

Molecular Theory of Geminate Recombination. V. Recombination of Polarons on the 2-D Square Lattice[†]

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A molecular theory of geminate recombination of charge carriers, previously developed, is generalized to study the recombination of polarons. The theory predicts recombination behavior in qualitative agreement with experimental data, and this behavior is governed over the entire range of field by molecular parameters. It is shown that the dissociation pathways available to the carrier depend strongly on its initial site. It is also demonstrated that the observed dissociation probabilities result from competition between rates for various processes along the dissociation pathway, and the effects of this competition on the field and temperature dependence of the dissociation probability are examined.

I. Introduction

Electric-field-dependent geminate recombination (GR) of photogenerated electron-hole pairs is the most fundamental mechanism determining the efficiency of photophysical processes in condensed phases. It is important even in perfect crystals. Geminate recombination limits the efficiency of dissociation of electron-hole pairs, and therefore contributes to the operational characteristics of photoelectronic devices.

In a series of papers,^{1–7} we have developed a lattice random walk approach to this problem, as an alternative to the Onsager theory^{8,9} which has been used to analyze much of the extensive body of experimental data on recombination.^{10–13} The latter is a continuum theory, and requires solution of the Smoluchowski equation for the mutual diffusion of the oppositely charged carriers under the joint influence of their Coulomb interaction and the external electric field. The continuum nature of the Onsager approach raises serious questions^{1,2,14} as to its applicability in many of the condensed phases which have been studied. The lattice random walk theory, on the other hand, takes account of the discrete nature of the materials and the symmetry properties of the lattice, and relates the physical process to molecular properties of the system.

In the present work, we extend our previous work, which dealt with bare carriers, to study the geminate recombination of electron and hole polarons. It will be shown that the recombination efficiency η for polarons exhibits the qualitative behavior observed experimentally, and that, in this case also, η can be related to molecular properties of the system. We shall also demonstrate that the method can be extended to study aspects of the dynamics of charge carriers which have not been previously treated. We shall be particularly interested in extracting information about carrier trapping, and about the relationship between initial conditions and dissociation pathways.

II. Methods

The basic model has been set forth in our previous work,^{1,2,4} to which the reader is referred for details of the calculation. We consider an electron polaron executing a nearest-neighbor random walk on a two-dimensional square lattice, in the presence of a hole polaron fixed at the origin. An electric field is applied to the system, and the polaron moves under the influence of both its Coulomb interaction with the hole and the external field. The hole site at the origin has two states accessible to the polaron: an excited state, which we denote by the index 1, and the ground state, 0. A polaron in state 1 at the origin can transfer either to a nearest-neighbor site, or to state 0. If the polaron goes to 0, recombination has occurred and the random walk is at an end. A polaron at any other site than the origin can only undergo nearest-neighbor transfer.

The formalism we developed in previous work^{1,2} can be generalized to the polaron case by using the chemical rate formalism of Scher and Holstein^{15–18} to calculate intersite transition probabilities. We have also applied this approach to a discussion of polaron transport.¹⁹ We consider a model in which an electron is transferred between two sites, for which the vibrational potentials are given by

$$V_1 = (\hbar\omega/2)(q + a/2)^2 + \Delta_0/2 \quad (1)$$

$$V_2 = (\hbar\omega/2)(q - a/2)^2 - \Delta_0/2 \quad (2)$$

respectively. Here q and a are dimensionless configuration coordinates, and Δ_0 is the intrinsic energy difference between sites 1 and 2. The frequency of the active vibrational mode is given by ω . Scher and Holstein showed that, in this model, the electron transfer rate is given by the expression

$$v_{\pm} = (2\pi J^2/\hbar\omega) \frac{\exp(\pm[\Delta/2kT] - F)}{[4\pi\gamma(\delta^2 + \operatorname{cosech}^2\xi)^{1/2}]^{1/2}} \quad (3)$$

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where

$$F = 2\alpha[\coth \xi - (\delta^2 + \cosh^2 \xi)^{1/2} + \delta \sinh^{-1}(\delta \sinh \xi)] \quad (4)$$

$$\Delta = \Delta_0 + \hat{\Delta}(E) \quad (5)$$

$$\delta = \Delta/4E_{\text{act}} \quad (6)$$

$$\alpha = 2E_{\text{act}}/\hbar\omega \quad (7)$$

$$E_{\text{act}} = \hbar\omega a^2/8 \quad (8)$$

and

$$\xi = \hbar\omega/2k_B T \quad (9)$$

J is the electron transfer matrix element. In eq 5, the intersite energy difference Δ has two contributions, one from the intrinsic energy difference in eqs 1 and 2, and the other arising from the externally applied electric field. In what follows, we shall take $\Delta_0 = 0$. We consider a two-dimensional square lattice with lattice constant a , and take the electric field in the x -direction:

$$\mathbf{E} = E\hat{\mathbf{x}} \quad (10)$$

Then, in the absence of Coulomb interactions, the energy difference for a step of one lattice constant in the x -direction is

$$\Delta_{i+1,i} = -eEa \quad (11)$$

The modification of the theory developed for bare carriers arises from the polaron transition rate (eq 3). Recall that, in the absence of Coulomb interactions, the transition probability per unit time for transition from the i th to the j th site is calculated from the intersite transition rate ν by^{1,2,4}

$$\psi(i \rightarrow j) = \frac{\nu(i \rightarrow j)}{\sum_k \nu(i \rightarrow k)} \quad (12)$$

Insertion of eq 3 into eq 12 gives the following expression for the polaron transition probability:

$$\psi(i \rightarrow j) = \frac{\exp[\gamma(x_j - x_i) - F(\delta_{ji})]}{\Phi(\delta_{ji})\{M(\delta_1)\cosh(\gamma) + M(0)\}} \quad (13)$$

