Nature of Charge Carriers in Disordered Molecular Solids: Are Polarons Compatible with Observations?

P.E. Parris
Department of Physics, University of Missouri-Rolla, Rolla, Missouri 65409

V.M. Kenkre and D.H. Dunlap
Center for Advanced Studies and Department of Physics and Astronomy, University of New Mexico, Albuquerque, New Mexico 87131

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Polaronic theories for charge transport in disordered organic solids, particularly molecularly doped polymers, have been plagued by issues of internal consistency related to the magnitude of physical parameters. We present a natural resolution of the problem by showing that, in the presence of correlated disorder, polaronic carriers with binding energies $\Delta \sim 50-500$ meV and transfer integrals $J \sim 1-20$ meV are completely consistent with the magnitudes of field and temperature dependent mobilities observed.

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Considerable debate continues regarding the nature of charge carriers in molecularly doped polymers [1–4] (MDP's) and other organic solids of current technological interest [5–8]. Experiments clearly show strong thermal activation of the field dependent mobility μ, that could arise equally well from a carrier's interaction with phonons (polaron binding), or from static properties of the material (energetic and spatial disorder). The latter was the primary motivation underlying the Gaussian disorder model (GDM) of Bässler *et al.,* in which activated mobilities arise from carriers hopping through a Gaussian density of transport states of energetic width $\sigma \sim 0.1$ eV, via Miller-Abrahams hopping rates [1]. Multiphonon processes typical of polaron transport are absent in such a model. Schein and co-workers, by contrast, suggested that carriers are polaronic and that crucial to the understanding of experiments was an adiabatic to nonadiabatic small polaron crossover [2]. Others combined these viewpoints with carriers assumed to be polarons moving in a disordered medium [3,4].

Whether charge carriers are polaronic or bare is also of obvious importance to ordered organics (crystals), where careful quantitative analysis [5] for naphthalene [6] has shown that the assumption of bare carriers leads to inconsistencies that are avoided when strong carrier interactions with phonons, particularly librations, are included. Such an analysis leads to the conclusion that carriers in napthalene are polaronic in all crystallographic directions [5]. Very recent work in other ultrapure organic solids has provided strong additional experimental evidence for the necessity of polaronic concepts in the explanation of charge carrier motion in organic materials [7].

In MDP's internal consistency seems to point in the opposite direction: *polaron*-based models appear to require unacceptable values of polaron binding energies or transfer integrals in these materials. It has been shown, e.g., by Schein and others [2,3], that to explain observed mobilities ($\mu \sim 10^{-6}$–10^{-3} cm^2/V s) using polaron binding energies Δ big enough to account for measured activation energies $E_a = \Delta/2 \sim 0.5$ eV, it is necessary to take nearest-neighbor transfer integrals $J \sim 1$ eV, if energetic disorder is assumed absent. Such values are unacceptable since they are even larger than the bandwidths for organic *crystals* [9]. Problems of interpretation also arise if energetic disorder is assumed to be the source of observed activation energies. Then, with hops requiring a typical energy jump $\Omega \sim 0.1$ eV, nonadiabatic small polaron hopping rates [10]

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

become strongly suppressed by an "inversion" factor $\exp(-\Omega^2/8\Delta kT)$ which reflects the difficulty of coincident events [10] when $|\Omega| \gg \Delta$. This suppression of the hopping rate again makes it difficult to explain the mobility without assuming an unreasonably large J. As emphasized almost a decade ago by two of the present authors [2,3], one is thus confronted by an unpleasant paradox: If carriers in ordered systems (crystals such as naphthalene) are polaronic in keeping with common expectations, they could hardly be expected to become bare in disordered systems. If they are polaronic in disordered systems, they could hardly be expected to have huge bare transfer integrals J uncharacteristic of organic solids.

