ is approximately equal to the empirical transit time t_T. This is called the critical trap criterion (CTC).

(iv) Superlinearity of t_T with L/E (sample thickness divided by the electric field) results from an increasing number of traps satisfying the CTC, or $M_i = L/\mu E \tau_i > 2$.

(v) Previous current traces fit with CTRW using a power–law waiting-time distribution function, $\psi(t) \propto t^{-(1+\alpha)}$, imply a power–law relation between the capture and release times, $\tau_i \propto \tau_{r,i}^{-\alpha}$.

(vi) The microscopic mobility can be determined from the transit time and the ratio of the initial current to the current at the transit time. $\mu = (L/t_T E) I(t \to 0)/I(t_T)$. This provides at least a lower bound.

(vii) The ratio of trap to transport states densities (N_i/N_v) can be determined from trap parameters (ω_i, γ_i), which in turn, can be determined by fitting the theory to experimental current traces.

(viii) Trapping and CTRW are equivalent in general.

The underlying conceptual differences previously envisioned between trapping and CTRW have also been explained. In fact, the cancellation of $\tilde{\phi}$ by $\tilde{\phi}^{-1}$ on the left-hand side of Eq. (102) can be traced to the definition of CTRW [cf. its GME, Eq. (94)] via the replacement of every site in a hopping array by an average site. This can be interpreted to mean the "relaxation" phenomena associated with the averages sites does not carry through to the transport states (or microscopic displacement events) themselves. Because of this, the association of "stochastic hopping" with CTRW acquires a questionable meaning. In fact, a more appropriate descriptor of CTRW might well be stochastic stopping, rather than stochastic hopping. The latter term could then be reserved to have a more specific meaning in connection with the more general master equation for hopping (cf. Appendix A), an idea which appears implicit in discussions by Scher.[22] The central question remains, however: How can stochastic hopping be redefined in a way which is distinguishable from trapping?

The importance of the above distinction appears more than semantical. The broad transit-time dispersion typically found in amorphous materials was previously thought to be a consequence of disorder. It is now found to be indicative of a rare trapping event. This implies very low trap densities, which are most likely due to defects such as dangling bonds, impurities, or combinations thereof, rather than disordered intrinsic material. It is conjectured that this broadly applies to both crystalline and amorphous materials, though the disorder in amorphous materials may very well be responsible for a spectrum of couplings (ν_i) to a particular defect.

Use of the theoretical results derived herein could find broad use as new tools for determining the microscopic mobility and localized state densities (traps) in all dielectric materials. Since the completion of this manuscript, another analytic solution of the multiple-trapping problem[23] has been published which appears different from the present solution except for the limit of a single trap.

For the purpose of probing localized trapping states, the present formalism for small signals should be adequate. But for completeness and application to certain imaging systems, it remains to extend the formalism to handle large signals.

As a first-order assessment of large signal effects, one might simply average the present small signal solution over a distribution of trap-free transit times, as determined, for example, by Batra and Schechtman.[24] Such an approach is nonrigorous, but the simplicity is appealing and it could prove to be adequate in many cases.

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APPENDIX A: DERIVATION OF THE TRAPPING PARAMETERS FOR MICROSCOPIC HOPPING

In this Appendix, we derive the capture and release rate constants (ω_i, r_i) for microscopic hopping on a lattice.

This is accomplished by deriving the trapping Eqs. (1)–(3) from the following master equation for hopping on a lattice:

$$\frac{\partial P(\bar{x}_l, t)}{\partial t} = \sum_{m \neq l} \omega'(\bar{x}_l - \bar{x}_m) P(\bar{x}_m, t) - \sum_{m \neq l} \omega'(\bar{x}_m - \bar{x}_l) P(\bar{x}_l, t). \tag{A1}$$

Here $P(\bar{x}_l, t)$ represents the probability that a carrier occupies a localized state centered at $\bar{x}_l$ and $\omega'(\bar{x}_l - \bar{x}_m)$ represents the transition probability per unit time from the site at $\bar{x}_m$ to the site at $\bar{x}_l$. Note that the net probability per unit time for release from the site at $\bar{x}_l$ is

