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What is Behind the $\sqrt{E}$?

D. H. Dunlap and V. M. Kenkre

Department of Physics and Astronomy and Center for Advanced Studies, University of New Mexico, Albuquerque, New Mexico

P. E. Parris

Department of Physics, University of Missouri-Rolla, Rolla, Missouri

That energetic disorder is the key behind the Poole-Frenkel mobility of photoinjected charges in molecularly doped polymers has always been suspected. In recent years, considerable experimental evidence for the importance of group dipoles has led to the realization that the charge-dipole interaction provides an important contribution to the Gaussian density of states. Here we discuss how the peculiarities of dipolar-disorder, in particular, the manner with which the dipolar disorder is spatially correlated, lead directly to the facts that (i) the mobility in these systems is strongly field-dependent at relatively low fields, (ii) the mobility increases exponentially with $\sqrt{E}$, and (iii) the field-dependence of the mobility is relatively insensitive to the nature of the underlying hopping rates.

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Introduction

The mobility of photoinjected charges in a variety of molecularly-doped, pendant-chain, and main-chain polymers has a field-dependence that, for electric fields E ranging from 10^4 to 10^6 V/cm, is given by the Poole-Frenkel law,[1]

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

where the “Poole-Frenkel factor” γ is found to be a decreasing function of the temperature. Soon after the first observations of this behavior in 1970,[2] the source of the distinctive, ubiquitous, and somewhat unusual field dependence (Eq. 1), was the subject of considerable debate, much of which focused on the role of the pervasive spatial and energetic disorder that was presumed to exist in these systems.[2–12] A brief sense of closure occurred in the late 1970s, when it was found[13] that the Poole-Frenkel mobility could be directly related to the highly-dispersive current-time transients observed during that period, through a single disorder parameter α as described in the Scher-Montroll theory of dispersive transport.[14] This temporary sense of closure was soon lost, however, largely as a result of improvements in materials technology that avoided the unintentional introduction into the polymer of various kinds of electron and hole traps. Indeed, in a seminal paper on TPA-doped polycarbonate, Borsenberger, Mey, and Chowdry[15] demonstrated in 1979 current-time curves featuring a distinct plateau, inconsistent with the predictions of Scher-Montroll theory. Because such a plateau is indicative of a steady drift of the injected charges, it was now felt that time-of-flight (TOF) experiments were measuring the bulk mobility of materials at hand, as opposed to artifacts of the TOF procedure. The observation of nondispersive transport implied that the disorder, while important for determining the mobility, was no longer so extensive as to prevent equilibration of carriers. This also implied, however, that a correct theoretical description of the mobility would require a more complete characterization of disorder. To this end, careful numerical investigations of hopping transport in a disordered matrix were vigorously pursued over the next decade. Particularly important were simulations of hopping on an energetically disordered lattice with a Gaussian density of states (DOS) carried out and characterized by Bässler and coworkers[16–18] in the context of what has come to be referred to as the Gaussian Disorder Model (GDM).

The Gaussian Disorder Model

The distribution of site energies appropriate for numerical simulations of the GDM was originally thought to arise from disorder-induced fluctuations in the electronic polarization energy arising from the interaction of a localized charge carrier with the surrounding medium.[16] In addition to this so-called van der Waals interaction, however, there are other sources of disorder, notable among them being the interaction of carriers with the permanent electric dipole moments of surrounding molecules, especially those of the dopants, which in most instances tend to be highly polar. For dopants that are randomly oriented and randomly packed, this charge-dipole interaction contributes strongly to the energetic

