Diffusion and Drift of Charge Carriers in a Random Potential: Deviation from Einstein's Law

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Employing Monte Carlo techniques, the diffusion and drift of charge carriers within an array of hopping states subject to a Gaussian distribution of site energies of width σ has been studied as a function of σ/kT and electric field. With increasing disorder and field, significant deviations from Einstein's law are noted. They are shown to be the consequence of anomalous, field-assisted diffusion while the mobility remains constant. The effect can account for anomalous transit-time dispersion observed in polymeric photoconductors exhibiting time-independent transport.

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A key experiment in determining the drift velocity of charge carriers in semiconductors under a bias field is to generate a sheet of carriers externally and follow its motion until discharge at the exit contact occurs. The mean arrival time directly translates into mobility, whereas its temporal distribution reflects the diffusivity of the carriers, a quantity that is difficult to measure directly. The signature of conventional Gaussian transport is that the ratio of diffusive spread to displacement is

$$\langle \Delta x^2 \rangle^{1/2} / \langle x \rangle = (kT/eE)(2Dt)^{-1/2}, \quad (1)$$

yielding a relative standard deviation $\Delta t_h/t_h = (2kT/eV)^{1/2}$ of the carrier arrival times at the sample boundary, V being the applied voltage. It implies the validity of Einstein's law relating carrier mobility μ to diffusivity D via $eD = \mu kT$. This behavior is found in an ideal crystalline sample.[1] The application of the Einstein relation to inhomogeneous and fractal systems is, however, nontrivial.[2,3] In the case of time-dependent dispersive transport, notorious in random systems, motion is often described in terms of a waiting-time distribution for carrier hops among localized sites of the form $P(t) \approx t^{-(1+\alpha)}$, $0 < \alpha < 1$. Equation (1) then has to be replaced by $\langle \Delta x^2 \rangle^{1/2} / \langle x \rangle \approx t^{-\alpha/2}$ indicating that the carrier packet spreads faster.[4]

Dispersive transport, characterized by the decay of the of the carrier velocity with time, can arise from energetic or positional disorder. In a sample of macroscopic dimension, transport will, however, become time independent if, after a time t_{rel}, the carriers have surveyed a representative fraction of the hopping sites,[5-8] except if hopping occurs in an exponential band tail.[9] One might intuitively assume that for times $t \gg t_{rel}$ transport begins obeying conventional Gaussian statistics again because the memory of the initial dispersion of hop rates is lost. In this Letter we argue against this notion by reporting on deviations from Einstein's law in cases of time-independent hopping within an intrinsic distribution of states. We shall use the term "dispersive Gaussian transport" (DGT) to characterize this type of transport.

The motivation for studying DGT came from time-of-flight (TOF) studies in various polymeric systems.[10-12] Although displaying well-developed plateau regions indicative of nondispersive transport, photocurrent transients are at variance with the conventional Gaussian transport concept, because the amount of charge contained in the leading current tail exceeds that predicted by Eq. (1) by orders of magnitude and increases with electric field, at variance with Eq. (1). It seems conceptually straightforward to associate the additional dispersion of carrier arrival times with the stochastic character of carrier motion in a random medium. However, the field dependence of the effect indicates that existing analytic theories for steady-state transport in systems with energetic disorder of the hopping sites[5,7] cannot provide a quantitative understanding because they apply to the linear-response regime only, i.e., to the case of low electric fields. On the other hand, it is of crucial importance for delineating the appropriate concept for rationalizing carrier transport in random organic media, such as molecularly doped polymers, to identify whether or not anomalous field-dependent diffusion and the concomitant deviations from Einstein's law are a consequence of the stochastic character of carrier transport. The method of choice for determining the behavior of a system, modeled in accord with the properties of real world samples, under conditions that may give rise to nonlinear response, is the Monte Carlo (MC) simulation.

