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Energetic Disorder, Spatial Correlations, and the High-Field Mobility of Injected Charge Carriers in Organic Solids

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In a large class of disordered organic solids, the observed field and temperature dependence of the mobility of photoinjected charge carriers arises from specific statistical features of the disordered potential energy landscape through which they move. In materials with polar constituents, energy fluctuations exhibit strong spatial correlations, with deep energetic valleys developing only over large length scales. We present a scaling analysis that shows how the hierarchical field-induced flattening of fluctuations of different magnitudes gives rise to field dependent (e.g., Poole-Frenkel type) mobilities characteristic of the spatial correlations from which they arise.

Introduction The hopping mobility of photoinjected charges in a large class of molecularly-doped polymers and molecular glasses has a field dependence that for electric fields E in a rather large range ($E \approx 10^4$ to 10^6 V/cm) is well described by the Poole-Frenkel law

$$\mu \propto \exp(\gamma\sqrt{E}), \tag{1}$$

in which γ (the Poole-Frenkel factor) is a material-dependent parameter that typically decreases with increasing temperature. The source of this unusual field dependence has been the focus of considerable experimental [1–11] and theoretical investigations [12–16] centering on the role played by spatial and energetic disorder. Recent efforts by a number of workers [17–24] have revealed that drift mobilities of this type can arise when injected carriers hop among sites distributed in a random potential energy landscape possessing the right type of spatial correlations. In many materials of interest, e.g., it has been established that significant energetic disorder arises from carrier interaction with random dopant or host molecules possessing permanent electric dipoles [25–31]. Since the charge-dipole interaction is long range ($\sim 1/r^2$), each injected charge interacts with many surrounding dipoles. To place a carrier at the n-th transport site, e.g., requires an energy $u_n = -\sum_i \mathbf{p}_i \cdot \mathbf{E}_{n,i}$ equal to its interaction with each dipole $\mathbf{p}_i$ in the medium, where $\mathbf{E}_{n,i}$ is the Coulomb field of the carrier evaluated at the location of the i-th dipole. For random dipole orientations $\mathbf{p}_i$, and locations $\mathbf{r}_i$, the site energy u_n has many independent contributions, and the resulting distribution tends towards a Gaussian with zero mean, as has long been assumed in numerical studies of Bässler and coworkers [14–16]. The energetic width σ of the distribution of site energies arising in

this dipolar disorder model has been calculated [18, 22, 31] for typical dipole moments and densities and found to be of the right order of magnitude, $\sigma \approx 60$ to 120 meV, to account for the thermally activated transport observed in these systems.

More importantly, the long range nature of the underlying interaction also gives rise to significant spatial correlations in the electrostatic potential arising from the random dipole distribution. Indeed, the potential energy autocorrelation function associated with a random distribution of dipoles decays very slowly [18, 24]

$$C(r) = \langle u(0)u(r)\rangle \sim \sigma^2 a/r \tag{2}$$

with intersite separation r, showing that in such a medium the energy at a given site tends to be close to that of neighboring sites, which are surrounded by nearly the same configuration of dipoles. Correlations of this type have been shown to have a critical effect on transport [17 to 20]. In a previous work [18], an analytical result

$$\mu = \mu_0 \exp\left[-\left(\frac{\sigma}{kT}\right) + 2\left(\frac{\sigma}{kT}\right)\sqrt{eaE/kT}\right] \tag{3}$$

giving a Poole-Frenkel mobility formally equivalent to Eq. (1) was derived for carriers hopping along one spatial dimension through a medium with 3D correlations as characterized by the dipolar correlation function of Eq. (2). A similar behavior has also been observed in recent 3D simulations [19], lending support to the essential idea that spatially-correlated energetic disorder is a necessary ingredient for obtaining field-dependent mobilities of the Poole-Frenkel type.