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DOS.[19–25] By way of illustration, consider a hole localized on a single dopant molecule and surrounded by other molecules of the medium, each with dipole moment p, and with positions restricted to lie on the points of a simple cubic lattice with lattice constant a_0. Because the field of an uncompensated charge injected into an insulator is long range, falling off as r^{-2}, the hole interacts with a large number of surrounding dipoles. If the hole is localized at a point $\vec{r}_n$, the electric field experienced by a dipole at $\vec{r}_i$ is

$$\vec{E}_i = \frac{e\left(\vec{r}_i - \vec{r}_n\right)}{4\pi \in \left|\vec{r}_i - \vec{r}_n\right|^3} \tag{2}$$

where the dielectric constant $\in \approx 3\in_0$. To place the hole at location $\vec{r}_n$ requires an energy

$$u_n = -\sum_i \vec{p}_i \cdot \vec{E}_i \tag{3}$$

equal to the sum of the interaction energy of the hole with each dipole $\vec{p}_i$ in the medium. For random orientations $\vec{p}_i$, and locations $\vec{r}_i$, the site energy u_n is the sum of a large number of independent contributions. For sufficiently high dipole concentrations, therefore, the distribution of site-energies tends naturally towards a Gaussian distribution with zero mean and a variance

$$\sigma^2 = \left\langle u_n^2 \right\rangle = 16.53 \times \frac{c}{3}\left(\frac{pe}{4\pi \in a_0^2}\right)^2 \tag{4}$$

that depends on the fraction c of lattice sites occupied by dipoles.[25,26] For a dipole moment of magnitude $p = 1.5$D, filling fraction $c = 1$, and lattice constant $a_0 = 8$Å, the width (Eq. 4) of the DOS is substantial, with $\sigma = 60$meV.

The rate with which a charge hops from one dopant molecule to the next, the key ingredient in the GDM, must satisfy certain requirements suggested by first principles considerations. One expects that the tunneling process from dopant n to dopant m should be described by a rate

$$R_{n,m} \propto \exp\,(-2\alpha r) \tag{5}$$

that exponentially decays with the dopant separation r. The principle of detailed balance requires that the ratio

$$\frac{R_{n,m}}{R_{m,n}} = \exp\left[-\frac{\left(u_n - u_m - eEr\cos\theta\right)}{kT}\right] \tag{6}$$

of forward and backward rates between two sites m and n equals a Boltzmann factor that depends on the site energy difference $u_n - u_m$, altered in the presence of an electric field by an amount $eEr \cos \theta$, where θ is the angle between the hopping direction and the field direction. For the purpose of the present discussion, consider the rate between two sites which differ in energy by an amount Δ, and denote by R_+ the rate for hops up in energy, and by R_- the rate for hops down in energy. Equation 6 implies

$$R_{\pm} \propto \exp\left[-\frac{\Delta}{2kT}(\eta \pm 1)\right] \tag{7}$$

where η, a factor that depends on the peculiarities of the electron-phonon coupling, determines the specific thermal behavior of the hopping rate. Small-polaron hopping rates have $\eta = 0$, and are referred to as having "symmetric" detailed balance. For Miller and Abraham hopping rates $\eta = 1$, and the detailed balance is said to be "asymmetric".

In typical transport simulations of the type performed over the last decade,[18] dopants are set up on the sites of a simple cubic lattice. Each site location $\vec{m}$ is assigned an initial energy $-eEam_z$ to account for an electric field in the z-direction, where m_z is its site-index in that direction. To this is added an energy $u_{\vec{m}}$ chosen, in the GDM, at random from a Gaussian distribution of width σ. Simulations are able to reproduce features of the TOF transients, showing cross-overs from non-dispersive to dispersive transport as a function of temperature similar to those seen in experiment.[27] For much of the field range probed in experiments, however, simulations on the GDM show better agreement with a linear ($\log \mu \propto E$) rather than a square root ($\log \mu \propto \sqrt{E}$) dependence of the mobility on field. While simulations do appear to show some agreement with $\sqrt{E}$ when (asymmetric) Miller and Abrahams rates[17] are employed, this agreement comes at fields too high for most experiments. It has also been argued recently that what agreement occurs at high fields arises not because of the disorder, but because hopping rates of this type exhibit a saturation in this region, as a result of their asymmetric nature.[28]