Here, Φ is the denominator of the second factor on the RHS in eq 3,

$$\Phi(\delta) = [4\pi\alpha(\delta^2 + \text{csch}^2(\xi))^{1/2}]^{1/2} \quad (14)$$

$$\gamma = eEa/2k_B T \quad (15)$$

is the dimensionless electric field,

$$M(\delta) = 2 \frac{\exp[-F(\delta)]}{\Phi(\delta)} \quad (16)$$

δ_1 is the reduced energy difference (eq 6) between two sites separated by a unit vector in the x direction, and δ_{ij} is the

reduced energy difference between sites i and j . This expression can be used to calculate the form factor

$$\Lambda(k,0) = \sum_l \psi(l,0) \exp(-i\mathbf{k} \cdot \mathbf{l}) \quad (17)$$

$$= 2[\hat{M}(\delta_1, \gamma, \xi)]^{-1} \{Q(\delta_1)e^{-F(\delta_1)} \cos(k_x + i\gamma) + Q(0)e^{-F(0)} \cos(k_y)\} \quad (18)$$

where $Q(x) = [\Phi(x)]^{-1}$, and

$$\hat{M}(\delta_1, \gamma, \xi) = M(\delta_1) \cosh(\gamma) + M(0) \quad (19)$$

This, in turn, gives the polaron Green's function for the two-dimensional square lattice:

$$G(l,m) = (2\pi)^{-2} \int_0^{2\pi} \int_0^{2\pi} d^2\theta \times \frac{\exp(i[l\theta_1 + m\theta_2])}{1 - 2\hat{M}^{-1}[Q(\delta_1)e^{-F(\delta_1)} \cos(\theta_1 + i\gamma) + Q(0)e^{-F(0)} \cos(\theta_2)]} \quad (20)$$

As in the case of bare carriers², it can be shown that the Green's function can be written in terms of an auxiliary function as follows:

$$G(l,m) = e^{i\gamma} f(l,m) \quad (21)$$

where

$$f(l,m) = (\pi)^{-2} \int_0^\pi \int_0^\pi d^2\theta \times \frac{\cos(l\theta_1) \cos(m\theta_2)}{1 - 2\hat{M}^{-1}[Q(\delta_1)e^{-F(\delta_1)} \cos(\theta_1) + Q(0)e^{-F(0)} \cos(\theta_2)]} \quad (22)$$

Note, however, that here, in contrast to the bare carrier case, $f(l,m) \neq f(m,l)$.

It is possible to develop recursion relations for the $f(l,m)$, as we did in the bare carrier case.^{2,4} In practice, however, it is more convenient and accurate to calculate the auxiliary functions using a two-dimensional integration algorithm, which avoids problems of numerical instability inherent in the use of recursion.

Once the $f(l,m)$ are calculated, giving the Green's functions (eq 21), the dissociation efficiency as a function of applied electric field $\eta(\gamma)$ is calculated as in the bare carrier case:

$$\eta(\gamma) = \psi_{10}(0)R(0,0) \quad (23)$$

where ψ_{10} is the transition probability/unit time from the excited state at the origin to the ground state, and $R(0,0)$ is the Laplace transform at $\mathbf{l} = 0$ and $\mu = 0$ of $\hat{R}(\mathbf{l},t)$, the probability that the electron has just reached site \mathbf{l} at time t . In previous work,^{2,4} we have shown that the R can be calculated as the solutions to a closed set of equations, if the lattice is divided into two sets of sites. The set L contains sites at which the transition rate for the electron to leave the site is affected by both the Coulomb interaction with the hole at the origin and the applied electric field. The complementary set L' contains sites at which only the applied field determines the transition rate to leave. We write the transition probability/unit time for transitions from site \mathbf{l}' to site \mathbf{l} as

$$\begin{aligned} \psi &= \psi(\mathbf{l} - \mathbf{l}') \quad \mathbf{l}' \in L' \\ &\psi(\mathbf{l} - \mathbf{l}'; \mathbf{l}') \quad \mathbf{l}' \in L \end{aligned} \quad (24)$$

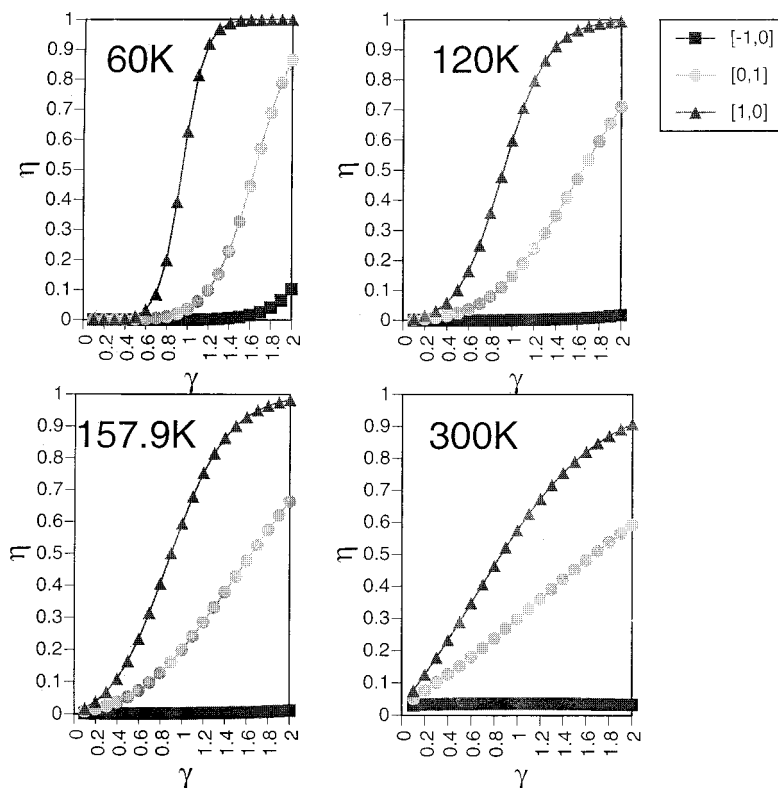


Figure 1. Plots of η vs γ for four values of T : 60, 120, 157.9, and 300 K. In this and subsequent plots, the parameter values are $(\epsilon_{\text{ex}}, \chi, R; \alpha, \xi) = (1.3, 1.2, 100.0; 10, 1)$.

Note that, in the first case, ψ depends only on $\mathbf{I}-\mathbf{I}'$, while in the second case, ψ depends explicitly on \mathbf{I}' . With this approximation, it was shown that the \hat{R} function can be calculated by inverting the matrix equation

$$G(\lambda - \mathbf{I}) = \sum_{\lambda'} M_{\lambda, \lambda'} R(\lambda') \quad (25)$$

where

$$M_{\lambda, \lambda'} = G(\lambda - \lambda'; 0) - \sum_{\mathbf{I}'} G(\lambda - \mathbf{I}'; 0) \psi(\mathbf{I}' - \lambda'; \lambda') \quad (26)$$

Note that the only sites which enter into the sum in eq 25 are those in the set L . Solution of the set (eq 25), followed by insertion into eq 23, gives the dissociation probability as a function of applied electric field.

