Small Polaron Hopping in the Inverted Regime and the Compensation Temperature

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Abstract

It has been recently shown that the Poole-Frenkel field dependence of the mobility of injected charges in molecuarly doped polymers arises as a natural consequence of the spatially correlated energetic disorder associated with the charge-dipole interaction. Small polaron hopping is compatible with this mechanism for disorder, provided that the polaron binding energy is in a range which is neither too large nor too small; If the binding energy is large, the size of the hopping matrix element which is required to account for the magnitude of the mobility must also be large, and may be unacceptable for an organic solid. If the binding energy is too small, on the other hand, the small polaron rates tend to become "inverted" by the energetic disorder. In this regime there is an increase in the Poole-Frenkel slope with decreasing temperature which may be described by Gill's compensation temperature.

Introduction

From the first time-of-flight mobility measurements on molecularly-doped polymers (MDP's) there has been considerable debate regarding the nature of the charge carriers that are photoinjected into these systems. In particular, there has often been disagreement as to whether the strongly activated field and temperature dependence of the observed mobility is related more to properties associated with the carrier and its interaction with phonons (e.g., the magnitude of the polaron binding energy, the degree and type of polaron formation), to static properties of the material (e.g., the amount and characteristics of energetic and spatial disorder), or to some combination of both. In the disorder formalism of Bässler, Borsenberger, and coworkers, it has been assumed that observed activation energies arise from activated hopping of carriers in an energetically disordered medium possessing a Gaussian density of localized transport states characterized by an energetic width $\sigma \approx 0.1$ eV. Within the context of this Gaussian disorder model (GDM) numerous simulations have been carried out using a specific functional form of the hopping rate in which polaron formation and multiphonon processes are assumed to be minimal (i.e., Miller-Abrahams rates [1]). In much of the work of Schein and coworkers, by contrast, significant effort has gone into explaining the concentration dependence of observed activation energies in terms of the polaron binding energy Δ of the carriers, the electron transfer integral J, and a crossover that has been suggested to occur between adiabatic and nonadiabatic small polarons [2]. Others have attempted to combine these two viewpoints by considering hopping with small polaron-like rates among energetically disparate sites [3, 4].

Until recently, however, quantitative difficulties have hampered the internal consistency of many of the polaron models. For example, in the absence of disorder, to predict mobilities of the right order of magnitude ($mu \sim 10^{-6}-10^{-3}$cm^2/Vs) using a polaron binding energy Δ big enough to give typical activation energies ($E_a = \Delta/2 \sim 0.5$ eV), it is necessary to assume transfer integrals J considerably larger than the bandwidth of an organic crystal [2, 3]. On the other hand, if the polaron binding energy is actually rather small, ostensibly allowing for a reasonable value of J, there would then need to be substantial energetic disorder to get an effective activation energy of the order of 0.5 eV. If the width σ of the energetic disorder needed to make up the difference represents actual energy jumps encountered in typical hops (as it does in the GDM and other models with uncorrelated energetic disorder), then an additional problem arises; the small polaron hopping rate tends to become "inverted". Inversion, in this context, refers to the strong suppression of the jump probability that occurs with small polaron type rates [5]

$$R = \frac{J^2}{\hbar}\sqrt{\frac{\pi}{2\Delta kT}}\, e^{-\Delta/2kT} \exp\left(-\frac{\Omega}{2kT} - \frac{\Omega^2}{8\Delta kT}\right) \tag{1}$$

for hops between sites with large intersite energy difference Ω, and arises as a result of the exponential factor $\exp\left(-\Omega^2/8\Delta\right)$ occurring in those rates which expresses the diminishing probability of having a "coincident event" when $|\Omega|$ is significantly greater than the polaron binding energy.[5] Such a reduction of the hopping rate for energetically disparate jumps makes it again difficult to obtain mobilities of the right order of magnitude without taking an unreasonably large value of J. In numerical work on the GDM such difficulties do not arise; the hopping rate is assumed to be of the Miller-Abrahams, single phonon-assisted type, having asymmetric detailed balance [6]. Indeed, numerical simulations of the Gaussian disorder model using symmetric rates are not consistent with formulae that have been extensively employed in the disorder formalism [4]. For this combination of reasons, it has been assumed by some that photoinjected charge carriers in molecularly-doped polymers are not polarons, but are implicitly associated with bare, disorder-localized electronic states.