Nevertheless, this limited agreement was taken as further evidence that energetic disorder is indeed the key behind the universal features in these systems. Simulation results were extensively tabulated in the "agreement regime", and many experiments were accordingly catalogued in order to draw conclusions concerning the underlying physical processes. This procedure of analyzing the mobility in terms of simulation data parameterized from the GDM was refined to a remarkable extent by the exhaustive and careful efforts of Borsenberger, Bässler, and coworkers, and is referred to in the literature as the "disorder formalism".[12] This disorder formalism provided a natural framework for discussing mechanisms of disorder and led to the identification of what is now considered by many to be the true source of the Poole-Frenkel mobility.

Indeed, perhaps the most important conclusion to come from this characterization concerned the role of dipole moments. In the 1990's, extensive analysis of materials based upon the disorder formalism showed a strong positive correlation between the inferred width of the DOS and the magnitude of group dipole moments of the molecular constituents.[21,26,29–34] In addition, the fact that only the asymmetric hopping rate gave partial agreement with the $\sqrt{E}$ field dependence was taken by some as evidence that injected charges in disordered organic solids do not form polarons. Although this implication was vigorously questioned by Schein and coworkers, who sought to interpret experimental results in terms of polaron formation,[35–39] the Poole-Frenkel field dependence did not appear explanable on the basis of polaronic arguments,[10] even in the presence of energetic and spatial disorder.[40] Against this backdrop, the theoretical focus began to center on the nature of disorder caused by the charge-dipole interaction, to see if there might be an important ingredient that had been omitted from the GDM which might explain the discrepancy between simulation and experiment.

Disorder Redux: Charge Dipole Interactions

In 1995, Novikov and Vannikov[41,42] calculated the energy correlation function

$$\langle u(r)u(0)\rangle \sim \sigma^2 \frac{a}{r} \tag{8}$$

for two sites separated by a distance r on a simple cubic lattice containing a set of randomly oriented point dipoles. It was found to decay algebraically with distance, asymptotically decreasing as r^{-1}, with an empirically determined scaling factor $a = 0.76a_0$ slightly less than a lattice constant.[41] In such a disordered dipolar medium, the energies of nearby hopping sites tend to be very similar; two neighboring sites are both likely to be high energy sites, or low energy sites, but it is very unlikely that one site will be of high energy and the other of low energy. Whereas in the GDM a charged particle experiences staccato transitions from high energy to low energy as it hops from dopant to dopant, in contrast, when the disorder is spatially correlated, the particle traverses a relatively smooth landscape of hills and valleys, each consisting of many individual hopping sites.[42] The local spatial correlation among site energies is another consequence of the long-range nature of the charge-dipole interaction. As previously mentioned, this range is such that a large number of distant dipoles contribute to the energy of any single site. The majority of these dipoles are so far off as to appear the same when "viewed" from neighboring molecules, making the energy of neighboring molecules very similar. The significance of correlations to transport, particularly as a means of understanding the Poole-Frenkel mobilities, was recognized by Garstein and Conwell.[43] They incorporated spatial correlations in the GDM and showed that the resulting field-enhancement of the mobility begins at a lower value of the field, and closely resembles $\sqrt{E}$.

With these important insights and the background of the GDM as inputs, an analytic result was obtained by the present authors[44] on the basis of a nonlinear response formalism[45] where the motion of charges is restricted to a one-dimensional path along the direction of the field. It was shown that Poole-Frenkel behavior is an exact consequence of spatially correlated energetic disorder, with a correlation function given by Eq. 8 for the charge-dipole interaction. Moreover, quantitative comparison with experiment showed the magnitude of the Poole-Frenkel factor, and its dependence on temperature, to be in reasonable agreement with those found in experiment. Further studies were subsequently carried out by Novikov, Vannikov, and the present authors[28] to investigate the consequences of having an unrestricted (three dimensional) transport path. These involved simulations on a 50 × 50 × 50 filled lattice for which the site-energies were calculated according to Eq. 3. The results showed some important differences from the GDM employed earlier.[18] The primary results of the new correlated disorder model (CDM) are twofold: (i) the mobility is described by the empirical relation