In what follows, as in previous work,⁴ we take the set L to include all sites up to and including third neighbors of the origin. This enables us to demonstrate the physical features of the approach, while retaining relative simplicity of calculation.

Another factor of critical importance in the study of geminate recombination is the initial distribution of the electron polaron about the hole polaron site. In previous work,² we considered three different distributions. The isotropic distribution is that in which the electron has an equal probability of being found at $t = 0$ at each of the nearest neighbors of the hole. In the Boltzmann distribution, the electron is localized at nearest neighbor sites of the hole, but the angular probability distribution is determined by the electric field strength at each site. In the Frenkel distribution, the electron is initially in state 1 at the origin. In the present work, we consider the behavior of carriers initially localized in particular states. We shall pay particular attention to the three nearest neighbors of the hole site at the origin.

Equations 3 and 5 give rise to three dimensionless molecular parameters, identical to those characteristic of the square lattice in previous work:⁴ ϵ_{ex} , χ , and R . The first is the reduced “ionization potential”—the energy required to transfer of the electron polaron from the excited state at the origin to a nearest-neighbor site

$$\epsilon_{\text{ex}} = E_{\text{ex}}/kT \quad (27)$$

The second is a measure of the dielectric screening in the material,

$$\chi = \frac{e^2}{2kTDa} \quad (28)$$

where D is the dielectric constant, and the third is the branching ratio for an electron polaron in state 1 at the hole site, measuring the relative intrinsic rates of recombination (at the origin) and nearest-neighbor transfer,

$$R = W(1 \rightarrow 0)/W_0 \quad (29)$$

These are *molecular* parameters, and they allow us to relate the details of the geminate dissociation process to the fundamental characteristics of the condensed phase in which it occurs.

III. Results and Discussion

The dissociation probability as a function of applied field behaves qualitatively in a manner similar to that observed for bare carriers.^{1–4} In Figure 1 are shown plots of η vs. γ for four values of T : 60, 120, 157.9, and 300 K. At each temperature, as a function of applied field, the curves are ordered as follows with respect to the initial site of the electron polaron:

$$\eta[1,0] > \eta[0,1] > \eta[-1,0] \quad (30)$$

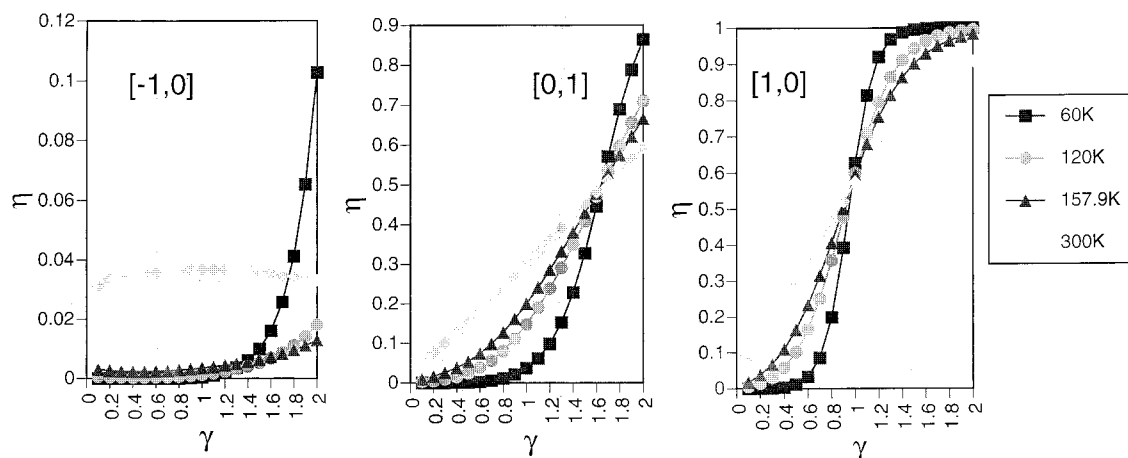


Figure 2. Behavior of η as a function of γ and T for specified initial sites.

This is precisely the behavior one would expect: electrons initially localized at the site upfield from the hole, $[-1,0]$ can be expected to have the largest probability of reaching the origin, where recombination becomes a possibility. The lowest probability of passing through the origin, and therefore the highest probability of dissociating, is expected from those electrons initially downfield from the origin, at $[1,0]$. Electrons initially localized at $[0,1]$ will have an intermediate probability of passing through the origin and recombining. It is also of interest to study the behavior of η as a function of γ and T for specified initial sites. Curves showing these data are given in Figure 2, but we defer analysis until after a discussion of charge carrier trapping.

Trapping can be defined precisely within our framework, as the probability of the electron passing through the origin at some time during its random walk. Carriers which pass through the origin fall into two classes—those which recombine, and those which escape to dissociate. The probability that a carrier will recombine is simply $1 - \eta$, and those carriers which do are not terribly interesting from the viewpoint of trapping. One is more interested in determining the probability η_0 that a carrier will pass through the origin and then dissociate, since it is those carriers which exhibit the *finite trapping times* conventionally associated with trapping experiments. We demonstrate that it is possible to calculate this quantity within the framework of the lattice random walk approach. [The total trapping probability can then be calculated, if desired, as $1 - \eta + \eta_0$.]

We first calculate the probability that the carrier, initially at \mathbf{l}_0 , will visit the excited state at the origin \mathbf{o}_1 for the first time at time t . Using notation introduced in earlier work,¹⁻⁴ we write

$$\hat{R}(0,t;\mathbf{l}_0) = \delta_{\mathbf{l}_0,\mathbf{o}_1}\delta(t) + \int_0^t d\tau \hat{P}(0,\tau;\mathbf{l}_0)\hat{R}(0,t-\tau;\mathbf{o}_1) \quad (31)$$

where $R(\mathbf{o}_1,t;\mathbf{l}_0)$ is the probability that the carrier has just arrived at \mathbf{o}_1 at time t , given that it was initially at \mathbf{l}_0 . $\hat{P}((\mathbf{o}_1,t;\mathbf{l}_0)$ is the probability that the carrier arrives at \mathbf{o}_1 for the first time at time t , having initially been at \mathbf{l}_0 . Laplace transforming both sides of eq 31 and rearranging gives

$$P(\mathbf{o}_1,s;\mathbf{l}_0) = \frac{R(\mathbf{o}_1,s;\mathbf{l}_0) - \delta_{\mathbf{l}_0,\mathbf{o}_1}}{R(\mathbf{o}_1,s;\mathbf{o}_1)} \quad (32)$$