In recent years, however, it has been recognized that disorder models with appropriate spatial correlations characterizing the random potential energy landscape[7] can explain most of the features associated with transport in these materials [8, 9, 10]. In particular, recent theoretical work has successfully explained the Poole-Frenkel field dependence, $\mu \propto \exp \gamma\sqrt{E}$, of photoinjected charge carrier drift mobilities commonly observed in these materials on the basis of spatial correlations naturally occurring as a result of the long-range charge-dipole interaction between charge carriers and permanent electric dipoles in the material [9, 10]. Moreover, this picture offers a natural explanation for the relationship that empirically exists between observed activation energies and dipole moments of the molecular constituents in a wide class of molecularly doped polymers, and organic molecular glasses. [11, 12, 13, 14, 15, 16, 17]

In this paper we point out that correlated disorder models (CDM's) of this type also offer the possibility of reconciling difficulties that have traditionally hindered polaron-based explanations of transport in these systems. Such a reconciliation is possible because, as pointed out previously, in correlated disorder models large potential energy fluctuations typically occur only over very large length scales. As a result, energy differences associated with nearest neighbor hops are typically much smaller than would be expected based upon the full width of the energetic disorder. Indeed, the activation energies that emerge in such models are the net result of many hops over spatially extended energetic hills and valleys [18]. Using an analytical extension of the approach developed in Refs. [9] and [19] (the details of which will be presented more fully in a subsequent paper), we show that the field and temperature dependence of the mobility in molecularly doped polymers is generally consistent with small polaron motion in a random energy landscape having correlations of the appropriate type. Through numerical studies based upon our theoretical expressions we are able to establish upper and lower bounds on the magnitude of polaron binding energies consistent with typical experimental data. Within the context of a 1D analysis of the underlying transport, we find that acceptable Poole-Frenkel-type behavior can be achieved with polaron binding energies in the range $\Delta = 0.1 - 0.5$ eV, and corresponding electron transfer integrals in the range $J = 0.01 - 0.1$ eV.

Approach

A formal extension of the theory presented in Refs. [9] and [19] makes it applicable to a rather general form of the hopping rate, including, as a special case, hopping rates of the type (1) that arise in the theory of molecular polarons. As in our earlier paper, the starting point of the analysis is an exact expression for the drift velocity [9, 20]

$$v = \frac{\rho}{\sum_{n=1}^{\infty} e^{-\beta(n-1)eE\rho} \left\langle {}^{\beta(u_n - u_1)} R_{n,n+1}^{-1} \right\rangle} \qquad (2)$$

for a particle moving along a one-dimensional transport path of sites separated by mean intersite spacing ρ through a 3-dimensional energetically disordered medium. In this expression $\beta^{-1} = kT$ is the mean thermal energy, $eE\rho$ is the potential energy drop induced by the field between neighboring sites, u_n is the site energy of the nth site along the path, and $R_{n,n+1}$ is the hopping rate connecting the n th site to its neighbor. The ensemble average in (2) was calculated in Ref. [9] by assuming a simple exponential dependence of the hopping rate $R_{n,n+1}$ on the energy difference $\Omega n = u_{n+1} - u_n - eE\rho$. In the present circumstance we take advantage of the fact that the hopping rate between two sites typically arises from a microscopic calculation as the Fourier transform of a memory function [21]. Thus, if the electron-phonon interaction is translationally invariant, the rate may be expressed in the general form

$$R_{n,n+1} = e^{-\beta\Omega_n/2} \tilde{W}\left(\Omega_n\right) = e^{-\beta\Omega_n/2} \int\limits_{-\infty}^{\infty} dt \; e^{i\Omega_n t} W\left(t\right) \qquad (3)$$

where the memory function $W\left(t\right)$ and its Fourier transform $\tilde{W}\left(\Omega\right)$ contain all model specific information about the electron phonon coupling. Following Ref. [22], we take advantage of this structure and formally introduce a function

$$\tilde{f}(\Omega) = \frac{1}{\tilde{W}(\Omega)} = \int_{-\infty}^{\infty} d\tau \; f(\tau) e^{i\tau\Omega} \qquad (4)$$

in terms of which the drift velocity can be written

$$v = \frac{\rho e^{\beta eE\rho/2}}{\sum_{n=1}^{\infty} e^{-\beta(n-1)eE\rho} \int_{-\infty}^{\infty} d\tau \; f(\tau) e^{-i\tau eE\rho} C_n} \qquad (5)$$

where

$$C_n = \left\langle e^{-(i\tau - \beta/2)u_n} e^{(i\tau + \beta/2)u_{n+1}} e^{-\beta u_1/2} \right\rangle. \qquad (6)$$

