Mean mobilities of charge carriers in disordered media

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Time-of-flight transient photocurrents in molecularly doped polymers are analyzed in terms of an effective velocity distribution, which is found to be normal. Combining this with a fractional power law to describe the current that would flow in a semi-infinite sample provides an accurate description of experimental data on many materials and allows the determination of mobilities with a precision significantly enhanced over previous graphical analysis. The mobilities are found to deviate systematically from the $\ln\mu \sim \sqrt{E}$ dependence previously suggested in the literature.

Since the work of Spear,[1] Leblanc,[2] and Kepler,[3] time-of-flight measurements have been routinely employed to determine photoexcited carrier mobilities in crystalline and amorphous semiconductors, in polymers, and in molecularly doped polymers.[4] In the last three cases the transient current is found to be more or less dispersive, in the sense that the current is not constant at short times (as would be expected for a sheet of charges propagating with constant velocity), and the spread of arrival times is much broader than expected on the basis of the Einstein relation between mobility and diffusion. It is generally accepted[5,6] that dispersive transport is due to wide variations in site-to-site hopping rates, which arises because of spatial (off-diagonal) and/or energetic (diagonal) disorder. Although theoretical methods have been applied to charge transport in these systems[5,7-10] the results involve approximations, which for example may not be valid at high electric fields, or Laplace transforms, which require numerical inversion using contour integration. Thus there is no *analytical* expression for the time dependence of the current that is generally applicable over the *entire* range of experimental interest. This has hindered the analysis of experimental data, and researchers have resorted to various *ad hoc* methods (usually graphical, and aimed at defining the "shoulder" in the transient, which is frequently the single most obvious feature) to extract a transit time, and thereby determine the mobility. Although convenient, this method of determining the mobility is not in accord with its definition in terms of (mean) drift velocity. It is desirable to find an analysis that lends itself to computational, rather than graphical, techniques, and that allows determination of experimental parameters for quantitative comparison with theory and simulation.

In this paper we introduce a general functional form for the shape of the transient that is useful for routine analysis of experimental data and permits the determination of a properly defined mobility. It is natural to analyze the photocurrent in terms of a function describing the current which would flow if the sample were semi-infinite, reduced by a factor that accounts for the arrival of carriers at the collecting electrode. It will be shown that the arrival times result from a velocity distribution that very closely approximates a Gaussian. As an example of the function for the infinite sample behavior, we use the fractional power law of Scher and Montroll[5] (SM). The subsequent data analysis then permits a more precise determination of mobility than previously obtained and reveals systematic deviations from its frequently cited field dependence.

In a standard,[4] constant-voltage mode, time-of-flight experiment let the photocurrent be $s(t)$, where t is the time after the (negligibly short) laser pulse. (See Fig. 1.) In most cases the current falls initially as a result of trapping,[9,11] dispersion,[5] and/or relaxation in a density-of-states energy distribution.[10,12,13] It can, in some cases, rise because of delayed generation effects.[14] Let $s_0(t)$ de-

