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NON-DISPERSIVE AND DISPERSIVE TRANSPORT IN RANDOM ORGANIC PHOTOCONDUCTORS

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Abstract A previously developed hopping concept for rationalizing charge transport in random organic photoconductors is further elaborated. It rests on the premise that random molecular packing gives rise to energetic disorder that can be accounted for in terms of a Gaussian-shaped density of hopping states (DOS). Computer simulations confirm that an array of randomly positioned dipoles generates a Gaussian DOS whose width is in excellent agreement with experiment. The existence of energetic disorder can explain in a quantitative manner the scaling behavior of the shape of time of flight signals with respect to sample length and electric field as well as the transition to dispersive transport at low temperatures.

Keywords: charge transport, hopping, dispersive, disorder, photocurrents

INTRODUCTION

The phenomenology of charge transport in glassy organic solids differs from that in crystalline counterpart structures in characteristic ways. Even in materials that are regarded as trap-free, the mobility μ is temperature activated featuring an activation energy of approximately 0.5 eV if analyzed in terms of an Arrhenius relationship. It follows a $\mu = \mu_0 \exp(\beta E^{1/2})$ law over at least one order of magnitude in field E [1] with ß changing sign at elevated temperatures.[2] At low temperatures, time-of-flight (TOF) photocurrent transients become dispersive, indicating that an operationally defined "mobility" is no longer a unique material property but depends on sample dimensions.[3] The above features are observed with pendant group polymers like poly(N-vinylcarbazole),[4] main chain polymers like σ-conjugated polysilanes,[5] π-conjugated polythiophenes[6] and polyphenylenevinylenes[7,8] and, notably, a variety of chemically quite different molecularly doped polymers.[9-12] Their obvious independence on chemical constitution and, hence, synthetic routes strongly suggests associating them with the randomness of the structure which is a physical property common to all of the materials mentioned above.

A model of hopping transport within a manifold of states with Gaussian-shaped density of states (DOS) profile has previously been developed on the basis of Monte Carlo simulations,[13] analytic effective medium theory,[14] and time-resolved optical spectroscopy.[15] It has been shown that it is able to account for the principal features of charge transport in molecularly doped polymers as well, indicating that structural relaxation leading to polaron formation,[16] though principally occurring, is of secondary importance only.

Unfortunately, the distribution of hopping states in organic glasses is not amenable to direct optical probing as the distribution of states of excitonic character is. On the other hand, the occurrence of inhomogeneously broadened, Gaussian-shaped absorption profiles of chromphores in supercooled liquids is a phenomenon well documented and well understood in terms of spatially random van der Waals and electrostatic interactions.[17,18] Guided by the functional similarity of dipole-dipole and dipole-charge interactions, it was straightforward to invoke a Gaussian as a first order choice also for the distribution function for charge transport states in glassy systems in which weak intermolecular coupling guarantees that all states be localized. Although this assumption established the basis for successful modelling of charge transport in random organic systems a more rigorous justification of the underlying premise seemed desirable.

This study is divided into two parts. The first one deals with the effect of permanent dipoles on the DOS function of a hopping system. It has been examined by summing up the individual contributions of randomly distributed dipoles to the total electrostatic potential at a given site of a model transport system and verifies that Gaussian-shaped DOS-functions are, in fact, appropriate as previously anticipated. The second part is devoted to an analysis of time of flight (TOF) signals. While early work emphasized the importance of universality as far as the shapes of dispersive TOF signals are concerned[19] more recent results indicated that this is rather a feature of non-dispersive hopping transport the reason being that the ratio of spatial broadening of a packet of transporting particles and its displacement under the influence of a drain field must become anomalously large in any random system in which the elementary transport step is controlled by a distribution of rates no matter whether or not dynamic equilibrium has been attained.