The purpose of this Letter is to show that this apparent paradox has a natural resolution in light of the recent experimental and theoretical characterization of the correlated, dipolar nature of the disorder through which carriers move in MDP's. It has been established, e.g., that the interaction between carriers residing on dopant molecules and molecular electric dipoles of the (electronically inactive) medium gives rise to a random potential energy landscape [11] with long range (i.e., algebraic) spatial correlations $\langle U(0)U(r)\rangle \sim \sigma^2 a/r$, where σ is the width of the energetic distribution arising from this mechanism, and $a \sim \rho/2$ a minimal molecular radius. The lack of an intrinsic length scale associated with such correlations has been recognized [12–15] as the key ingredient needed to explain the Poole-Frenkel (PF) field dependence $\mu \sim \exp(\sqrt{\gamma E})$ of charge carrier mobilities in these materials [12–15]. As we have previously discussed in detail [15], with r^{-1} energetic correlations, the spatial width of large site energy fluctuations scales algebraically with their depth. Rate-limiting activation energies arise not from individual hopping events, but from the escape from energetic valleys comprising many sites. It is the hierarchical flattening of these larger scale energetic structures that is responsible for the PF behavior. We show here using the techniques of Refs. [13] and [14] that mobilities of MDP's are entirely compatible with small polaron motion in a random energy landscape provided it has the algebraic spatial correlations of the charge-dipole type. First, we derive analytic results for 1D polaron motion through a 3D dipolar medium. We then present a series of numerical calculations for a fully 3D system. Numerical calculations confirm essential features of the 1D analysis, and more importantly, allow realistic bounds to be placed on polaron binding energies compatible with experimental observations and known properties of organic solids.

Following Ref. [13], we begin with an exact relation [13,16]

$$\mu = \frac{\rho/E}{\sum_{n=1}^{\infty} e^{-\beta(n-1)eE\rho} C_n}, \qquad C_n = \langle e^{\beta(u_n-u_1)} R_{n,n+1}^{-1} \rangle, \tag{2}$$

for the mobility of a particle moving along a 1D nearest-neighbor transport path among dopant molecules separated by mean intersite spacing ρ through a 3D disordered dipolar medium. In (2), $eE\rho$ is the energy drop induced by the field E between neighboring sites, u_n is the energy of the nth site, $R_{n,m}$ is the rate from site m to n, and $\beta^{-1} = kT$. In contrast to earlier calculations [13] which assumed $R_{n,n+1}$ to have a simple exponential dependence on the energy difference $\Omega_n = u_{n+1} - u_n - eE\rho$, we use here a more realistic hopping rate expression [10,17,18] allowing for multiphonon (polaron) processes.

Two specific features allow us to proceed. The first is the well-known Fourier transform expression [19] which naturally arises for hopping rates derived from linear response theory:

$$R_{n,n+1} = e^{-\beta\Omega_n/2}\tilde{W}(\Omega_n), \tag{3}$$

where $\tilde{W}(\Omega_n) = \int_{-\infty}^{\infty} W(\tau) e^{i\tau\Omega_n}$ contains model-specific information about electron-phonon coupling. Since the electron-phonon interactions are associated with short-range distortions of the lattice, while energetic disorder in a dipolar material arises from the long-range interaction between charge carriers and random dipoles in the medium, we make the natural (and simplifying) assumption that electron-phonon interactions are uncorrelated with the energetic disorder. The second ingredient is a prescription [20] for writing the integral of a correlation function such as $W(\tau)e^{i\tau\Omega_n}$ as the reciprocal of the integral of *another* correlation function. Of relevance to the general theory of the calculation of transport coefficients [20,21], this prescription is used here in the simplified form $1/\tilde{W}(\Omega_n) = \int_{-\infty}^{\infty} f(\tau) e^{i\tau\Omega_n}$ employed in Ref. [22]. This allows us to express C_n in (2) as

$$C_n = \int_{-\infty}^{\infty} d\tau\, f(\tau) e^{-i\tau eE\rho} \left\langle \frac{e^{(i\tau+\beta/2)u_{n+1}} e^{-\beta u_1}}{e^{(i\tau-\beta/2)u_n}} \right\rangle. \tag{4}$$