$$\mu = \mu_0 \exp\left[-A_1\left(\frac{\sigma}{kT}\right)^2 + A_2\left(\left(\frac{\sigma}{kT}\right)^{3/2} - A_3\right)\sqrt{\frac{eEa_0}{\sigma}}\right], \tag{9}$$

where the parameters $A_1 = 0.35$, $A_2 = 0.78$, and $A_3 = 1.97$, and (ii) the Poole-Frenkel behavior is insensitive to the nature of the underlying hopping rate. Indeed, the only parameter in Eq. 9 that depends on the choice of detailed balance is the overall scale factor μ_0.

The empirical characterization (Eq. 9), and the analytical results for one-dimensional transport,[44] therefore, both support the idea that correlated disorder is a necessary ingredient for obtaining field-dependent mobilities of the Poole-Frenkel type. Unfortunately, analytical details of the 1D calculation and the numerical work represented in Eq. 9 provide little physical insight into just how correlations of the type that arise in dipolar materials can give rise to a field dependence of the form observed in so many materials. In what follows, we attempt to provide a physically motivated explanation for the source of the Poole-Frenkel law which gives an easily understandable picture of the mechanisms that give rise to the $\sqrt{E}$ mobility.

Physical Explanation of the Field Dependence

When the energetic disorder in a charge transport material is very large, there will be a small fraction of molecules in the system which act as traps, in the sense that the average time a charge resides on these sites is so large that the process of escaping from them is the rate-limiting step for transport. Under these circumstances the mobility

$$\mu \sim \frac{\langle \rho_z \rangle}{E\langle \tau \rangle} \tag{10}$$

depends on the ratio of the mean distance $<p_z>$ between traps sites visited (in the direction of the field) to the average dwell (or escape) time $<\tau>$ for those traps that most limit transport. When the disorder is uncorrelated, a trap typically consists of a single site with an extraordinarily low energy. When the disorder is correlated, on the other hand, a low energy site will have a tendency to be surrounded by neighboring sites of similar energies, so that what constitutes a trap is actually a group of sites at the bottom of a deep energetic bowl or valley. To escape from such a valley, a particle must migrate some distance, hopping over those sites which connect the valley floor to the rim, or saddle point.

In either case, the field-dependence of the mobility arises from that of the average escape time from rate limiting traps. Escape from such a trap is a thermally activated process, with an activation energy equal to the energy difference between the bottom of the trap and the rim. In the presence of a field, the trap is tilted, and the activation energy is reduced. Assuming that particles escape the trap in the direction of the field, the activation energy is lowered by the amount eEr, where r is the distance between the bottom and the rim of the trap, and the associated escape time is reduced by a factor of exp $(-eEr/kT)$. From Eq. 10, it follows that the essential field dependence of the mobility

$$\mu \propto \frac{1}{\langle \tau \rangle} \propto \exp(eEr_c / kT) \tag{11}$$

arises from the field-induced decrease in the escape time associated with the most rate limiting traps. In Eq. 11, the length r_c represents the characteristic width of those "critical traps" that most limit transport through the material. In a system with uncorrelated disorder the critical traps are simply isolated sites with deep energies and the characteristic width $r_c = \rho$ associated with such a trap is just the mean interdopant spacing. Because this is independent of the field, the mobility $\mu \propto \exp eE\rho/kT$ for a system with uncorrelated disorder depends in the activated regime exponentially on the first power of the field. In the case of dipolar disorder, the width of critical traps arises from a relatively subtle competition between trap depth, trap width, and the field induced lowering of the associated potential barrier. As we show below, this leads to a critical trap width $r_c = r_c(E)$ that actually depends on the field, and thus leads, through Eq. 11, to a Poole-Frenkel field dependence.