SHAPE OF THE DOS FUNCTION IN THE PRESENCE OF DIPOLES

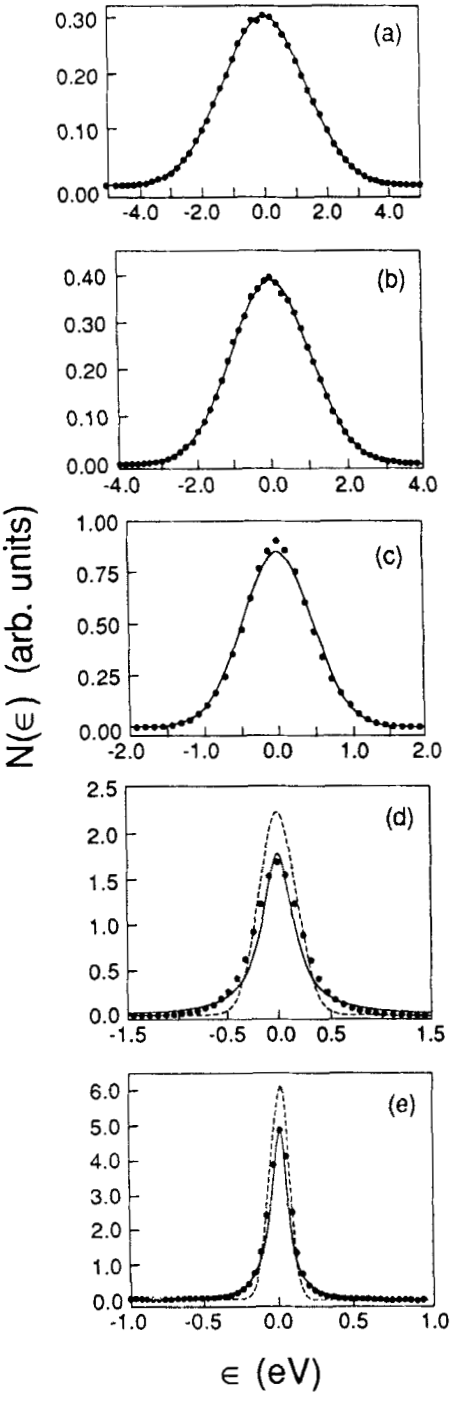

Fig. 1 shows a series of DOS profiles computed by numerical summation of the contribution of randomly oriented permanent dipoles on the electrostatic potential at a given site of a cubic lattice. For a relative concentration $c > 0.2$ it is indistinguishable from a Gaussian while at lower concentrations the wings gain intensity and the profile approaches a Lorentzian. For $c < 0.2$ the variance σ_d of the dipolar DOS varies as $c^{2/3}$ and approaches $\sigma_d \sim c^{1/2}$ above. If one ignores the deviations from a $\sigma_d \sim c^{2/3}$ law at large c one can derive a scaling law that allows predicting σ_d once the dipole moment (in Debye units), the intersite separation a (in Å) and the dielectric constant ε are known:

$$\sigma_d(p,a,\varepsilon,c) = 3.0\,[c^{1/3}/a]^2\,(p/\varepsilon) \quad (1)$$

For a = 6Å, ε = 3, c = 1 and p = 2.5 D, σ_d = 0.07 eV is obtained in excellent agreement with experimented data derived from an analysis of the temperature dependence of the charge carrier mobility in molecularly doped polymers and glasses. Recall

Fig. 1: A series of DOS profiles calculated for a relative concentration: (a) c = 1.0, (b) c = 0.5, (c) c = 0.15, (d) c = 0.05, and (e) c = 0.01 of dipoles with moment 6 D randomly positioned as sites of a hypothetical cubic lattice with lattice constant a = 3.5Å and ε = 1. Full curves are Gaussian fits, dashed curves are Lorentzians.

that hopping theory predicts $\mu(T) = \mu_0 \exp[-(2\sigma/3kT)^2]$ where $\sigma = (\sigma_{vdw}^2 + \sigma_d^2)^{1/2}$ is the sum of van der Waals and dipolar contributions.