Unfortunately, exisiting analytical [18] and numerical calculations [19] provide little physical insight into how correlations that arise in dipolar materials cause the field dependence of the form observed, or, indeed, how other correlations might be expected to give rise to similar field dependencies. In this paper we present a scaling analysis that we believe captures the essential physics behind the high-field mobility associated with hopping transport in systems possessing extensive spatially-correlated energetic disorder. The essence of the analysis, developed in the following section, is that in materials in which potential energy fluctuations exhibit strong spatial correlations, deep energetic valleys develop only over correspondingly large length scales. In such systems, the hierarchical field-induced flattening of fluctuations of different magnitudes (and thus lengths) leads to the establishment of critical traps, i.e., regions associated with potential energy fluctuations of a critical field-dependent size that limit transport.

Charge Transport in a Correlated Random Potential We consider the hopping of charge carriers among localized transport sites embedded in a correlated Gaussian random potential. For large enough disorder, a small fraction of low energy transport sites in the system will act as traps, with the average time spent on these sites large enough that escape from them is rate-limiting for transport. Under these circumstances the mobility

$$\mu \sim \frac{\langle \varrho_z \rangle}{E\langle \tau \rangle} \tag{4}$$

will depend on the ratio of the mean distance $\langle \varrho_z \rangle$ between traps (along the field direction) to the average dwell (or escape) time $\langle \tau \rangle$ for those critical traps that most limit transport. When the underlying random potential in which the transport sites are embedded is uncorrelated (or has a very short correlation length), a trap is just a single

low energy site, but with correlated disorder low energy sites are typically surrounded by neighboring sites of similarly low energy. Thus, by definition, what constitutes a trap is a group of such sites lying in an extended region associated with a deep potential energy fluctuation, escape from which requires a particle to move from the sites connecting the valley floor to the rim.

In this circumstance, the field dependence of the mobility is dominated by that of the average trap escape time; the latter being thermally activated, with an activation energy Δ equal to the energy difference between the bottom of a trap and the rim. In the presence of a field, the trap is tilted, and the activation energy is reduced, assisting escape. Along the field direction, the activation energy is lowered by the potential drop eEr induced by the field, where r is the distance between the bottom and the rim. The escape time τ is then reduced by the Boltzmann factor $\exp(-eEr/kT)$. From Eq. (4), the field dependence of the mobility

$$\mu \propto \frac{1}{\langle \tau \rangle} \propto \exp(eEr_c/kT) \tag{5}$$

will reflect the field-induced decrease in escape time associated with the most rate limiting, or critical, traps, which will be of some characteristic linear extent r_c. With uncorrelated disorder, r_c is just the nearest-neighbor spacing ϱ, and the corresponding mobility $\mu \propto \exp(eE\varrho/kT)$ depends on the first power of the field. With correlated disorder, however, the width of critical traps is determined by a competition between the trap depth, the trap width, and the field induced lowering. This leads to a critical width r_c that depends upon field strength.

The origin of the Poole-Frenkel law and other possible field dependent mobilities associated with hopping transport in correlated media lies in the statistical relationship between the depth and the spatial extent of typical energetic fluctuations in the material. This relationship is characterized by the mean-square potential energy difference

$$\langle \Delta^2(r) \rangle = \langle [u(r) - u(0)]^2 \rangle = 2\left[\langle u^2 \rangle - \langle u(r)u(0) \rangle\right] = 2\left[\sigma^2 - C(r)\right] \tag{6}$$

between two sites in the medium separated by a distance r. With the correlation function (2) appropriate to a disordered dipolar medium the mean-square energy difference $\langle \Delta^2(r) \rangle \sim 2\sigma^2(1 - ar^{-1})$ between two sites in such a medium approaches a maximum of $2\sigma^2$, rising monotonically with increasing site separation as r^{-1}. Thus, statistically, the energy difference between two sites becomes greatest when, at infinite separation, they are influenced by two completely independent arrangements of surrounding dipoles. By the same token, this energy difference tends to zero as the site separation decreases, since in this limit two nearby points are influenced by the same configuration of surrounding dipoles. In what follows, we consider transport in a class of correlated Gaussian potentials which generalize the dipolar situation studied previously and which include, e.g., correlations arising from a carrier's interaction with localized charge distributions possessing higher multipole moments. Specifically, we consider Gaussian potentials described by a general power law correlation function of the form

$$\langle \Delta^2(r) \rangle \sim \sigma^2\left[1 - \left(\frac{a}{r}\right)^p\right], \qquad p \geq 1. \tag{7}$$