We can write the probability that a carrier initially at \mathbf{l}_0 will dissociate by passing through the excited state at the origin as follows:

$$\eta_0(t) = \int_0^t d\tau \hat{P}(\mathbf{o}_1,\tau;\mathbf{l}_0)\eta_F(t-\tau) \quad (33)$$

Here, $\eta_F(t)$ is the probability of dissociating at time t , given that the initial site of the carrier is the excited state at the origin—the Frenkel initial condition.^{1,2}

The total probability of dissociation by pathways leading through \mathbf{o}_1 is then

$$\eta_0 = \int_0^\infty dt \hat{\eta}_0(t) = \eta_0(s=0) \quad (34)$$

But, from eq 33,

$$\eta_0(s) = P(\mathbf{o}_1,s;\mathbf{l}_0)\eta_F(s) \quad (35)$$

$$\eta_0 = P(\mathbf{o}_1,0;\mathbf{l}_0)\eta_F(0) \quad (36)$$

and therefore, from eq 32,

$$\eta_0(0) = \frac{[R(\mathbf{o}_1,0;\mathbf{l}_0) - \delta_{\mathbf{l}_0,\mathbf{o}_1}]}{R(\mathbf{o}_1,0;\mathbf{o}_1)}\eta_F(0) \quad (37)$$

This is the answer we seek. We have previously developed methods^{2,4} to calculate the R functions and η_F . We are therefore in a position to calculate η_0 . It is also useful to define a trapping ratio, denoted by

$$\Xi(\mathbf{l}_0) \equiv \eta_0(\mathbf{l}_0)/\eta(\mathbf{l}_0) \quad (38)$$

This quantity, which depends on the initial site \mathbf{l}_0 , is the ratio of the probability of dissociation by pathways which pass through the excited state at the origin \mathbf{o}_1 to the total probability of dissociation by any pathway. It is therefore a measure of the prevalence of finite-time trapping processes in the system.

It is clear from eq 37 and 38 that the values of η_0 and Ξ will reflect a complex interplay between the rates of the various processes available to the carrier. We begin to examine this point in Figure 3, in which the behavior of η_0 is shown as a function of field and initial site, at specified temperatures. At each temperature, and for every field value, the probability of dissociating through \mathbf{o}_1 is greatest when $\mathbf{l}_0 = [-1,0]$. It is physically reasonable that both the $[-1,0] \rightarrow [0,0]$ transition rate and the dissociation probability from \mathbf{o}_1 are increasing functions of field. For the two remaining \mathbf{l}_0 we observe a bending over ($[0,1]$) or a maximum ($[1,0]$) in η_0 . Clearly, for values of γ greater than some threshold, processes becomes important which decrease in rate with increasing field. This is seen more clearly in Figure 4, in which the same data are plotted as a function of field and temperature, for specified initial sites. Two points are readily seen from this plot: (1) There is a difference

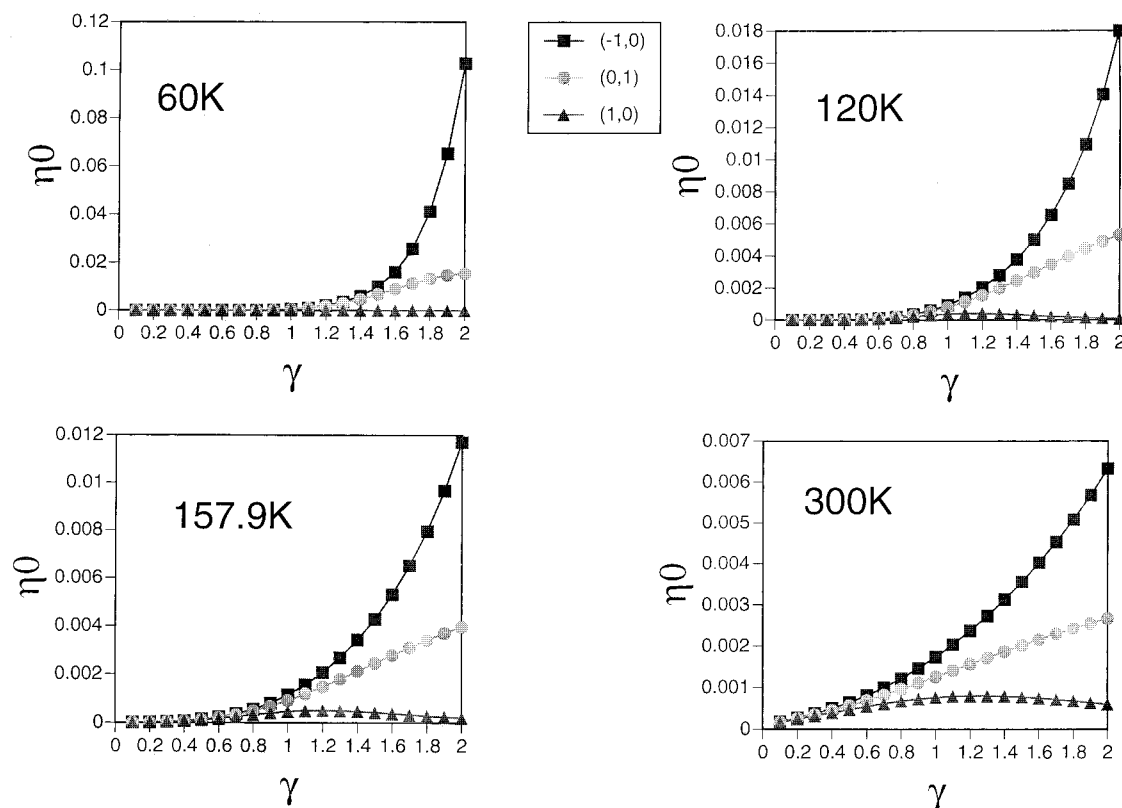


Figure 3. η_0 as a function of applied field and initial site, at different temperatures.