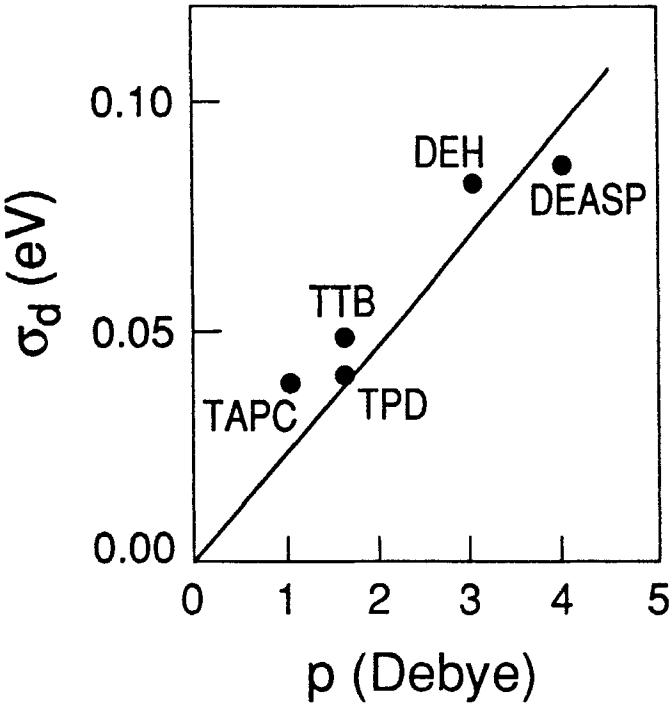

Fig. 2: Experimental data for the dipolar contribution σ_d to the total width of the DOS for vapor deposited single component glasses of 1,1 -bis(di-4-tolylamino-phenyl)cyclohexane (TAPC), N,N ,N, N -tetrakis(4-methylphenyl)-(1,1 -biphenyl)-4,4 -diamine (TTB),N,N -diphenyl-N,N -bis(3-methylphenyl)-(1,1 -biphenyl)-4,4 -diamine (TPD),1-phenyl-3-p-diethylaminobenzaldehyde diphenylhydrazone (DEH), and 1-phenyl-3-p-diethylaminostyryl-5-p-diethylphenylpyrazoline (DEASP) (from[20])

Fig. 2 shows experimental data[21] for a series of single component glasses as a function of the dipole moment of the transport molecules. The line is a fit based upon Eq.(1) with c = 6Å and ε = 3.5. The reason for the success of this simple concept for dipolar interaction is that on the one hand the number of interacting particles is sufficiently large that central limit theorem applies and on the other hand the strength of interaction is weak enough to render dipolar rearrangements, ignored in the computations, unimportant.

SCALING PROPERTIES OF TOF SIGNALS

Upon drifting across a film of a dielectric material under the action of an applied electric field E an initially δ-shaped sheet of externally generated charge carriers spreads with time because of diffusion. The signature of conventional Gaussian transport is that the ratio of the diffusive spread to displacement is time dependent,

$$<\Delta x^2>^{1/2}/<x> = (kT/E)(2Dt)^{-1/2} \quad (2)$$

V being the applied voltage. Eq.(2) implies validity of Einstein's law relating carrier mobility μ and diffusivity D via $eD = \mu kT$ and predicts that time of flight (TOF) signals recorded at variable electric field and/or sample thickness L and plotted on a time scale normalized to t_{tr} become broader upon either lowering E at constant L or reducing L at a given field. For L = 10 μm and V = 500 V, i.e. $E = 5x10^5$ Vcm^{-1}, $\Delta t_{tr}/t_{tr} \simeq 10^{-2}$ follows. In random media TOF signals are much broader and often dispersive.

It was a major success of the Scher-Montroll-Lax[19] treatment of stochastic transport in random media to explain these anomalies in terms of the disorder of the sample if cast into a heuristically defined, algebraic waiting time distribution. With the advent of clean and reproducibly manufacturable molecularly doped polymers it became clear, however, that dispersive TOF signals are not a requirement for observing anomalously broad tails. This fact was first documented by Tahmasbi and Hirsch[22] on the basis if TOF signals for polyvinylcarbazole exhibiting well-developed plateau regions and broad tails yet yielding transit times that scaled exactly linearly with sample thickness. Meanwhile there is growing evidence[23,24] that universality of TOF signal shapes, for long considered to be a hallmark of dispersive transport, is rather an inherent feature of non-dispersive transients in random photoconductors.