Now if in (6) and (7), $u(0)$ refers to the energy at the bottom of a valley, and $u(r)$ to that at the rim, then Eq. (7) implies an approximate relation between the mean width r

of a valley and its depth Δ, i.e., wider valleys tend to be deeper and deeper valleys tend to be wider. One might expect that in such a situation the broadest (i.e., deepest) valleys always form the most rate-limiting traps. This is not generally correct, however, because the concentration of very deep valleys is also very small, decreasing exponentially with increasing valley depth (reflecting the assumed Gaussian density of states). More importantly, however, the energy barriers associated with wide (i.e., deep) energetic valleys become reduced more in the presence of a field than do narrower (shallower) ones, as we illustrate in Fig. 1. Thus, in a correlated medium of this type, the most effective traps for a given field strength are neither the widest nor the narrowest, but those of some intermediate critical dimension $r_c(E)$.

To determine this critical trap width we consider the diffusional escape of a particle[32] from an energetic valley of width r and depth $\Delta(r) = u(r) - u(0)$. The rate at which a particle escapes from such a trap is known to be proportional to the ratio of the probability $P(r)$ that the particle is on the rim, to the probability $P(0)$ that the particle is at the bottom of the trap[33]. If the escape rate is low (rate-limiting), local equilibrium will be obtained within the trap region, and the ratio of interest can be written as a detailed balance factor,

$$\frac{P(r)}{P(0)} = \frac{g(r)}{g(0)} \exp\left(-\frac{\Delta(r) - eEr}{kT}\right), \tag{8}$$

where $g(r)$ and $g(0)$ give the site density near the trap rim and bottom, respectively. Once a particle reaches the rim, there is then a characteristic time

$$\tau_D \approx \frac{\delta^2}{D_0} = \frac{\delta^2}{R_0 \varrho^2}, \tag{9}$$

to hop a distance δ across the dividing surface, with hops occurring at some characteristic rate R_0. The overall trap escape time from a given energetic valley of width r is

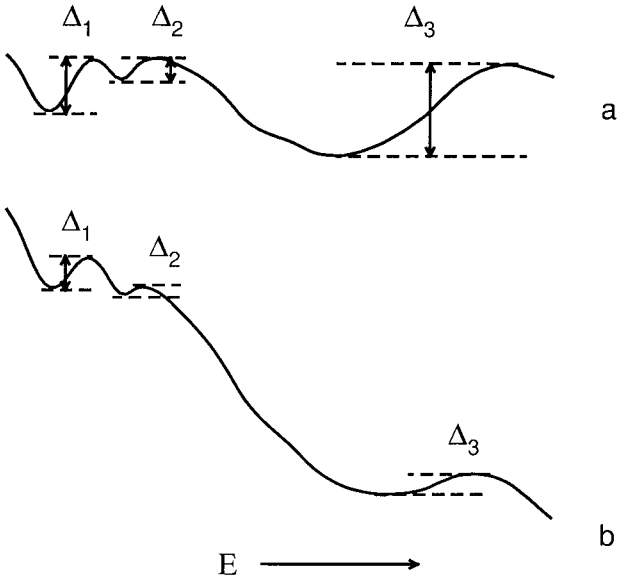

Fig. 1. Correlated random potential with and without an applied field. Note that in the absence of a field the deepest potential wells are also the widest. When a field is applied in b), wider potential wells are tilted more, and hence experience much greater barrier reduction