$$r_l = \sum_{m \neq l} \omega'(\bar{x}_m - \bar{x}_l). \tag{A2}$$

Hence, each state may be characterized by its mean release time $\tau_{r,l} \equiv r_l^{-1}$. If the transitions which determine r_l do not significantly involve transitions to other states for which the release constant (r_m say) is less than or equal to r_l, then the state in question is effectively isolated from all similar (or slower) states. Such isolated states shall be defined as traps. It may be noted that this definition is consistent with the general notion of a trap indicated earlier (immobilization for an observable length of time) even though some $\tau_{r,l}$ may be too brief to be manifest in the measured current trace. (Restrictions on observability are discussed in depth later.) Now, all states that do not satisfy the above criterion of a trap are strongly interconnected, and therefore represent another example of what is defined herein as transport states. An additional assumption that is now made concerning these transport states is that the differences between the release times $\tau_{r,l}$ from one transport state to another will not be observable and may be replaced by an average value, designated τ^*. Now the location of the traps will generally not be known *a priori*. Thus it is appropriate to turn to an ensemble description in which the traps are distributed at random (i.e., that the samples are homogeneous). And since a trap is now characterized by its release time τ_r, not its location, it is also appropriate to replace the subscript l (on r_l) by i, to indicate that $\tau_{r,i} = r_i^{-1}$ is of a certain magnitude. Use of i, j to indicate traps in this way is consistent with previous notation for release to extend states.

The capture of a carrier from a transport state is basically release in reverse. However, the capture event is *conditional* on the fact that the final site is a trap. Thus the capture probability per unit time by trap i can be written

$$\omega_i = \sum_l \omega_i'(\bar{x}_m - \bar{x}_l) N_i / N_h, \tag{A3}$$

where the subscript i on $\omega_i'(\bar{x}_m - \bar{x}_l)$ indicates the fact that $\omega'(\bar{x}_m - \bar{x}_l)$ may now be conditional on the nature of the trap that is tacitly assumed to exist at site $\bar{x}_m$. Of course, $\bar{x}_m$ can be any site and the probability that it is a trap having a release time in the range quantified by $\tau_{r,i}$ is N_i/N_h. If ω_i' is only weakly dependent on the nature of the final state (so $\omega_i' \approx 1/\tau^*$), then ω_i is predominantly determined by the probability that a transition from any transport state will simply end in a trap. But it should be emphasized that $\omega_i'(\bar{x}_m - \bar{x}_l)$ is not, in general, the simple inverse of the corresponding transition in r_i even though the same initial and final states are involved. They may differ because a complex sequence of intermediate transitions may be involved which require activation (cf. Fig. 2 in text).

Given Eqs. (A2) and (A3) as the definitions of ω_i and r_i for capture and release from localized transport states (i.e., hopping states), it remains to show that they are consistent with Eqs. (1)–(3). Now, a populated state depends on its nature. To quantify this, we denote the occupation probabilities of the transport states and traps by $p(\bar{x}_l, t)$ and $p_i(\bar{x}_l, t)$, respectively. The net rate of filling trap i may therefore be written.

$$\frac{\partial p_i(\bar{x}_l, t)}{\partial t} = \sum_{m \neq l} \omega_i'(\bar{x}_l - \bar{x}_m) \frac{N_i}{N_h} p(\bar{x}_m, t) - r_i p_i(\bar{x}_l, t), \tag{A4}$$

where we have made explicit use of the fact that $\bar{x}_l$ is now trap i. Next, we assume that the average of $p(\bar{x}_m, t)$ for the states neighboring trap i (assumed to occur here at $\bar{x}_l$) is $p(\bar{x}_l, t)$ (i.e., the same as if the trap did not exist at $\bar{x}_l$). Whence,

$$\frac{\partial p_i(\bar{x}_l, t)}{\partial t} = \omega_i p(\bar{x}_l, t) - \gamma_i p_i(\bar{x}_l, t), \tag{A5}$$

which is identical to Eq. (2). The reverse of the processes on the right-hand side of Eq. (A5) also act as a sink or source of mobile carriers, and this must be taken into account as we next turn to the derivation of Eq. (1).

We next focus on the master equation, Eq. (A1), for the population of a transport state which is coupled to other transport states alone. If we assume only nearest-neighbor transitions are important and renormalize all the transitions from a particular site, then one can write $\tau^*\omega'(\bar{x}_l - \bar{x}_{l\pm1}) = \gamma_\pm$, where γ_+ and γ_- are the conditional probabilities from transitions "with" and "against" the electrostatic force, respectively. Assuming further that the transport state population, $p(\bar{x}_l, t)$ is slowly varying, then a Taylor expansion of $p(\bar{x}_{l\pm1}, t)$ may be used for the following conversion of a difference relation into a differential relation:

$$\frac{1}{\tau^*} p(\bar{x}_l, t) - \sum_{m \neq l} \omega'(\bar{x}_l - \bar{x}_m) p(\bar{x}_m, t) = -\frac{\partial f_p}{\partial x}, \tag{A6}$$