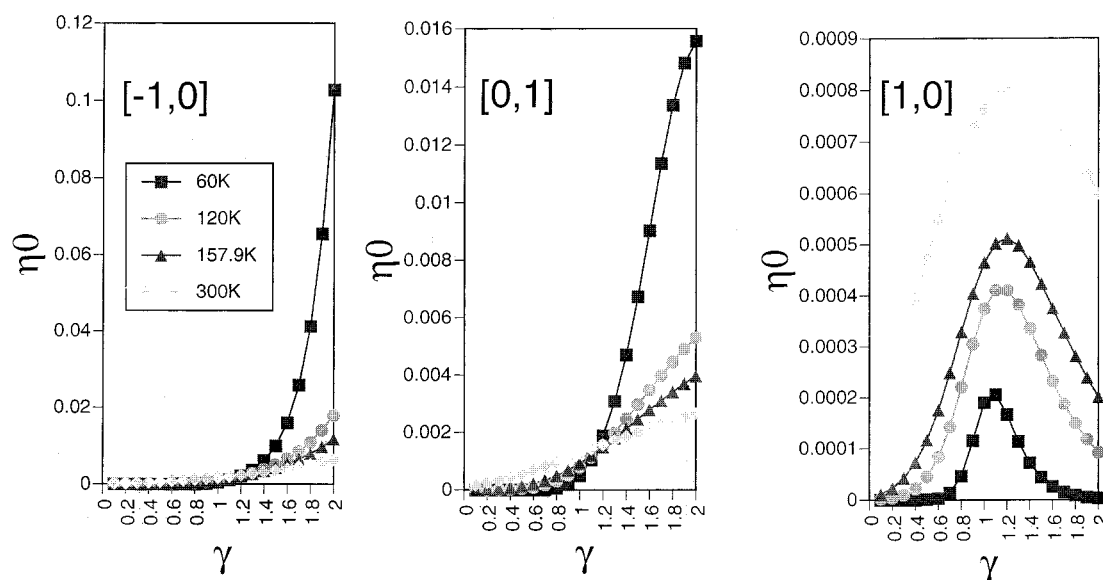


Figure 4. η_0 as a function of applied field and temperature, for different initial sites.

in the T -ordering between the three initial sites. When $\mathbf{l}_0 = [-1,0]$, η_0 decreases with increasing temperature at higher fields. This ordering is reversed at all fields when $\mathbf{l}_0 = [1,0]$. When $\mathbf{l}_0 = [0,1]$, a curve crossing is observed, at a value of γ at which there is essentially no temperature dependence of η_0 . (2) There is a difference in the field dependence in the three cases. η_0 is strictly increasing with γ over the range studied when $\mathbf{l}_0 = [-1,0]$. When $\mathbf{l}_0 = [0,1]$, signs of a downturn in η_0 are visible at high field. When $\mathbf{l}_0 = [1,0]$, η_0 goes through a maximum for all temperature values.

As a preliminary to understanding these observations, we note that in this system the character of the energy surface is determined by γ (as shown in Figure 5), and the pathways

available to the carrier are determined by \mathbf{l}_0 and T . We further note that an increase in probability with increasing temperature, at a given field value, is the fingerprint of processes which involve the absorption of energy. Conversely, a decrease in probability with increasing T is characteristic of processes involving the emission of energy. While these facts don't provide a microscopic mechanism for carrier migration, they do suggest a possible framework within which our calculations can be interpreted. When $\mathbf{l}_0 = [-1,0]$, at larger field values, the $\mathbf{l}_0 \rightarrow [0,0]$ (trapping) step and the dissociation from the Frenkel state both involve downward steps in energy. On the other hand, when $\mathbf{l}_0 = [1,0]$, there is always an uphill step in the carrier pathway: at a given field strength, either trapping