With a correlated Gaussian energy landscape having the dipolar correlations [11] $\langle U(0)U(r)\rangle \sim \sigma^2 a/r$ relevant to the materials at hand, the three-point correlation function in (4) can be computed using the techniques of Refs. [13]:

$$\left\langle \frac{e^{(i\tau+\beta/2)u_{n+1}} e^{-\beta u_1}}{e^{(i\tau-\beta/2)u_n}} \right\rangle = \frac{e^{\beta^2\sigma^2 a_n} e^{i\beta\sigma^2 b_n \tau}}{e^{\sigma^2(1-a/\rho)(\beta^2+\tau^2)}} \tag{5}$$

with $b_n = \rho^{-1}[\delta_{n,1}(\rho - a) + (1 - \delta_{n,1})a/n(n-1)]$ and

$$a_n = \frac{\delta_{n,1}(\rho - a)}{2\rho} + (1 - \delta_{n,1})\left(1 - \frac{(2n-1)a}{2\rho n(n-1)}\right). \tag{6}$$

In formal transport theory [20,21] $f(\tau)$, sometimes called a force-force correlation function, is calculated directly from microscopic interactions. Here, for small polaron rates, if (1) is assumed in (3), $f(\tau)$ is seen immediately to be given by

$$f(\tau) = \sqrt{\frac{\Delta kT}{2\pi^2 J^4 \eta}} \exp(-\tau^2/4\eta), \tag{7}$$

where $\eta = -(8\Delta kT)^{-1}$. The integral resulting from substitution of (5) and (7) into (2) and (4) then gives

$$\mu = \frac{J^2\rho}{\hbar E\Delta}\sqrt{\frac{\pi}{2}}\,\beta\tilde{\Delta}\, \frac{e^{\beta eE\rho/2} e^{-\beta\tilde{\Delta}/2}}{\sum_{n=1}^{\infty} e^{-\beta eE\rho(n-1)} e^{\beta^2\sigma^2 a_n} G_n}. \tag{8}$$

Thus, aside from a modified binding energy $\tilde{\Delta} = \Delta - \frac{1}{2}\beta\sigma^2(1 - a/\rho)$, the effects of inversion are entirely contained in the factors

$$G_n = \exp\left[\frac{\frac{1}{4}(\beta^2\sigma^2 b_n - \beta eE\rho)^2}{2\beta\tilde{\Delta}}\right]. \tag{9}$$

Except for G_n, the sum in Eq. (8) is identical to those in earlier expressions which predict the PF field dependence [13].

In the earlier analyses, the corresponding summand was observed to be a sharply peaked function of n, and the sum well represented by a small number of terms lying near the peak. In the present situation, when Δ is sufficiently large, G_n is slowly varying. Moreover, in this limit the factor G_n does not affect the location (in n) of the dominant terms of the sum. The resulting mobility then exhibits the same asymptotic PF form derived in Ref. [13], i.e.,

$$\mu = \mu_0 e^{-\beta\tilde{\Delta}/2} \exp(-\beta^2\sigma^2) \exp(2\beta\sigma\sqrt{\beta eEa}), \tag{10}$$

but with a modified activation due to the polaron binding energy. Thus, for large Δ, the 1D model predicts the characteristic PF field dependence, but with a mobility reduced by the activated factor $\exp[-\beta\tilde{\Delta}/2]$. For small Δ, the individual factors G_n become exponentially large, and cause significant deviations from PF behavior.