then the ratio

$$\tau = \frac{\delta^2}{R_0 \varrho^2} \frac{g(0)}{g(r)} \exp\left(\frac{\Delta(r) - eEr}{kT}\right) \tag{10}$$

of (9) and (8). Now the mobility is related to the ensemble average of the escape time from the critical traps. This average may be evaluated by taking advantage of the fact that for large enough disorder (or low enough temperatures) the r and Δ dependence of the pre-factor in (10) is weak compared to the exponential factors, so that the mean escape time from valleys of width r takes the form

$$\langle \tau(r) \rangle = \tau_0 \left\langle \exp\left[\frac{\Delta(r) - eEr}{kT}\right] \right\rangle, \tag{11}$$

where τ_0 is a characteristic time that will depend, at most, algebraically on field and distance. The average over the Gaussian correlated random potential energy field reduces, in this case, to an average over the distribution

$$P(\Delta; r) = \frac{1}{\sqrt{2\pi \langle \Delta^2(r) \rangle}} \exp\left(-\frac{\Delta^2}{2\langle \Delta^2(r) \rangle}\right), \tag{12}$$

of site-energy differences Δ at a given distance r, which is assumed to have zero mean and a variance $\langle \Delta^2(r) \rangle$ given, e.g., by (7). Performing the average we find that

$$\langle \tau(r) \rangle = \tau_0 \exp\left[-\frac{eEr}{kT} + \frac{\langle \Delta^2(r) \rangle}{2(kT)^2}\right]. \tag{13}$$

Now the critical traps are those for which the escape time is the longest. Maximizing this last expression with respect to r gives for a correlation function of the form (7), a critical width

$$r_c = a\left(\frac{p\sigma^2}{2eEakT}\right)^{\frac{1}{1+p}}. \tag{14}$$

It is traps of this critical size that for large enough disorder are the most important in determining the mobility at a given field strength. Note that at very low fields the widest traps become important ($r_c \to \infty$ as $E \to 0$), consistent with the idea that they are also the deepest. As the field increases, however, the widest traps are flattened strongly by the field, reducing their release times dramatically. The rate limiting step is then determined by traps of smaller spatial extent. For power law correlations (7), the critical trap width decreases monotonically as $E^{-1/(1+p)}$, leading to a characteristic field dependent mobility, which we compute by evaluating the mean escape time (13) for traps of critical width (i.e., at $r = r_c$) and substituting into (4) to obtain

$$\mu = \mu_0 \exp\left[\left(\frac{\sigma}{kT}\right)^2 - p\left(\frac{\sigma}{kT}\right)^{\frac{2+p}{1+p}} \left(\frac{2eEa}{p\sigma}\right)^{\frac{p}{1+p}}\right]. \tag{15}$$

Naturally, this reduces for $p = 1$ to Eq. (3), recovering the Poole-Frenkel field dependence (1) derived previously [18] and long seen in experiment.

The field dependence of the mobility arises, therefore, from the fact that the size r_c of critical traps is field-dependent. Clearly, however, the characteristic scaling (14) of

the critical trap width with the field cannot persist to lengths smaller than the mean interdopant spacing ϱ. Thus, with increasing field a regime is reached where the mobility crosses over to a field dependence that is activated with the first power of the field, i.e., $\mu \propto \exp(eE\varrho/kT)$. By equating Eq. (14) to the mean intersite spacing ϱ we deduce the following threshold field

$$E_c = \frac{p\sigma^2}{2eakT}\left(\frac{a}{\varrho}\right)^{1+p} \tag{16}$$

associated with such a crossover.

Summary We have argued that the key behind the Poole-Frenkel mobilities in disordered molecular solids lies in spatial correlations associated with the energetic disorder. These correlations lead to sites located close together in space having similar energies. For large disorder, charges can become trapped in naturally forming energetic valleys associated with local regions containing sites of atypically low energy. The field dependence of the mobility comes about, in this picture, from the field-dependent modification of the release time from traps of a critical size determined by a competition between trap depth, trap width, and the degree to which traps of a given width are tilted by the field.

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