Using well tested MC techniques[13] we simulated transport of charge carriers by jumps on a cubic lattice of $70 \times 70 \times 70$ sites with periodic boundary conditions and equidistant spacing a. Motion of a carrier was governed by site-specific energies resembling a Gaussian density of states (DOS) centered at ϵ_0 with standard deviation σ. A carrier was generated at an arbitrary site and allowed to execute a random walk under the action of an external electric potential. Following the theory of hopping transport,[14] whose applicability is well manifested,[15] we determined the carrier motion on the basis of the Miller-Abrahams[16] jump rate between two sites i and j which reads

$$v_{ij} = v_0 \exp(-2\gamma \Delta r_{ij}) \exp(-\Delta \epsilon_{ij}/kT), \quad (2)$$

where γ is the inverse wave-function localization radius ($2\gamma a = 10$) and $\Delta\epsilon_{ij}$ is the difference in site energies including the field energy. For jumps down in energy $\Delta\epsilon_{ij}$ was set equal to zero. A crucial test for this assumption is provided by experimental studies of the energetic relaxation of triplet excitations in a benzophenone glass.[17] Triplet excitons are known to migrate via exchange interactions as charge carriers do. These experiments yielded perfect agreement with the predictions of both the MC simulation and analytic theory, not expected if the rate for energy-releasing jumps were restricted by an energy-matching condition.

All sites within a cube of $(5a)^3$ were considered as target sites for jumps within a sphere of radius of $\sqrt{12}a$. A restriction to both nearest-neighbor jumps and a lattice of $25\times25\times25$ sites had no significant effect on the results, provided that the effective sample length of $300a$ was maintained.

The simulation allowed monitoring of the moments of the distributions of position, energy, and energy barriers until the carrier reached the collecting electrode at a distance of 300 lattice planes. On average, the transit signals of 200 carriers were accumulated. Simulations were carrier out for variable intrinsic disorder quantified in terms of σ/kT and electric fields ranging from 2×10^4 to 3×10^5 V/cm. Upper limits for disorder and electric field were determined by the condition of the carriers attaining an equilibrium mobility within the time of flight. The evaluation concentrated on the mobility μ and the diffusion constant D parallel to the field given by $\mu = (1/E)d\langle x\rangle/dt$ and $D = \frac{1}{2}d\langle(x-\langle x\rangle)^2\rangle/dt$, respectively.

The simulated current transients exhibit an initial dispersive regime, governed by energy relaxation of the carriers within the DOS. In the long-time limit carriers settle at an equilibrium occupation density. By virtue of thermodynamic arguments[7] this holds for any DOS falling off faster than an exponential. Under this condition transport is subject to a time-independent distribution of jump rates, its signature being a plateau within the current trace. In the following we focus on this nondispersive transport regime for which the simulations yield a linear variation of the mean position of the carrier packet with time.

For dispersion parameters $\sigma/kT > 2$ both the energy and diffusion coefficient continue to decay slightly after the current has equilibrated. This reflects the slow energy redistribution of carriers temporarily trapped within the tail states of the DOS.[18] Consequently, the simulation results for a large disorder parameter are not equilibrium values but represent lower limits for the deviations from Einstein's law since $eD/\mu kT$ rises until true equilibrium conditions are attained. This is indicated in the inset of Fig. 2 for $\sigma/kT = 2.5$, $E = 10^5$ V/cm, and a sample length of $3000a$. Bearing in mind that the time required for resolving the long-time limit for $eD/\mu kT$ increases drastically with σ/kT, this would involve unrealistically large computation times if realized for the complete set of simulations. True stationary conditions are attained only if the distribution of carrier energies remains unaltered in the course of the transport. By thermodynamic arguments this final occupational density is also a Gaussian of width σ but displaced to lower energies by σ^2/kT. Despite carrier discharge at the counter electrode, this ultimate density of energies is perfectly revealed by the present model simulation as documented elsewhere.[18]