where f_p is given by Eq. (3), with

$$\mu E \equiv (\gamma_+ - \gamma_-)(\bar{x}_{l+1} - \bar{x}_l)/\tau^* \tag{A7}$$

and $\bar{x}_l = x$. Note that $P(\bar{x}_l, t)$ is replaced here by $p(\bar{x}_l, t)$ because we are dealing exclusively with the population of transport states alone. It can be seen from this if there were no traps, Eq. (A6) for the continuum limit (after adding the photogeneration source) would reduce to Eq. (1). Therefore, when one takes into account that a given lattice site may be a trap, the net accumulation on an ensemble averaged site (at $\bar{x}_l = x$) may be written

$$\frac{\partial P(x, t)}{\partial t} = g_\nu(x, t) - \frac{\partial f_p}{\partial x}, \tag{A8}$$

where

$$P(x, t) \equiv p(x, t) + \sum p_i(x, t) \tag{A9}$$

is now the sum of the conditional occupational probabilities given that the accumulation point is either a transport state or a trap. Substituting Eq. (A9) into Eq. (A8), and replacing the time derivatives of p_i with their equivalent given by Eq. (A5), one arrives at Eq. (1). This fulfills the objective of this Appendix.

One might argue that Eq. (A6) cannot be used for states connected to traps. However, this is a small error because there are very few traps. In addition, one can remove this error in the analysis by superposing transport states at all the trap positions, and redefine the capture and release constants given by Eqs. (A2) and (A3) to represent capture and release between the actual traps and the virtual transport states superposed at the trapping sites. It is not likely, however, that the corrections that can be made in this manner are observable.

APPENDIX B: DIFFUSION VERSUS TRAP CONTROLLED TRANSIT TIME DISPERSION

By comparing the effect of diffusion alone with the effect of trapping alone, a simple criterion may be constructed for when the effect of diffusion may be neglected. In addition, it becomes readily apparent how the effect of diffusion can be incorporated in the trap controlled transport problem with little added complexity.

It is well known that the solution to Eq. (1) with diffusion and recombination included, but no carrier release (all $\gamma_i = 0$), is simply

$$p(x, t) = \frac{q\eta N_0}{(4\pi D t)^{1/2}} \exp\left(-\frac{(x - \mu E t)}{4Dt} - \omega_0 t\right), \tag{B1}$$

where the diffusion coefficient D is related to the microscopic mobility μ by the Einstein relation. This ignores any effect of the upstream boundary (at $x = 0$), but it can be shown that the effect of this boundary may be included via a modified quantum efficiency η.

If $L \gg (2Dt)^{1/2}$ when $t \sim t_0 = L/\mu E$, then it is an excellent approximation to replace t by t_0 in $(2Dt)^{1/2}$ during the short time interval during which the carriers cross the downstream boundary (at $x = L$). The dispersion in transit times resulting from diffusion is then given by

$$Y_D(t) = \frac{1}{(2\pi)^{1/2}\sigma_D} e^{-(t - t_0)^2/2\sigma_D^2}, \tag{B2}$$

where

$$\sigma_D^2 \equiv t_{\sigma,D}^2 = 2Dt_0/(\mu E)^2 = 2kT/\mu^2 E^3. \tag{B3}$$

This is the diffusion dispersion cited and compared in the text to the dispersion due to trapping. For a single trap, the latter is simply given by

$$t_\sigma^2 = 2M_1\tau_{r,1}^2. \tag{B4}$$

As also stressed in the text, the most effective way of establishing whether t_0 or $t_{\sigma,D}$ is dominant, is to normalize them with respect to the mean transit time, whence,

$$\frac{t_{\sigma,D}^2}{t_0^2} = \frac{2kT}{qEL} = \frac{2kT}{qV}, \quad \text{for diffusion} \tag{B5}$$

and

$$\frac{t_\sigma^2}{t_m^2} = \frac{2M_1\tau_{r,1}^2}{(t_0+M_1\tau_{r,1})^2}, \quad \text{for trapping} \tag{B6}$$

$$\rightarrow \frac{2}{M_1} = \frac{2\mu E}{\omega_1 L}, \quad \text{for } M_1\tau_{r,1} \gg t_0.$$

It is easy to verify that trapping can produce a broader relative dispersion than diffusion whenever traps are present for which $\tau_r > t_0 kT/qV$.