The source of this unusual behavior lies, ultimately, in the statistical relationship between the depth of energetic fluctuations that occur in dipolar media to the spatial extent with which they are associated. This relationship is often expressed in terms of the mean-square potential energy difference

$$\left\langle \Delta^2(r) \right\rangle = \left\langle [u(r)-u(0)]^2 \right\rangle = 2\left[\left\langle u^2 \right\rangle - \left\langle u(r)u(0) \right\rangle\right] \quad (12)$$

between two sites in a disordered medium separated by a distance r. Substituting the correlation Eq. 8 into Eq. 12, we see that in a disordered dipolar medium the mean-square energy difference

$$\left\langle \Delta^2(r) \right\rangle \sim 2\sigma^2\left(1-\frac{a}{r}\right) \quad (13)$$

between two sites approaches a maximum of $2\sigma^2$, rising monotonically with increasing site separation as r^{-1}. Equation 13 expresses the fact that, statistically, the energy difference between two sites becomes greater the further they are apart, and becomes greatest when, at infinite separation, they are influenced by two completely independent arrangements of surrounding dipoles. On the other hand, this equation also implies that the energy difference between two sites tends to zero as they get closer together, since in this limit any two nearby points are influenced by the same configuration of surrounding dipoles. In a dipolar medium this reduction can occur for sites separated by relatively large distances. Thus, as we have asserted, a site on the floor of an energetic valley is typically surrounded by neighbors of similarly low energy.

Moreover, if we consider $u(0)$ to be the energy at the bottom of a valley, and $u(r)$ to be the energy at the rim, Eq. 13 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. At first sight, one might expect that the broadest (i.e., deepest) valleys always form the most rate-limiting traps. This is not correct, however, because of the already mentioned tilting of the energetic valleys by the field. Indeed, the energy reduction eEr between the valley floor and the rim is clearly greater for wider (and therefore deeper) valleys than it is for narrower ones (see Fig. 1). On the other hand, the most narrow valleys, although they are tilted to a lesser extent, are also very shallow. Thus, in a dipolar medium, the valleys which act as the most effective traps for a given field strength are neither the widest nor the narrowest, but rather those of some intermediate critical dimension $r_c(E)$.

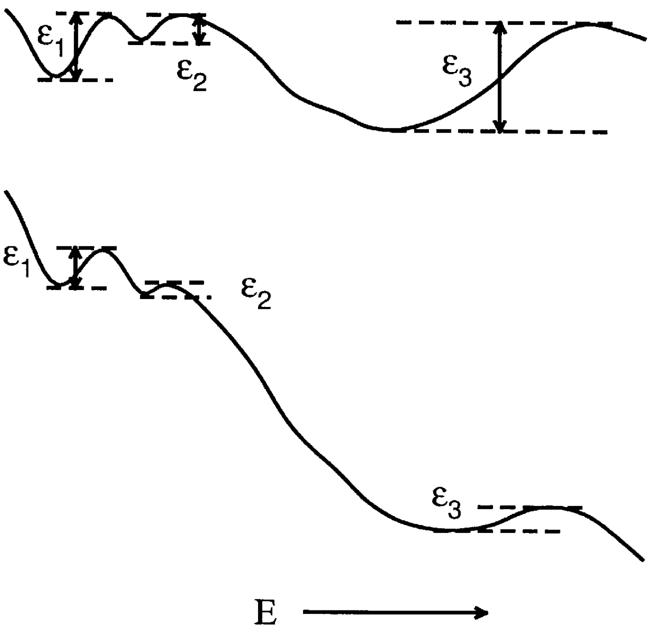

Figure 1. Correlated random potential with and without an applied field. Note that in the absence of a field (top) the deepest potential wells are also the widest. When a field is applied (bottom), wider potential wells are tilted more, and hence experience much greater barrier reduction.