The key result is qualitatively indicated in Fig. 1 which shows different current profiles for $\sigma/kT = 0$ and 3 on a time scale normalized to the mean transit time τ_{tr}. While the $\sigma = 0$ case reveals true Gaussian transport, defined via the fulfillment of Einstein's law, additional spreading of arrival times is observed for $\sigma/kT = 3$, reflecting the spatial spread of the packet. The inset in Fig. 1 shows that in either case the current profile is accurately described by

$$I(t) \sim \int_{-\infty}^{\infty} (4\pi Dt)^{-1/2} \exp\left[-\frac{(x-\mu Et)^2}{4Dt}\right] dx = 1 - \tfrac{1}{2}\,\mathrm{erfc}\left[\frac{l-\mu Et}{(4Dt)^{1/2}}\right], \quad (3)$$

as expected if the carriers, contributing equally to the current, are subject to time-independent diffusion and mobility. The fact that Eq. (3) provides a perfect fit to the simulation data over almost three decades in current clearly indicates that the spatial distribution of the carrier packet follows a Gaussian profile. Note that Eq. (3) yields $I(t)$ on the basis of normal Gaussian transport statistics irrespective of any relation between diffusivity D and mobility μ.

Figure 2 quantifies the deviation from Einstein's law by showing how $eD/\mu kT$ varies with the degree of disor-

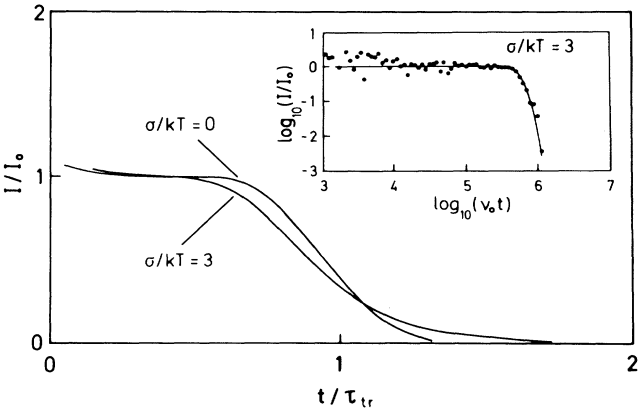

FIG. 1. Simulated current transients normalized to both mean transit time and plateau current for $E = 10^5$ V/cm and σ/kT as indicated. Inset: The $\sigma = 3kT$ profile (dots) as above on a log-log scale together with $I(t)$ following Eq. (3) (line) taking μ and D from Fig. 3.

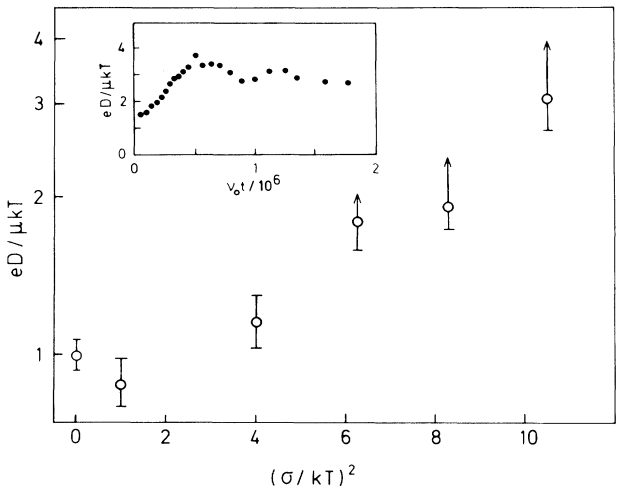

FIG. 2. Dependence of $eD/\mu kT$ on the dispersion parameter σ/kT for a field $E=10^5$ V/cm. Note that an extrapolation of the data to $\sigma=0$ would yield $eD/\mu kT=\frac{1}{2}$ due to the energetic asymmetry introduced to the rates via Eq. (2). Inset: The gradual increase of $eD/\mu kT$ as it approaches its long-time limit for the case $\sigma/kT=2.5$ and $E=10^5$ V/cm.