Are the conclusions of the 1D analytical calculation applicable to 3D materials? To test, we performed numerical calculations similar to those of Ref. [14], as follows: First, point dipoles with random orientations are placed on a periodic cubic lattice of 50^3 sites, and the potential energy at each site due to the dipole distribution calculated. Hopping rates $R_{n,m}$ between lattice sites are computed using Eq. (1) with $J_{n,m} = J(r_{n,m}) = J_0 \exp[-\alpha(r_{n,m} - \rho)]$, with $\alpha^{-1} = 1$ Å, and with the field directed along one axis. Using a relaxation algorithm that explicitly includes hopping rates from each site to its 26 nearest neighbors, we then obtain the steady-state site probabilities p_n, from which the mean velocity $\vec{v} = \sum_{n,m} \vec{r}_{n,m} R_{n,m} p_m$, and mobility are calculated.

In Fig. 1, calculated mobilities for physically *reasonable* parameters, $\sigma = 80$ meV, $J = 1$ meV, $\Delta = 150$ meV, and $\rho = 10$ Å, show that polaron transport is compatible with PF mobilities for temperatures in the range $T = 225$–325 K and fields in the range $E = 10^4$–10^6 V/cm. Straight lines in Fig. 1 are least-square fits to data in the range $\sqrt{E} = 300$–900 $(\mathrm{V/cm})^{1/2}$ typically probed in experiments. In Fig. 2 we present parameters characterizing those linear fits, specifically, the PF factors $\gamma = \partial \ln(\mu)/\partial\sqrt{E}$, which give the slope of each fit in Fig. 1, and the extrapolated zero field mobility $\mu_{\mathrm{ext}}(0)$ associated with the intercepts. From (10) and the recent 3D numerical work of Ref. [14], these quantities are predicted to scale with temperature as $\gamma \propto (\sigma/kT)^{3/2}$ and $\ln[\mu_{\mathrm{ext}}(0)\exp(\Delta/2kT)] \propto (\sigma/kT)^2$, respectively. The data clearly support the predicted scaling laws. By fitting the data to an obvious generalization of the form proposed by Novikov *et al.* in Ref. [14]

$$\mu = \mu_0 e^{-\beta\Delta/2} e^{-A_1\beta^2\sigma^2} e^{A_2(\beta^{3/2}\sigma^{3/2} - A_3)\sqrt{eEa/\sigma}}, \tag{11}$$

we obtain $\mu_0 = 3.6 \times 10^{-3}$ cm^2/V s, $A_1 = 0.31$, $A_2 = 0.78$, and $A_3 = 1.75$ for the 3D polaron mobility for these parameters.

The 1D calculation suggests that deviations from the PF law occur for small Δ, when rates become "inverted." This is confirmed in Fig. 3, where μ is calculated with parameters of Fig. 1, but with Δ reduced to 10 meV. Here, the field range of PF behavior is small, and the mobility drops after reaching a maximum near 5×10^5 V/cm. That this results from inversion follows from the open circles in Figs. 1 and 3 where μ is calculated at $T = 325$ K without the inversion factor in (1). Inversion has been studied in systems with no correlations [4,23]; its effects on systems with correlated disorder have not.

Thus, observed PF behavior is consistent with small polarons and realistic values of J, provided the binding energy is sufficiently *large* to avoid the inversion effects of Fig. 3. Since μ decreases exponentially with Δ, a large Δ again requires an unphysical J. When Δ becomes too large, values of J required for mobilities in the right range again become unphysical. To obtain the same room temperature μ in Fig. 1 with Δ increased to 500 meV, J must increase from 1 to 20 meV, at the high end expected for polyaromatic hydrocarbon crystals [9]. Figure 3 shows that a Δ of 10 meV is too small except, possibly, for a few systems at high fields and low dopant concentrations,