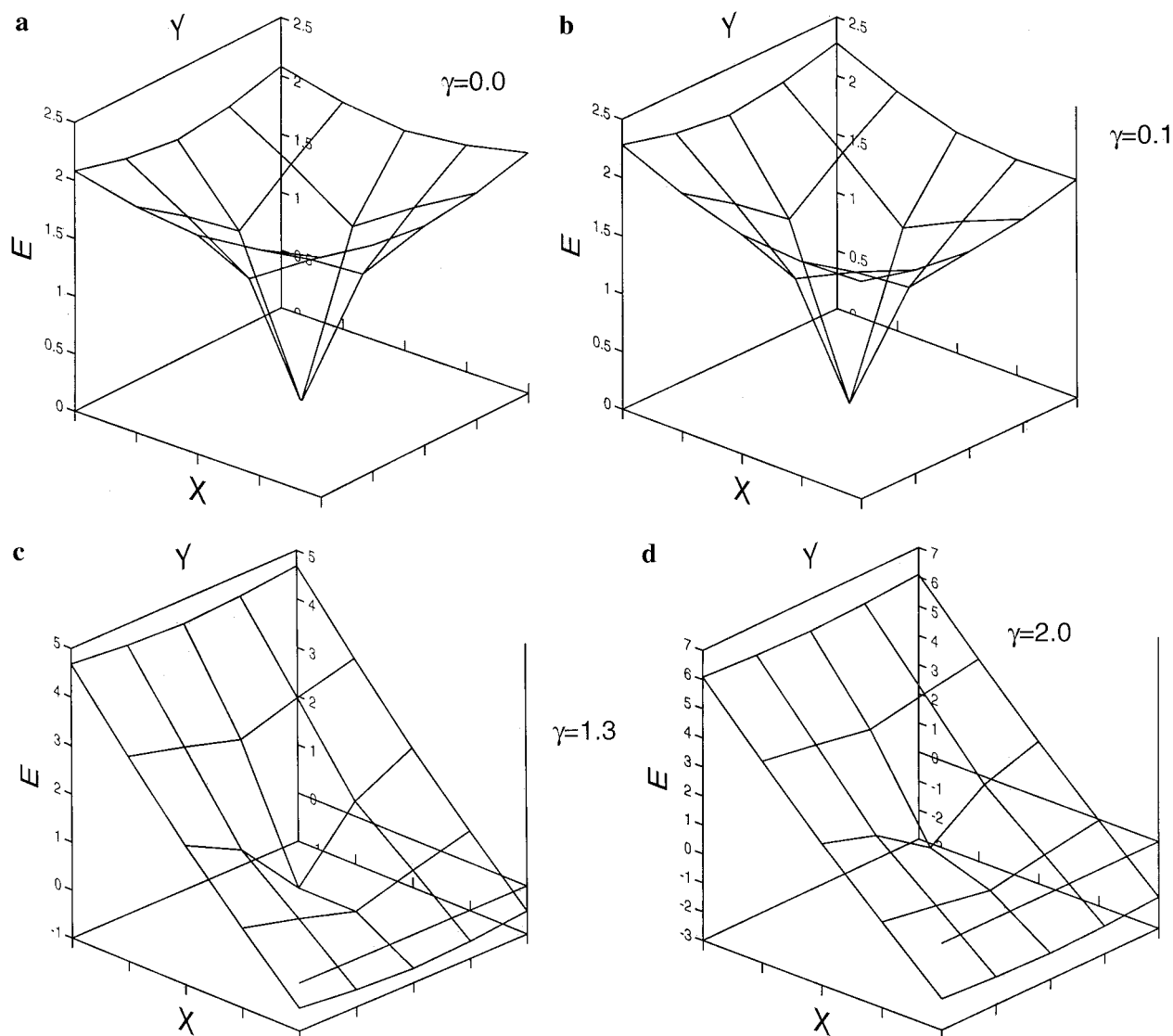


Figure 5. The energy surface on which the electron polaron moves in the neighborhood of the hole at the origin, for four different values of γ : (a) $\gamma = 0.0$, (b) $\gamma = 0.1$, (c) $\gamma = 1.3$, (d) $\gamma = 2.0$. A square neighborhood of the origin is shown, including sites with $-2 \leq x, y \leq 2$. The electric field, which is identically oriented in all three cases, points in the $+x$ direction.

or dissociation requires a step upward in energy. When $\mathbf{l}_0 = [0,1]$, the trapping step is *always downward in energy*, since that step is in a direction which is orthogonal to the applied field. The energetics of the Frenkel dissociation, however, vary with field. At low field dissociation requires steps upward, while higher fields invert the energy surface (Figure 6). A field strength exists at which the various energetic steps precisely compensate, and there is no T -dependence. We are thus able to account for the temperature ordering of η_0 noted as point 1 above.

The effects summarized in point 2 can be accounted for by the following observations. A maximum in the $\eta_0(\gamma)$ curve must arise from competition between two probabilities, one of which increases with γ while the other decreases. The specific probabilities involved will differ for each \mathbf{l}_0 . Clearly, however, the mechanism involves interaction between a trapping process whose probability decreases with field (Figure 7), and the Frenkel dissociation process, the probability of which increases with field (Figure 6).

Finally, we note that η_0 is at least an order of magnitude larger when $\mathbf{l}_0 = [-1,0]$ than in the other two cases. This suggests that, when $\mathbf{l}_0 = [-1,0]$, a substantial fraction of all

dissociation must proceed through the trapping state. We investigate this point by inspecting results for the trapping ratio Ξ .

In Figure 8 we show Ξ for each of the three initial sites, as a function of γ and T . These plots are consistent with physical intuition, and with previous figures. When the electron is initially at $\mathbf{l}_0 = [-1,0]$, the site immediately upfield from the hole, the trapping ratio at all temperatures shows saturation behavior, asymptotically approaching $\Xi = 1$ at higher values of γ . Saturation is much more rapid at lower temperatures. The origin of this behavior is clear. The external field and the Coulomb interaction between the hole and electron act in concert to drive the electron polaron to the hole polaron site at the origin. Therefore, with increasing field, the probability of dissociating through the state $\mathbf{0}_1$ grows. At high fields the overwhelmingly probable dissociation process is that in which the electron transfers to the excited state at the origin and then dissociates. As T is increased, competing pathways become more accessible, and the saturation of Ξ slows.

When the initial site is $[0,1]$ or $[1,0]$ different behavior is obtained. In each case, and for each temperature value, a maximum is observed in the curve of Ξ vs γ . This mirrors the

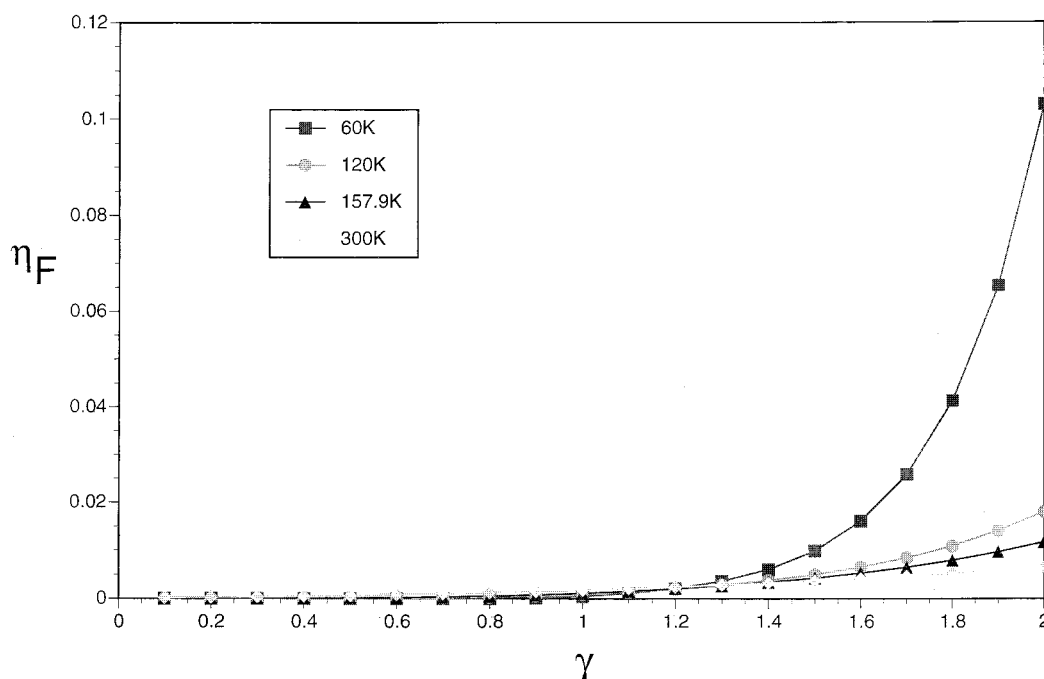


Figure 6. Frenkel ($l_0 = 0_1$) dissociation probability as a function of field, for different temperatures.