For concentration, temperature, and field ranges of interest, the site energy distributions of the dipolar disorder model[7] are well approximated by a Gaussian[23], and the ensemble average of the product of exponentials in the denominator is straightforward to compute using the techniques of Refs. [9] and [19]. The essential result is that

$$C_n = e^{\beta^2\sigma^2 a_n} e^{i\beta\sigma^2 b_n \tau} e^{-\sigma^2 \frac{(\rho-a)}{\rho}\tau^2} \tag{7}$$

where $\sigma^2 = \langle u_n^2 \rangle$ is the variance of the energetic distribution associated with the dipolar disorder, and the quantities a_n, b_n, and c_n are defined through the relations

$$a_n = \frac{1}{4}\frac{\delta_{n,1}(\rho - a)}{\rho} \tag{8}$$

$$+\frac{1}{4}(1-\delta_{n,1})\left(\frac{3\rho+1}{\rho} - \frac{2a}{\rho n(n-1)}\right) \tag{9}$$

$$b_n = \frac{\delta_{n,1}(\rho-a)}{\rho} + \frac{(1-\delta_{n,1})a}{n\rho} \tag{10}$$

in which a, representing a minimal molecular radius, is typically about one-half the mean intersite spacing, a relationship that we assume in what follows.

For the small polaron rate (1), we have, through Eqs. (3 and (4), the specific result that

$$f(\tau) = \sqrt{\frac{\Delta kT}{2\pi^2 J^4 \eta}} \exp\left(-\tau^2/4\eta\right) \tag{11}$$

where $\eta = -8\Delta kT$. Because η is negative in this instance, we perform the integral resulting from the substitution of (11) and (7) into the denominator of (5) by formally treating η as a complex variable and analytically continuing the result to the value of η appropriate for the small polaron rate. After dividing by the field, the final result of the calculation is the following exact expression for the small polaron mobility

$$\mu = \frac{J^2\rho}{\hbar E\Delta}\sqrt{\frac{\pi}{8}\beta\left(4\Delta - \beta\sigma^2\right)} \tag{12}$$

$$\times \frac{e^{\beta eE\rho/2} e^{-\beta\Delta/2}}{\sum_{n=1}^{\infty} e^{-\beta eE\rho(n-1)} e^{\beta^2\sigma^2 a_n} \exp\left[2\frac{(\beta^2\sigma^2 b_n - \beta E\rho)^2}{4\beta\Delta - \beta^2\sigma^2}\right]}.$$

Equation (12) allows, through a numerical evaluation of the sum in the denominator, calculation of the mobility for small polaron hopping rates as an explicit function of the transfer integral J, the polaron binding energy Δ, the width σ of the energetic disorder, and the temperature $T = 1/k\beta$.

Results and Discussion

In Fig. 1 we present calculations of the field dependent mobility using Eq. (12) for a specific set of microscopic parameters, demonstrating that hopping rates of the small polaron type are indeed consistent with a strongly activated Poole-Frenkel mobility of the right magnitude over the range of temperatures $T = 230 - 330$ K and fields $E = 2.5 \times 10^3 - 1.5 \times 10^6$ V/cm typically probed in experiment. The filled data points in these figures were produced using (12) with polaron parameters $J = 10$ meV and $\Delta = 0.15$eV that are reasonable for molecular solids. In addition we have assumed a mean intersite spacing $\rho = 10$ Å, a molecular radius $a = 5$ Å, and have included correlated energetic disorder characterized by a width parameter $\sigma = 80$ meV. For the data points shown, numerical convergence of the sum in the denominator of (12) occurs within about 10^3 terms of the series. The straight lines accompanying the numerical data are the results of linear least-square fits performed in the restricted range $\sqrt{E} = 300 - 900$ (V/cm)$^{1/2}$.