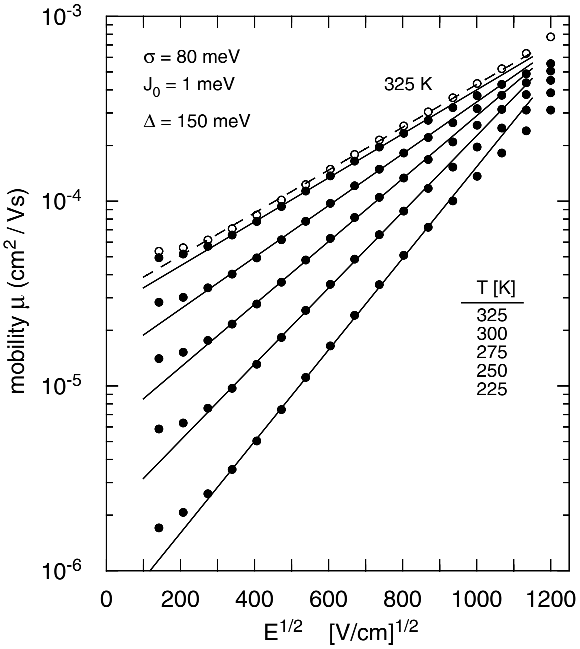

FIG. 1. Field dependent mobility for polaron transport in a dipolar solid with indicated parameters.

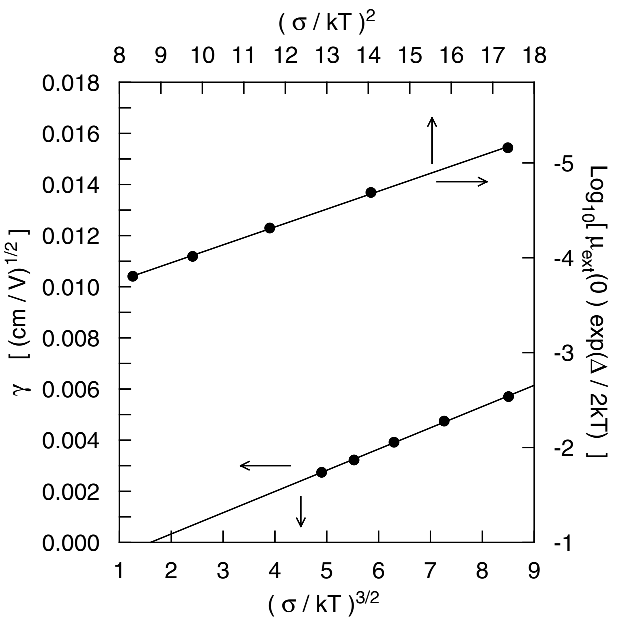

FIG. 2. PF factor γ and zero field mobility for data in Fig. 1. Arrows indicate axes to be used for each.

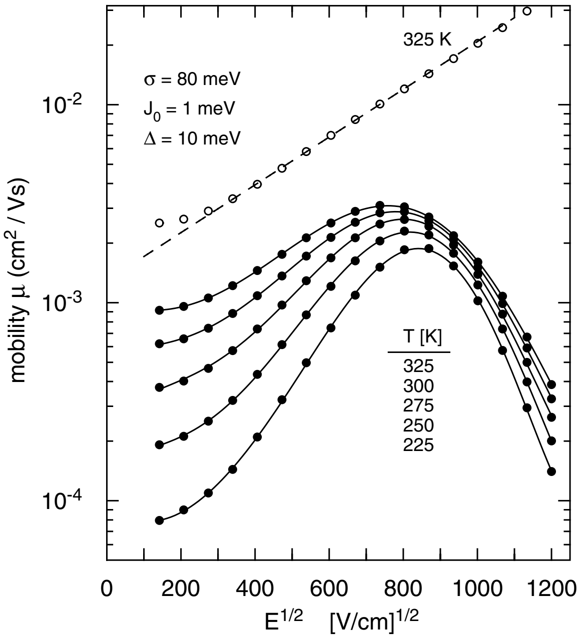

FIG. 3. Field dependent mobility for polaron transport in a dipolar solid with indicated parameters.

where mobilities that decrease with field are observed [23]. For the level of energetic disorder ($\sigma = 80$ meV) used here we conclude that, for $\Delta = 50$–500 meV, PF-like mobilities of observed magnitude *are consistent* with small polaron motion in a correlated dipolar landscape.

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