To determine the critical trap width in the case of dipolar disorder we consider the well-known dynamical problem of the diffusional escape of a particle[46] from an energetic valley of width r and depth $\Delta = u(r) - u(0)$. 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, or "dividing surface", to the probability $P(0)$ that the particle is at the bottom of the trap.[47] If the escape rate is sufficiently low (i.e., rate-limiting), the system will have achieved a local equilibrium within the trap region. This ratio can then be written as the detailed balance factor,

$$\frac{P(r)}{P(0)} = \frac{g(r)}{g(0)}\exp\left(-\frac{\Delta(r)-eEr}{kT}\right) \quad (14)$$

where the degeneracy factors $g(r)$ and $g(0)$ give, respectively, the number of hopping sites in the neighborhood of the rim and the trap bottom. Once a particle reaches the rim, there is a characteristic time

$$\tau_D \approx \frac{\delta^2}{D_0} = \frac{\delta^2}{R_0\rho^2}, \quad (15)$$

to diffuse across the dividing surface, which depends on the rim thickness δ and a diffusion constant $D_0 = R_0\rho^2$ associated with hops in the vicinity of the rim, which occur at some characteristic rate R_0. The overall trap escape time from a given energetic valley of width r is then the ratio

$$\tau = \frac{\delta^2}{R_0\rho^2}\frac{g(0)}{g(r)}\exp\left(\frac{\Delta(r)-eEr}{kT}\right) \quad (16)$$

of Eqs. 14 and 15. 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 prefactor in Eq. 16 is weak relative to the exponential factors, so that the average escape time from valleys of width r can be written

$$\langle \tau(r) \rangle = \tau_0 \left\langle \exp\left[\frac{\Delta(r) - eEr}{kT}\right] \right\rangle. \tag{17}$$

For dipolar disorder, the distribution $P(\Delta;r)$ of site-energy differences Δ at a given distance r is approximately Gaussian,

$$P(\Delta; r) = \frac{1}{\sqrt{2\pi \langle \Delta^2(r) \rangle}} \exp\left(-\frac{\Delta^2}{2\langle \Delta^2(r) \rangle}\right), \tag{18}$$

with zero mean, and variance $<\Delta^2(r)>$ given by Eq. 13. Using this to perform the average over the energy barriers Δ leaves, for traps of width r, the mean escape time

$$\begin{aligned} \langle \tau(r) \rangle &= \tau_0 \exp\left[-\frac{eEr}{kT} + \frac{\langle \Delta^2(r) \rangle}{2(kT)^2}\right] \\ &= \tau_0 \exp\left[-\frac{eEr}{kT} + \left(\frac{\sigma}{kT}\right)^2 \left(1 - \frac{a}{r}\right)\right] \end{aligned} \tag{19}$$

The critical traps are those for which the escape time is the longest. Indeed, because of the exponential factors in this last expression, the escape time is strongly peaked at a width r for which the exponentiated quantity is a maximum. This occurs at that radius r for which

$$\frac{d}{dr}\left[-\frac{eEr}{kT} + \left(\frac{\sigma}{kT}\right)^2 \left(1 - \frac{a}{r}\right)\right] = 0. \tag{20}$$

The solution to Eq. 20 gives the critical trap width

$$r_c = a\sqrt{\frac{\sigma^2}{eEakT}}. \tag{21}$$

It is traps of this critical width that, for large enough disorder, are the most important in determining the mobility at a given field strength. Note that at very low fields it is the widest traps that become important ($r_c \to \infty$ as $E \to 0$), consistent with the idea that these constitute the deepest traps in the system. As the field increases, however, the widest traps are tilted over very strongly by the field. This reduces their release times dramatically. The rate limiting step is then determined by traps of finite width. Thus, the critical trap width decreases monotonically as $E^{-1/2}$. Indeed, it is precisely this dependence of the critical trap width on field that is the real source of the Poole-Frenkel law. To quantify this last point, we evaluate the mean escape time (Eq. 19) for traps of critical width (i.e., at $r = r_c$) to obtain

$$\langle \tau \rangle = \tau_0 \exp\left[\left(\frac{\sigma}{kT}\right)^2 - 2\left(\frac{\sigma}{kT}\right)^{3/2} \sqrt{\frac{eEa}{\sigma}}\right]. \tag{22}$$