The goal of previous Monte Carlo simulations[25,26] was to delineate the evolution of TOF signals as a function of temperature T, electric field E and sample length L in hopping systems with built-in energetic and positional disorder. For moderate energetic disorder, $\sigma/kT = \sigma < 4$, TOF signals show well-developed plateaus yet the dispersion

$$w = (t_{1/2} - t_0)/t_{1/2} = (\pi D/\mu EL)^{1/2}, \quad (3)$$

$t_{1/2}$ being the time after which the current has decayed to 1/2 of its plateau value and t_o the intersection point of the asymptotes, remains anomalously large. (On the

basis of $\mu kT = eD$ Eq. (3) would predict $w = (\pi kT/eV)^{1/2}$). The simulations indicated that this is due to a field-induced spreading of the carrier packet translating into an apparent field-dependent diffusity D_e. Analytic work[27] confirmed this result. Interestingly, for $\hat{\sigma} > 3.5$, D_e varies almost linearly with E and L equivalent to w being independent of both electric field and sample length implying universality of TOF signals plotted on time scale normalized to the transit time.

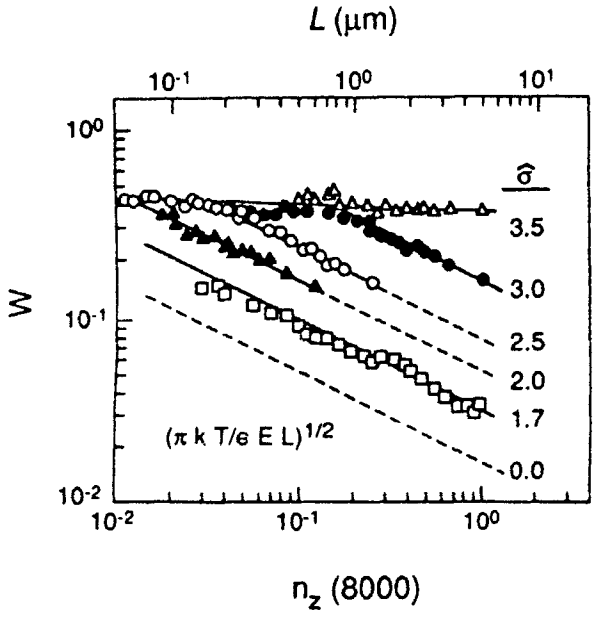

Fig. 3: Simulation result for w vs sample length normalized to the number of lattice planes in a cubic system with a = 6 Å.

Fig. 3 further predicts a turn-over of w(L) from $w \propto L^{-1/2}$ for $\hat{\sigma} < 3$ to w = const $\simeq$ 0.4...0.45 for $\sigma > 3.5$. This effect has been verified with glassy DEH by measuring w(L) at two different temperatures below the glass transition temperature (fig. 4).

The key result of this study is the prediction and its experimental verification that the dispersion w of a non-dispersive TOF signal is in a unique way related to the disorder of the sample its functional dependence on sample length L undergoing a characteristic change upon varying the degree of disorder. The observation that the w(L)-dependence changes from $w \propto L^{-1/2}$ to w = const. in one and the same sample solely as a result of a temperature change provides compelling evidence that the relative energetic disorder is indeed the main origin of TOF pulse broadening. Recall

that below the glass transition temperature, where the frozen-in disorder potential is constant, $\hat{\sigma}$ changes reversibly upon changing T.

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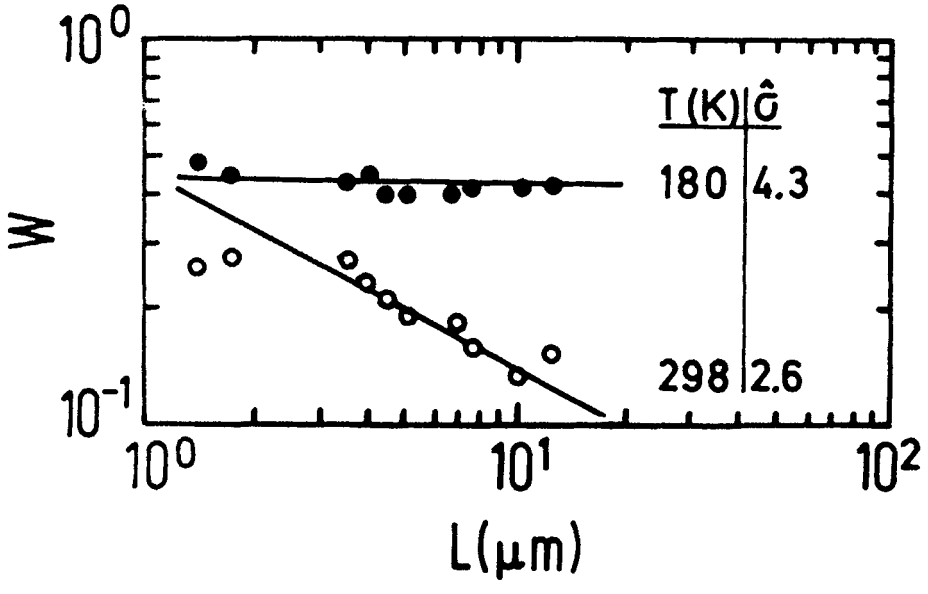