It follows that the transient current due to diffusion alone may be written

$$I(t) = \frac{1}{L}\int_0^L \mu E p(x,t)\,dx$$

$$\approx \frac{q\eta N_0 e^{-\omega_0 t}}{t_0}\left(1 - \int_0^t Y_D(t)\,dt\right). \tag{B7}$$

This may be compared to the single-trap case in the limit of no release. From Eq. (67), it can be seen that $A_0 \rightarrow 0$, $A_1 \rightarrow 1$, $s_1 \rightarrow \omega_1 = \omega_0$, and $F_1(t) \rightarrow 0$ as $r_1 \rightarrow 0$. Hence Eq. (66) reduces to

$$I(t) = \frac{q\eta N_0}{t_0} e^{-\omega_0 t}[1 - u(t - t_0)]. \tag{B8}$$

Hence the effect of diffusion is to replace the step function by the integral of $Y_D(t)$. It is thus apparent that the effect of diffusion is simply to broaden the dispersion of transit times.

A general solution with both trapping and diffusion included may now be guessed. One should simply replace $\delta(t - t_0)$ in Eq. (38) by $Y_D(t)$. This is justifiable from a statistical point of view as well, because the diffusion mechanism for broadening the transit time dispersion is independent of the trapping mechanism. The total dispersion due to both mechanisms is then simply

$$t_{\sigma,\text{tot}}^2 = t_{\sigma,D}^2 + t_\sigma^2 = \frac{2kTL}{\mu^2 E^3} + \frac{2\omega_1 L\tau_{r,1}^2}{\mu E} \tag{B9}$$

for a single frequently visited trap. In principle then, one should be able to shift trap controlled dispersion to diffusion controlled dispersion by simply lowering the electric field. There are no known cases for which this has been observed. To observe the effect experimentally, however, one should probably study electronic grade materials, since there is apparently always such an abundance of traps in electrophotographic materials that the transient current becomes immeasurably small at sufficiently low fields.

[1] W. E. Spear, Proc. Phys. Soc. Lond. Ser. B70, 669 (1957); 76, 826 (1960); J. L. Hartke, Phys. Rev. 125, 1177 (1962); H. P. Grunwald and R. M. Blakney, Phys. Rev. 165, 1006 (1968); M. D. Tabak, Phys. Rev. B 2, 2104 (1970).

[2] H. Scher and E. W. Montroll, Phys. Rev. B 12, 2455 (1975).

[3] A. Many and G. Rakavy, Phys. Rev. 126, 1980 (1962).

[4] R. M. Blakney and H. P. Grunwald, Phys. Rev. 159, 658 (1967).

[5] W. E. Teft, J. Appl. Phys. 38, 5265 (1967).

[6] I. P. Batra and H. Seki, J. Appl. Phys. 41, 3409 (1970); H. Seki and I. P. Batra, J. Appl. Phys. 42, 2407 (1971).

[7] M. Silver, K. S. Dy, and I. L. Huang, Phys. Rev. Lett. 27, 21 (1971); J. Non-Cryst. Solids 8, 773 (1972).

[8] R. Enck (private communication).

[9] G. Pfister and H. Scher (unpublished).

[10] S. W. Ing, Jr., J. H. Neyhart, and F. Schmidlin, J. Appl. Phys 42, 696 (1971).

[11] G. Pfister, Phys. Rev. Lett. 33, 1474 (1974); G. Pfister, *Photoconductivity and Related Phenomena*, edited by J. Mort and D. Pai (Elsevier, Amsterdam, 1976), Chap. VII.

[12] S. J. Fox and H. C. Locklar, Jr., J. Non-Cryst. Solids 8, 552 (1972).

[13] J. M. Marshall and A. E. Owen, Philos. Mag. 24, 1281 (1971).

[14] F. D. Fisher, J. M. Marshall, and A. E. Owen, Philos. Mag. 33, 261 (1976).

[15] L. Onsager, J. Chem. Phys. 2, 599 (1934).

[16] M. E. Scharfe, Phys. Rev. B 2, 5025 (1970).

[17] G. Juska, A. Matulionis, and J. Viscakas, Phys. Status Solidi 33, 533 (1969).

[18] H. B. Dwight, *Tables of Integrals and Other Mathematical Data* (MacMillan, New York, 1949).

[19] S. W. Ing, Jr. and J. H. Neyhart, J. Appl. Phys. 43, 2670 (1972).

[20] F. W. Schmidlin, in Ref. 11, Chap XI.

[21] V. M. Kendre, E.W. Montroll, and W. E. Shlesinger, J. Stat. Phys. 9, 2 (1973).

[22] H. Scher, in Ref. 11, Chap III.

[23] A. I. Rudenko, J. Non-Cryst. Solids 22, 215 (1976).

[24] I. P. Batra and B. H. Schechtman, J. Phys. Chem. Solids 32, 769 (1971).