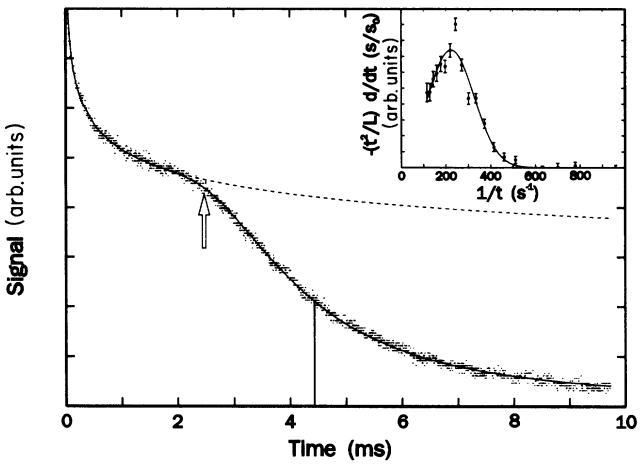

FIG. 1. Time-of-flight photocurrent transient signal $s(t)$. The data are the dots and the solid curve is a fit to Eq. (6), giving the mean transit time t_0 indicated by the solid vertical line. The arrow marks the "traditional" transit time extracted by graphical analysis to define the shoulder of the transient, and the dotted line corresponds to s_0. In this example, 50% diethylaminobenzaldehyde-diphenylhydrazone (DEH) in polystyrene, thickness 11.5 μm, at 260 K and 31.3 V/μm, the fitting parameters are $t_0 = 4.433 \pm .005$ ms, $w_v = 0.442 \pm .001$, and $\alpha = 0.8643 \pm .0006$. (Quoted errors are statistical, one standard deviation.) $\chi_r^2 = 1.25$. The inset shows the velocity distribution obtained as described in the text, with the curve giving a Gaussian fit to the data.

scribe the time dependence that the current would take, due to these processes, in the absence of a second sample surface. As carriers arrive at the collecting electrode they cease to contribute to the current. Hence,

$$s(t)=s_0(t)\left[1-\int_0^t p_t(t')dt'\right], \quad (1)$$

where $p_t(t)$ is the probability that a carrier arrive between times t and $t+dt$. The arrival time distribution can be related to a distribution of effective velocities $p_v(v)$:

$$p_t(t)=(L/t^2)p_v(L/t), \quad (2)$$

where L is the thickness of the sample. The velocities are "effective" in the sense that no carrier maintains a unique velocity throughout its entire transit, but rather the velocity of each carrier is averaged over its path. The velocity distribution then counts the number of paths that result in a particular value of v.

Once p_v is determined, it is a trivial matter to obtain the mean carrier mobility, since, by definition

$$\langle\mu\rangle=\frac{\langle v\rangle}{E}=\frac{1}{E}\int_{-\infty}^{\infty} vp_v(v)dv . \quad (3)$$

This is clearly the physically proper form for the mobility, in contrast to any definition based on a single point of the current-time profile, such as its shoulder.

Given this formulation of the problem, the task of the experimentalist is to determine which functions, $s_0(t)$ and $p_v(v)$, best describe the data, and to compare their parameters with theory. We have found a pair of simple functions that fit a wide variety of our own experimental measurements. Our choice of these functions was motivated by a desire to make contact with the existing body of literature on dispersive transport, keeping to a minimum, at least initially, the number of adjustable parameters. Accordingly, we choose first for $s_0(t)$ the fractional power-law form of SM:[5]

$$s_0(t)=At^{-(1-\alpha)}, \quad 0<\alpha\lesssim 1 . \quad (4)$$

The two parameters are A, which provides an overall scale for the signal, related to the laser-pulse energy and the charge generation efficiency, and the dispersion parameter α, which tends to 1 for a nondispersive signal (i.e., one having a time-independent current until carriers start to leave the sample). This power-law form can even empirically describe delayed generation, if α is allowed to be greater than unity, in which case the current increases at short times.

The velocity distribution function is normal to a very good approximation. We were led to this surprisingly simple result by examining several current transients in the following way: (1) fit the signal, for times short compared to the traditional transit time, to the form of Eq. (4) obtaining the parameters A, α; (2) divide the entire transient by s_0; (3) using the derivative form of Eq. (1),

$$\frac{d}{dt}\left[\frac{s}{s_0}\right]=-p_t(t) , \quad (5)$$

differentiate to find the arrival time distribution; (4) following Eq. (2), multiply by t^2/L to obtain the velocity distribution, and plot vs $1/t$. The results, an example of which is shown as the inset to Fig. 1, follow a Gaussian within the accuracy allowed by the digital differentiation. By analyzing transients in this way, we became convinced that the Gaussian form was appropriate, and subsequently analyzed the entire time dependence in terms of the four-parameter function:

$$s(t)=At^{-(1-\alpha)}\left[1-\int_0^t \frac{1}{\sigma_I t'^2\sqrt{2\pi}}\exp\frac{-(1/t'-1/t_0)^2}{2\sigma_I^2}dt'\right] . \quad (6)$$