Fig. 4: w as a function of sample length for a DEH glass at different temperatures

This work demonstrates that the scaling behaviour of non-dispersive TOF signals in random organic photoconductors is an inherent property of transport systems with Gaussian type energetic disorder onto which positional disorder may yet need not be superimposed. It is not bound to the observation of what has conventionally been referred to as dispersive transport, although both phenomena have the same physical origin. This origin is identified as the electronic relaxation of an ensemble of carriers hopping within a Gaussian distribution of localized states. Transport will obey

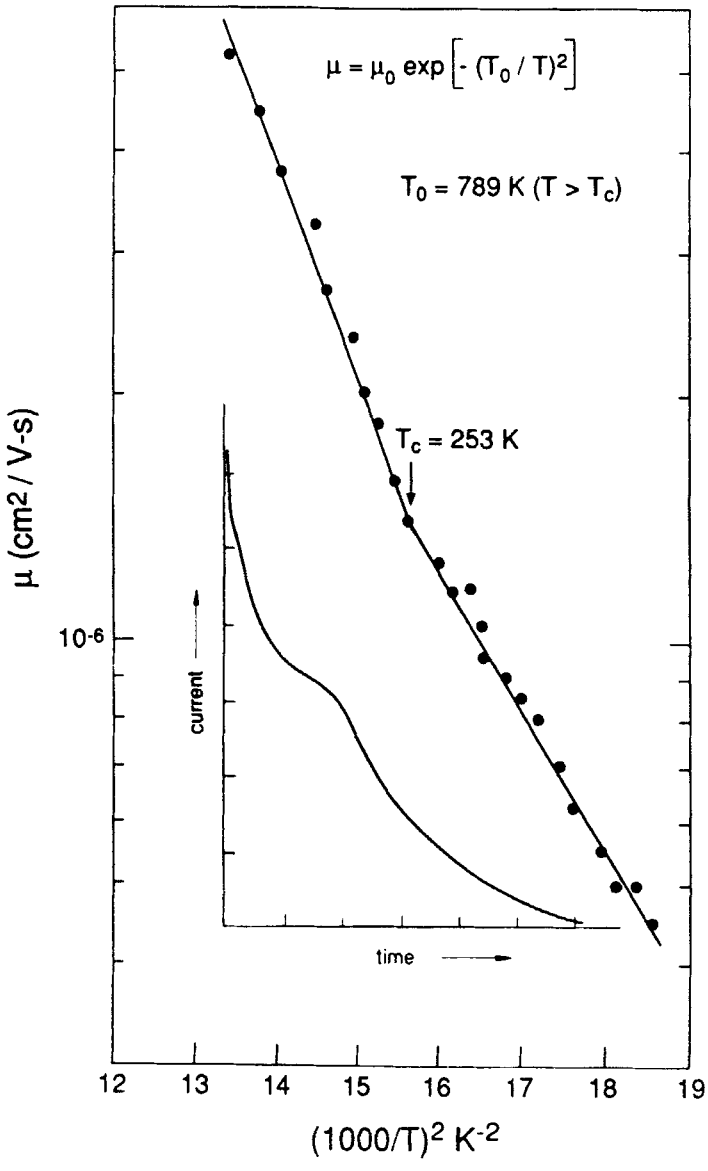

Fig. 5: Temperature dependence of the operationally defined hole mobiltity in a DEASP glass (from [28]). The inset shows the shape of a TOF signal at $T = T_c$ as predicted by simulation (from [3]).