A final substitution of Eq. 22 into Eq. 10 then gives the familiar Poole-Frenkel mobility

$$\mu = \mu_0 \exp\left[-\left(\frac{\sigma}{kT}\right)^2 + \gamma\sqrt{E}\right], \tag{23}$$

with a Poole-Frenkel factor

$$\gamma = \sqrt{\frac{4\sigma^2 ea}{(kT)^3}}. \tag{24}$$

and a prefactor mobility $\mu_0 = <\rho_z>/\tau_0 E$.

Symmetric versus Asymmetric Rates

The crux of the explanation for a $\sqrt{E}$-dependent mobility comes, therefore, from the fact that the size r_c of critical traps is field-dependent. Indeed, from Eq. 21, we see that the amount by which the floor-to-rim energy difference is reduced by the tilting of the field,

$$\Delta u = eEr_c = \sigma\sqrt{\frac{eEa}{kT}}, \tag{25}$$

is proportional to $\sqrt{E}$ (as it was in the original argument for the Poole-Frenkel law,[1] wherein it arises from the field-induced lowering of the barrier associated with a particle escaping from a Coulomb trap.) With this basic picture, we can also understand why it is that recent simulations using dipolar disorder have shown that the Poole-Frenkel mobility is independent of whether the underlying hopping rates are of the symmetric or asymmetric type.[28] This independence of the way in which detailed balance is implemented arises because the time to escape from broad valleys depends on the probability of finding a charge at the rim, relative to that of finding it at the valley floor. Because the system relaxes to a quasi-equilibrium in each trap, this relative probability is given by a Boltzmann factor. Under these conditions, relaxation to such a state of local thermal equilibrium is assured as long as the hopping rates are related to one another through detailed balance, but is independent of the particular way that detailed balance is implemented.

On the other hand, the trap escape time is also proportional to the time for a particle to diffuse across the rim, which in turn depends on the properties of the individual hopping rates, and therefore, potentially, on the form of detailed balance. This turns out to be unimportant, however, because the Boltzmann factors for the hopping rates between neighboring dopants depend exponentially on the ratio $eE\rho/\mathrm{kT}$, whereas the Boltzmann factor connecting the floor of a valley to its rim depends exponentially on the factor eEr_c/kT. As long as E is sufficiently low, so that $r_c >> \rho$, the field dependence of the latter will dominate the field dependence of the former. Following this line of argument a bit further, we should expect, in fact, that as the field strength increases there will be a cross-over to a regime where the symmetry of the hopping rates does actually matter. Such a cross-over would occur when the critical trap width r_c becomes of the order of the interdopant spacing ρ. From Eq. 21 we deduce the following threshold field

$$E_t = \frac{\sigma^2}{kT}\frac{a}{e\rho^2} \tag{26}$$

associated with such a crossover. For typical values σ = 0.1 eV, T = 300K, and $\rho = a$ = 10Å, the field strength above which the symmetry of the hopping rates is revealed is roughly $E_t = 3 \times 10^6$V/cm, considerably higher than the field strengths probed in most experiments.