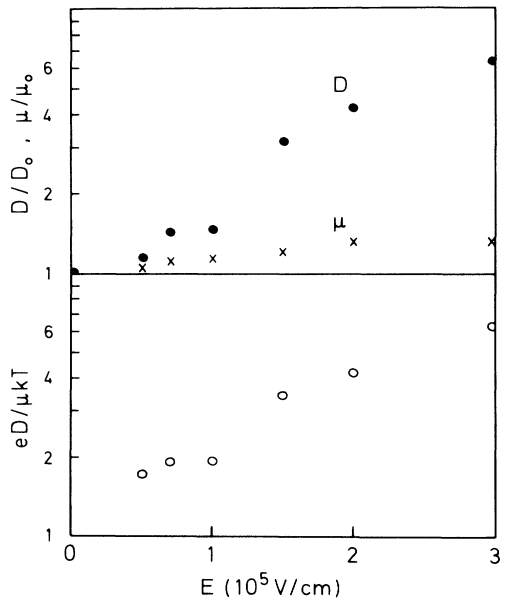

FIG. 3. Field-induced increase of D and μ relative to the low-field limit for $\sigma/kT=3$ (upper plot). The lower plot indicates the resulting ratio $eD/\mu kT$ as a function of field.

der expressed via σ/kT. This unambiguously demonstrates that diffusion of a carrier packet within a static random potential subject to a biasing field follows Gaussian statistics, documented by the linear growth of the mean-square displacement with time, yet does not in general obey Einstein's law. We note that the usual derivation of Einstein's law involves the assumption that the medium is isotropic and electric fields are low enough to guarantee linear response.

To explain the above results we examine in Fig. 3 the field dependences of both the diffusivity D and mobility μ of the charge carriers for $\sigma/kT=3$. For regular systems the linear-response domain is restricted by the condition $\cosh(eEa/kT)=1$, approximately fulfilled in the present simulations as documented by the only marginal dependence of μ on E. Remarkably, however, the diffusivity increases much more rapidly with field than does μ. The Einstein relation is recovered in the $E\rightarrow 0$ limit only, deviations becoming significant for $E>5\times10^4$ V/cm.

At present we can only speculate on the interpretation of this novel effect. Consider a system with $\sigma/kT=3$. After initial relaxation a carrier will, on average, occupy sites at energy 3σ below the center of the DOS at ϵ_0 where the fraction of sites with energy $\epsilon<\epsilon_0-3\sigma$ is 3×10^{-3} only. In order to continue its motion the carrier has to be excited to a site of higher energy unless it finds an energetically favorable path to new sites. In any case, predetermined paths defined by highest exchange frequencies will govern carrier motion with certain configurations being likely to override the tendency of a carrier to follow the biasing field. On a microscopic scale the assembly of sites is, therefore, not an isotropic continuum but a network of reduced dimensionality. It is well known that for diffusion in a one-dimensional system under a biasing field the linear-response theory already breaks down at very low fields.[19,20] We therefore conjecture that the observed nonlinearity in the diffusivity is the signature of reduced local dimensionality of the random walk a carrier executes within an array of hopping sites subject to energetic (diagonal) disorder. On a macroscopic scale, however, the topology of the random walk is three dimensional with the consequence that the drift velocity varies in proportion to E. This idea clearly calls for rigorous analytic work which we hope this Letter will stimulate.

To outline the relevance of the present results for real systems we draw on the experiments of Yuh and Stolka[11] on photocurrent transients in molecularly doped polymers. These authors analyzed the tails of TOF signals exhibiting well-developed plateau regimes and observed anomalous broadening of the tails with electric field. The inferred field dependence of the charge-carrier diffusivity turns out to be in accord with the present simulations. Quantitative comparison requires an extension of the simulation data to larger electric fields and an inclusion of both the effect of a fluctuation of intersite distances and possibly additional trapping by extrinsic traps.

In conclusion, we have shown that charge carriers executing a random walk in a statistical potential are subject to anomalous field-assisted yet time-independent diffusion while exhibiting conventional drift behavior at fields of practical interest. This leads to significant devi-

ations from Einstein's law at increasing energetic disorder and electric field although TOF profiles are correctly described by Guassian transport statistics. The equivalence of diffusion and mobility of charge carriers in random systems is thus restricted to the very-low-field regime.

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