Gaussian statistics, i.e. be time independent and the TOF signals revealing a width w proportional to $L^{-1/2}$ if the carriers attain dynamic equilibrium characterized by the theoretical asymptotic occupational density of states (ODOS) which for a Gaussian

DOS of width σ is also a Gaussian of width σ yet shifted by an energy σ^2/kT relative to the origin of the DOS. The dispersion w of the TOF signal will be anomalously large, though, because the structure of the ODOS implies a distribution of individual jump rates. The other extreme is the situation in which the disorder is so large that carriers traverse the sample before relaxing to their mean equilibrium energy. In that case TOF signals will be dispersive because relaxation is accompanied by a slowing down of the hopping motion. There is an intermediate regime in which the energy of those carriers that occupy the upper states of the ODOS (and it is those carriers that contribute most to the current) has attained its infinite time limit yet the bottom part of the ODOS has not fully evolved because of the long equilibration times. For this reason the width of the distribution of jump rates of the ensemble continues to become broader with time. It is this process that translates into a time dependence of the apparent diffusivity and, concomitantly, the growth of D_e with the distance of the carrier packet from the injecting contact although the photocurrent has attained its plateau value already. It turns out that under realistic values of electric field and sample dimension this case is realized for σ-values around 4, i.e. σ~0.1 eV and room temperature. Since 0.1 eV is a typical value for the DOS in molecularly doped polymers[13] as well as σ-[1] and π-[7] conjugated main chain polymers it is all but surprising that the scaling behaviour of TOF signals is a frequently encountered phenomenon.

Finally, an example for the turn-over to dispersive transport for $\hat{\sigma} \gtrsim 5$ shall be presented. Simulation work had indicated that loss of a plateau in a TOF signal in double linear representation is insufficient for concluding on the importance of dispersion effects. It turned out that the change in the temperature dependence of the kink in a TOF signal, conventionally used to determine the carrier mobility, is a less ambiguous way to identify the ND→D transition.

Fig. 5 is an example for this behaviour based upon data for a one component DEASP glass.[28] The shape of the TOF signal at the critical temperature T_c, that translates into a critical disorder parameter $\hat{\sigma}_c$ is shown as an inset. Since in a thick sample carriers have more time to relax towards dynamic equilibrium as compared to a thin sample, $\hat{\sigma}_c$ must increase, i.e. T_c decrease, with increasing sample length L. This effect has been observed with DEASP in quantitative agreement with model predictions (Fig. 6).

The results summarized above add further support to the notion that the disorder formation, though simple, is able to recover all basic features of transport in random organic solids in a surprisingly quantitative way.

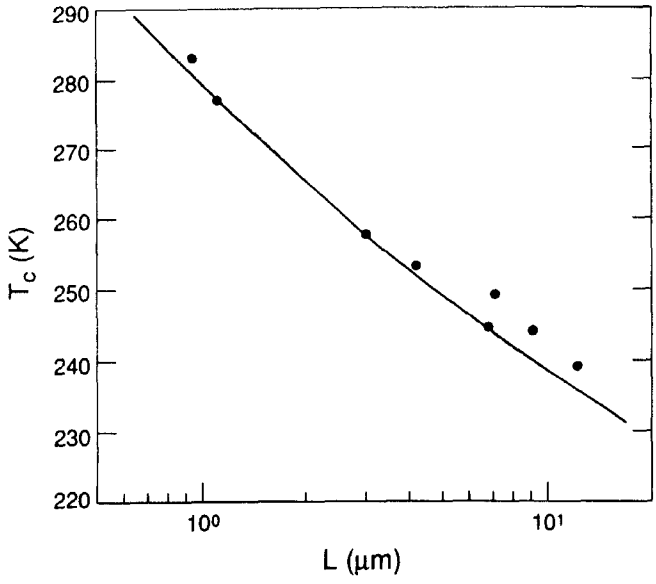

Fig. 6: T_c as a function of sample length. Data points are experimental (DEASP, from[28]), the full curve is the simulation result based upon an intermolecular distance of 6 Å.

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