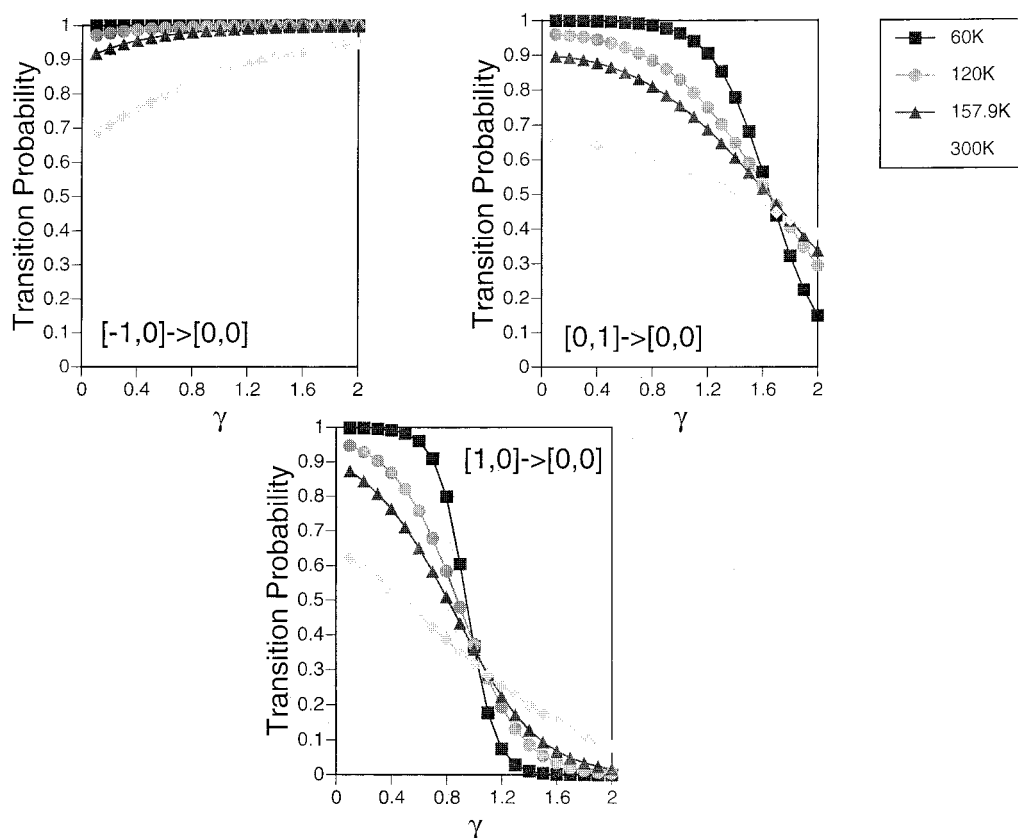


Figure 7. Transition probabilities to $[0,0]$ from each of the three initial sites as functions of T and applied field.

behavior of η_0 shown in Figure 4 and reflects a field-driven increase in the probability of dissociation through non-trapping pathways. In Figure 9, we show the same data plotted to illustrate the difference in behavior between the three initial sites at each temperature. It is seen that the trapping ratios for different initial sites can differ by an order of magnitude or more at each temperature. Note that the magnitude of Ξ in both these cases is very small, reflecting the fact that carriers whose initial

site is not upstream from the trapping site have a very small probability of dissociating with trapping.

We are now in a position to discuss the results shown in Figure 2. Recall that this plot shows results for η , the probability of dissociating by *any* pathway. Processes involving the state 0_1 are of negligible importance in dissociation from $l_0 = [0,1]$ or $[1,0]$. We are therefore essentially plotting the field dependence of $\bar{\eta}_0 = \eta - \eta_0$, the probability of dissociating without

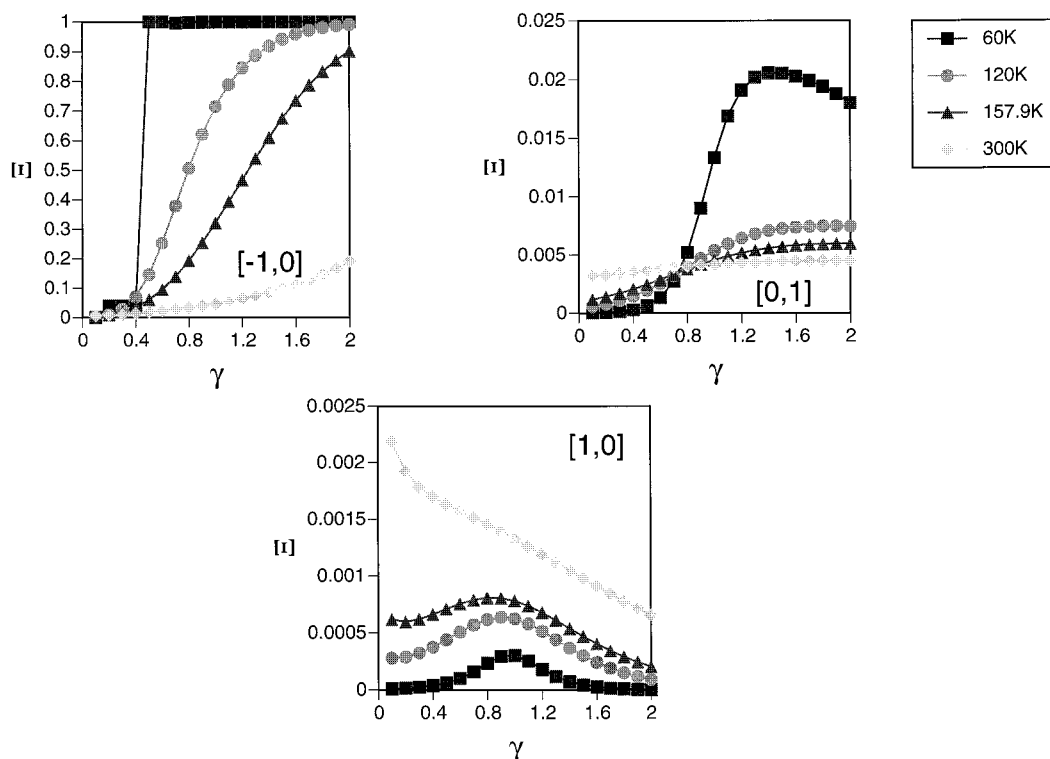


Figure 8. Trapping ratio Ξ for each of the three initial sites as a function of γ and T .