Here $t_0=L/\langle v\rangle$ is the relevant mean transit time, and $\sigma_I=\sigma_v/L$ is the standard deviation of inverse arrival times, giving the width of the velocity distribution σ_v. We have successfully used this formula to fit transients (for an example, see Fig. 1) obtained on 20 different samples, over temperature ranges from 215 to 400 K, and electric fields from 1 to 120 MV/m. Values of α range from 0.65 to 1, and the relative width $w_v=\sigma_v/\langle v\rangle$ from 0.3 to 1. We expect and find that the parameters α and w_v are not totally independent of each other in this description, since both reflect the physics giving rise to dispersion of the carrier packet. The quality of fit (defined using the reduced χ^2 statistic, which is between 0.5 and 2.0 in more than 95% of the cases) is excellent over these entire ranges and shows no obvious trend. Because the fit is highly overdetermined (typically 2000 data points and only four fitting parameters) the precision with which the parameters are determined is excellent—usually better than one part in 10^3, an improvement of one or two orders of magnitude over graphical methods. Further details of the fitting procedure and additional results will be given in future publications.

We have used this procedure to reanalyze the mobility of several materials, an example of which is illustrated in Fig. 2: diethylaminobenzaldehyde-methylphenylhydrazone (DEMPH[15]) doped into polycarbonate (PC) at a concentration of 50%. The axes are $\log_{10}\mu$ and $\sqrt{E}$, which would be appropriate for Poole-Frenkel emission from charged traps.[16] Plots of this type, using the shoulder as transit time, generally yield straight lines within the scatter of the data. The new analysis not only gives mobility values that are considerably lower (about a factor of 2), but are sufficiently precise to reveal a systematic discrepancy. The inset of Fig. 2 shows that the deviation has a distinct upward curvature in this case. In some other materials the curvature is downward or sigmoid.

One might wonder whether the deviations from $\ln\mu\sim\sqrt{E}$ result from a bias produced in the data by the parametrization of s_0 in terms of α. This is a difficult question to answer in general, since the method implies

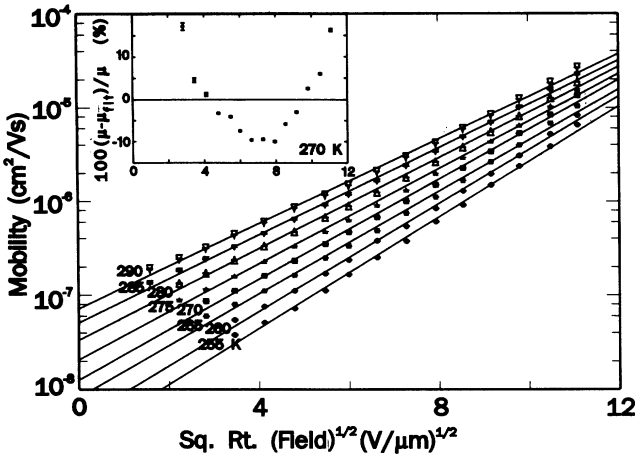

FIG. 2. Field dependence of the mobility of 50% DEMPH in polycarbonate at the temperatures indicated. The (frequently indistinguishable) pair of bars through the symbols show the errors. The lines are attempted fits to $\ln\mu \sim \sqrt{E}$. The relative deviations of the fit at 270 K are shown in the inset.

the extrapolation of s_0 through the region of the transit time, where, by definition, its validity cannot be quantitatively verified. However, since the power-law form always has a rather weak time dependence in the region of interest, we find that unreasonably large errors, or time dependent changes, in α (~ 0.05, which is of order 50 times the error estimate in α itself) are required to account for the deviations. Moreover, in DEMPH:PC, α is virtually independent of field above about 30 V/μm; yet the curvature persists in this range.