Of course, because it is exp (eEr_c/kT) that gives the Poole-Frenkel mobility, there is no compelling reason to expect perfect agreement with the Poole-Frenkel law once factors on the order of exp $(eE\rho/kT)$ become important. Indeed, the characteristic scaling (Eq. 21) of the critical trap width with the field obviously cannot persist over lengths smaller than the mean interdopant spacing. Thus, the threshold field E_t can also be interpreted as the field above which the mobility departs from a $\sqrt{E}$ dependence. That the threshold field is, for reasonable parameters, above the field strengths probed in most experiments, accounts for the well-known robustness of the Poole-Frenkel law. On the other hand, the form of Eq. 26 shows that the onset of deviations from Poole-Frenkel behavior would be expected to occur sooner in more diluted systems, where ρ is larger. It is interesting to note that such deviations have been observed in molecularly-doped polymers with very low concentrations.[48] Finally, we note that, insofar as the preceding analysis presumes a significant component of dipolar disorder, a robust Poole-Frenkel field dependence would not necessarily be expected among systems with very little dipolar disorder. Thus, even for systems with a small σ, the threshold field E_t could fall in the experimental range.

Summary

In this article we have argued that, as originally believed by many workers, energetic disorder is the key behind the Poole-Frenkel mobilities in disordered molecular solids. However, a clear picture of the particular mechanism by which this field dependence arises from energetic disorder has emerged only recently. As we have attempted to elucidate here, the field dependent mobility of these materials has its source in the interaction between injected charges and polar molecules in the medium, which gives rise to a spatially-correlated distribution of site energies. These correlations are such that sites located close together in space tend to have very similar energies. For large enough disorder, charges become trapped in naturally forming energetic valleys associated with local regions containing sites all of which have an atypically low energy. The $\sqrt{E}$-dependence of the mobility comes about, in this picture, from the field-dependent modification of the release time from traps of a critical size, a critical size which itself comes about as a competition between trap depth (and thus width) and the degree to which traps of a given width are tilted by the field. This basic picture has been verified directly from an exact calculation in which transport is modeled as a random walk along a one-dimensional path through a medium containing randomly-placed and randomly-oriented point dipoles,[44] and has been empirically supported by extensive numerical simulations of hopping transport in three dimensional dipolar media.[28]

Nonetheless, there remain further details that have yet to be understood. For example, Gill's compensation temperature T_0 (or the off-diagonal disorder parameter Σ of the disorder formalism), which characterizes the fact that there is, in some systems, a temperature at which the Poole-Frenkel factor vanishes, does not arise in a natural manner from the calculations of Section IV. Nor does the fact that in molecularly-doped polymers the compensation temperature is generally observed to decrease as the mean dopant spacing increases.[49,50] Conventional wisdom is that the Poole-Frenkel factor γ develops a more subtle temperature dependence as a result of spatial disorder, an effect which has not been considered in the simple picture developed above. According to Eq. 23, the extrapolated-zero-field mobility should show a temperature-dependent activation energy $E_A \sim \sigma^2/kT$ which decreases with increasing temperature. Also, because the squared width σ^2 of the DOS is proportional to the dipole moment, one expects to find a larger activation energy E_A with dopants having higher dipole moments. Both of these tendencies are, in fact, observed.[12,51–54] Because σ^2 is also proportional to the concentration of dipoles, one would expect E_A to decrease as the concentration of polar dopants is reduced. Except in a few cases,[55] however, the activation energy is found to either increase or remain constant with decreasing dopant concentration.[12,49,56] Finally, there exist systems in which a robust $\sqrt{E}$ field dependence is observed even though permanent group dipole moments of the molecular constituents are vanishingly small.[11,57] It is clear from the above description that what is required to obtain a Poole-Frenkel field dependence is a component of disorder that has long-range correlations, falling off with distance as the first power of the intersite separation. In principle, any disorder mechanism that can produce such correlations will also generate a field dependent mobility of this type. Do Poole-Frenkel type mobilities in non-polar materials provide evidence of such a nonpolar mechanism, or do they suggest the possibility of polar contaminants that have not been identified? It is interesting to note on simple electrostatic grounds that a dipolar field is the longest range interaction that charge carriers can have with any neutral chemical or topological defect.

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