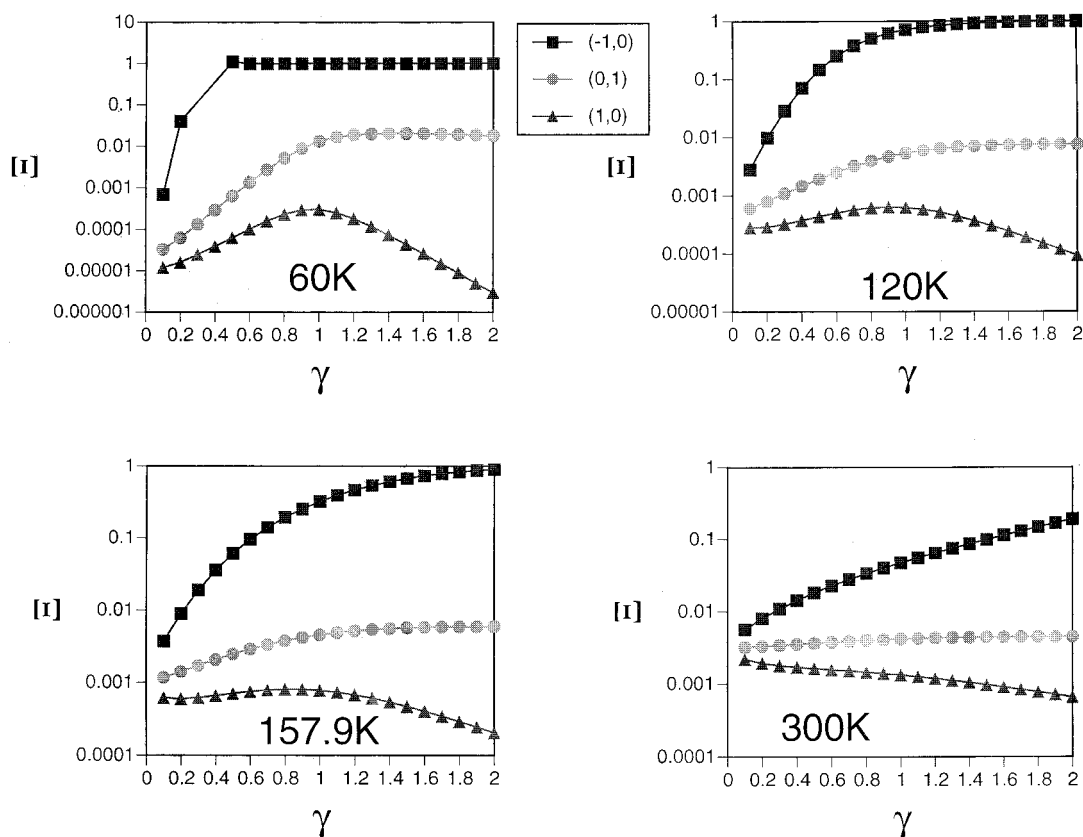


Figure 9. The same data as shown in Figure 3, plotted to illustrate the difference in behavior between the three initial sites at each temperature.

trapping. In both of these cases we observe an inversion of temperature ordering at some field value. As before, we understand this to reflect a change in the nature of the energy surface explored by the carrier as the applied field increases. At lower field values, dissociation probability is primarily determined by processes which involve upward steps in energy.

At higher fields, the principal determinants of η are processes taking place through downward steps in energy.

When $\mathbf{l}_0 = [-1,0]$ a different picture emerges. As we have remarked above, at lower temperatures, pathways involving $\mathbf{0}_1$ contribute a substantial fraction of the total dissociation probability. At $T = 300$ K, however, nontrapping pathways

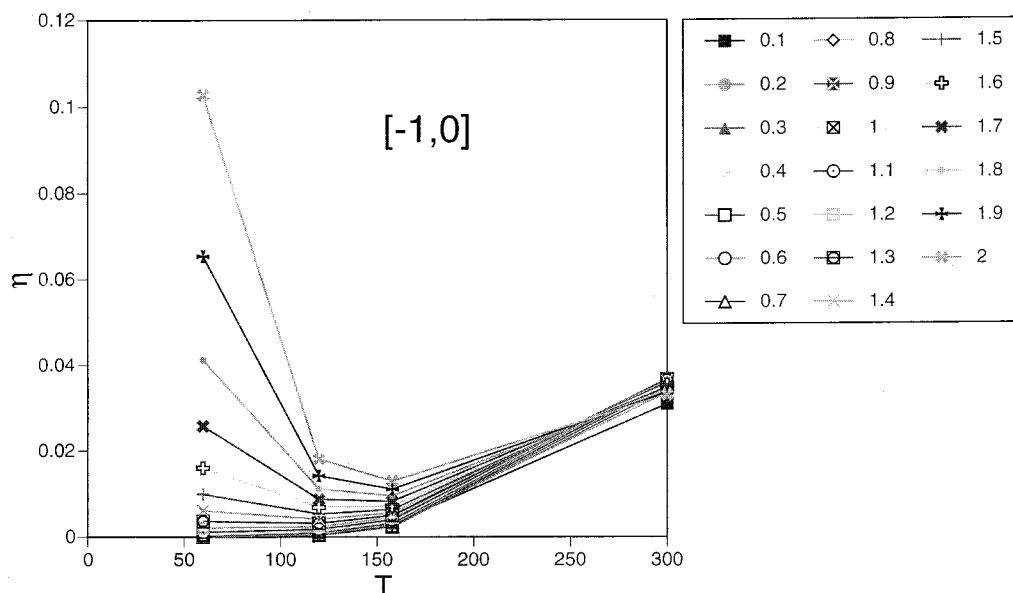


Figure 10. Temperature dependence of η for fixed values of γ , when $l_0 = [-1, 0]$.

contribute the overriding fraction of total probability. This separation of temperature regimes is evident in the $\eta(\gamma)$ plot, and more clearly in Figure 10. At low temperatures, the T dependences are similar to those of the other initial sites—governed by uphill processes at low field and downhill processes at high field. At $T = 300$ K uphill processes dominate at all fields.

IV. Summary

We have calculated the dissociation probability of electron and hole polarons using the lattice random walk formalism. It was demonstrated that the dissociation pathways available to the carrier depend strongly on the site on which it is initially localized. We have also shown that the temperature and field dependences of the dissociation probability can give information about the rates for various processes along the dissociation pathway. The use of the lattice random walk method enables us to examine the behavior of geminate recombination/dissociation as a function of fundamental molecular parameters. We hope to explore the parameter space more fully in forthcoming work.

Acknowledgment. This work is dedicated to my friend and collaborator Harvey Scher with affection and respect, and with warmest wishes for many happy and productive years.

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