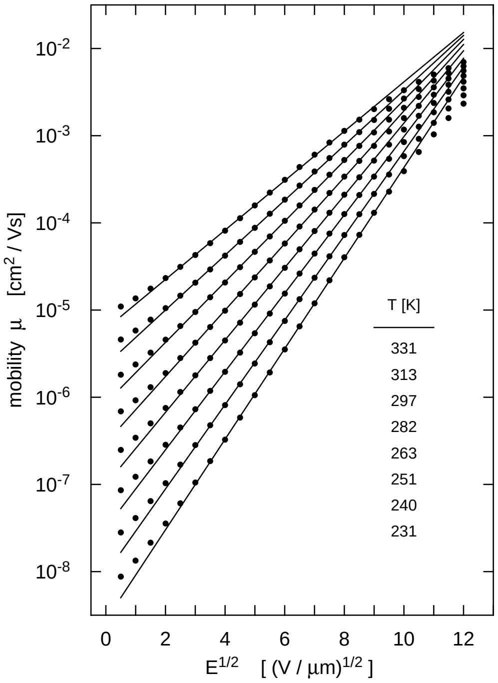

Figure 1: Field dependent mobility for the model described in the text, parametric in temperature, as indicated.

In addition to the data presented in Fig. 1, we have performed a more extensive investigation of the mobility over a wide range of polaron and disorder parameters. For the same values of σ, a, and ρ, and polaron binding energies in the range $\Delta = 0.1 - 0.5$ eV, the agreement with the Poole-Frenkel law remains undiminished. For Δ smaller than 0.1 eV, we begin to see significant deviations from

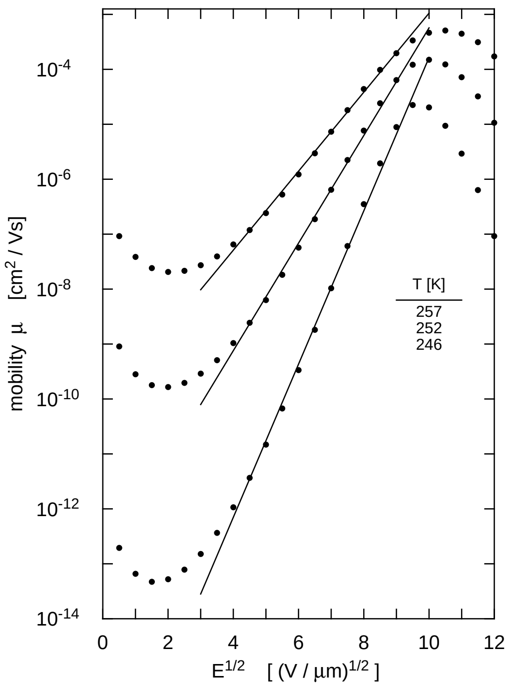

Figure 2: *Mobility for $\Delta = 0.08$ eV, at temperatures just above threshold. The initial decay with field is followed by an increase spanning many orders of magnitude.*

the Poole-Frenkel law which arise when a large enough fraction of the hopping rates becomes extremely slow in the “inverted” regime. These deviations are naturally exaggerated in our one dimensional calculation, where it is impossible to avoid a slow hop, to the extent that a steady state mobility does not exist for $4\Delta \leq \beta\sigma^2$. Such a transition to an anomalous transport regime is well-known in this context [20], and has been discussed previously[22]. In Fig. 2 we show the mobility versus field for $\Delta = 0.08$ eV, for temperatures $T = 257$, 252, and 246K which are just above the transition threshold. At low fields the mobility drops with increasing field. This is expected since for downhill hops the field increases the degree of energy mismatch between sites, and pushes some fraction of hopping rates further into the inverted regime. The subsequent increase in the mobility at higher fields shows an enhanced Poole-Frenkel dependence, but in a narrower range of field. The sensitivity of the Poole-Frenkel factor to temperature is indicative of the effect of the compensation temperature proposed by Gill[24]. A more complete analysis of this transition, along with a more comprehensive discussion of other aspects of the present model will appear in a subsequent publication.

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Biography

David Dunlap is an associate professor of physics at the University of New Mexico. His work has focused on transport phenomena in the solid state such as Anderson localization, Bloch Oscillations, polaron formation, and hopping transport with spatial and energetic disorder in molecular solids.

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