Next we consider whether the choice of function, $s_0(t)$, might affect the mobility. The Scher-Montroll form used in these initial analyses may not be totally consistent with the data. It has been shown, for example, that a single power law does not describe all the early time photocurrent for polysiloxanes with pendant carbazole groups.[17] Similarly, we have found the SM form to be less accurate for tritolylamine (TTA) doped polycarbonate[18] than for hydrazones, the deviation being consistent with a time-dependent α.[19] Other forms of s_0 might be used to model better this behavior, for example, the Kohlrausch-Williams-Watt function,[20] which is well known to give an empirical description of phenomena involving dispersive relaxation. In a simple attempt to account for an α increasing with time, as well as to test the sensitivity of the moblitiy to the choice of the s_0 function, we let $s_0(t)=a+b/t$, which interpolates between the completely dispersive case ($\alpha=0$) at $t=0$ and the nondispersive case ($\alpha=1$) at long times. Except for the case of TTA/PC, which showed marginal improvement, this led to poorer fits ($\chi_r^2 \gtrsim 3$) apparently because this two-parameter form does not properly account for the time scale of the relaxation. Most importantly, it did not qualitatively change the nature of the deviation of the mobility from $\exp\sqrt{E}$. We therefore conclude that the discrepancies are not an artifact of the analysis procedure.

The experimental observation of an $\exp\sqrt{E}$ dependence has been difficult to account for.[21] Our result indicates that it is not necessary to consider theoretical models in which $\ln\mu$ is *exactly* proportional to $\sqrt{E}$. Unfortunately, it is not yet clear what functional form does provide a better description of the data. We note that disorder simulations[22] do show similar, though larger, deviations. The lack of a functional form limits the accuracy of obtaining the activation energy of the mobility by extrapolation to zero field.[21,23]

The accuracy of the Gaussian form for $p_v(v)$ is intriguing. It is reminiscent of the central limit theorem as it might apply to the sequence of hops made by each carrier. One can define an instantaneous velocity in terms of the microscopic parameters associated with each hop: $v_i = l_i \cos\theta_i / \tau_i$, where l_i is the length of the ith hop, making an angle θ_i with the applied electric field, and τ_i is the residence time preceding the hop. Apparently the distributions of l, θ, and τ lead to a v_i distribution that obeys the central limit theorem when summed over a large number of hops ($\sim 10^4$) on each carrier's path and the large number of carriers ($\sim 10^9$). It should be emphasized that it is the effective velocities (or *inverse* arrival times), and not the arrival times, which have the normal distribution. Indeed, one of the major features of dispersive transport theory is that the SM waiting time distribution[5] $\psi(\tau) \sim \tau^{-(1+\alpha)}$ has no finite mean when $\alpha < 1$ and does not obey the central limit theorem.

We find values of the relative width of the velocity distribution $w_v = \sigma_v / \langle v \rangle$ lying mostly between 0.3 and 1 for the data that we have examined. This implies a significant probability of zero and even negative velocities, i.e., some carriers either never leave the sample or presumably recombine at the illuminated electrode. Although this is surprising, it is physically reasonable, and properly accounted for in the average effective velocity.

In summary, we have described a method of analyzing photocurrent transients to determine physically relevant parameters that enter two functions, one describing the current as it would evolve in a semi-infinite sample, and the second accounting for the arrival of carriers at the collecting electrode. We have demonstrated by a particular choice of these two functions, namely a Scher-Montroll power law and a normal velocity distribution, that a straightforward fitting procedure can be successfully applied to a wide variety of data. The analysis reveals that the commonly cited $\sqrt{E}$ mobility behavior is merely an approximation for these kinds of material. Theoretical input to the choice of the two functions, and further careful data analysis, are required in order to refine the methodology described here, and to determine, with the enhanced precision that it affords, the field, temperature, concentration, and time dependence of charge-carrier mobilities in disordered media.

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