PHYSICAL REVIEW B, VOLUME 65, 014305

Electric field dependence of charge mobility in energetically disordered materials: Polaron aspects

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(Received 8 February 2001; revised manuscript received 30 May 2001; published 13 December 2001)

In order to understand the electric-field dependence of charge mobility in molecularly doped organic materials, we consider the one-dimensional migration of carriers between sites with Gaussian energetic disorder. The transition rate of carriers to neighboring sites is assumed to be given by the Marcus rate equation. An exact analytical expression is derived, and is compared to the measured data. A phenomenological Gill's relation occurs in the intermediate region of the S-shaped field dependence of the mobility. The recently observed anomalous field dependence of the mobility, which shows that the mobility increases with field strength at low fields, passes through a maximum, and then decreases with increasing field strength, is reproduced. The increase followed by the decrease of the mobility with increasing field strength is interpreted as a result of energetic disorder and the Marcus inverted region.

DOI: 10.1103/PhysRevB.65.014305 PACS number(s): 71.38.−k, 72.10.Bg, 72.40.+w

I. INTRODUCTION

Charge transport in many doped organic materials shows a strong response to external electric fields E_0 and temperature T. The mobilities are very low, and the field dependence is well described by Gill's empirical law, $\log \mu \propto \sqrt{E_0}$, in a wide range of the field strength, $E_0 \approx 10^4 - 10^6$ V/cm, for various combination of the dopant molecules and host materials.[1,2] Most of the experimental results showed a positive slope;[1] $\log \mu$ increases with $\sqrt{E_0}$. A negative slope was also observed at sufficiently low concentrations of dopant molecules and high temperature.[3] The origin of such a universal field dependence has been of both theoretical and experimental interest.[1] Among many theoretical studies a particularly important mechanism was proposed by Dunlap *et al.*[4] They demonstrated that Gill's law arises naturally from the interaction of charge carriers with randomly distributed permanent dipoles.[4] In some experiments Gill's law is observed at an intermediate field strength. At high fields the mobility passes through a maximum and even decreases.[5–8] To cast some light on such a field dependence of the mobility, namely, Gill's law and the appearance of a maximum, we have developed analytical expressions for the charge mobility by assuming a physically plausible but simple enough charge transport mechanism. It is generally accepted that charge transport occurs due to a hopping transition between adjacent donor or acceptor molecules.[9] In solution, the Marcus rate equation is well established for such charge-transfer processes.[10] In Marcus theory the contribution to the reorganization energy comes from both the reorientation of dipoles in the solvent and the intramolecular vibration.[10,11] In the solid phase dipoles cannot rotate, and the reorganization should be governed solely by the vibrational relaxation.[11] Indeed, a corresponding equation exists in the description of a small polaron, and the reorganization energy E_r is twice the polaron binding energy due to the coupling of the charge with low-frequency phonon modes.[12,13] The localization of the charge required for the small polaron picture is justified for several reasons. As we will explain below, site energies spread with a deviation of ~ 0.1 eV which is much larger than the value of the transfer integral, resulting in an Anderson-Mott localization.[14] Furthermore, the reorganization energy of 0.1–0.3 eV, which is typical of the low-frequency vibronic relaxation, is also large compared to the value of the transfer integral. Under such conditions a polaron is well localized, and is termed a Holstein small polaron.[15,16] A transition takes place to neighboring sites by hopping, because the bandwidth is considerably reduced due to the lattice distortion around the charge. The most important manifestation of the Marcus rate equation is the appearance of a so-called inverted region where the transition rate decreases by decreasing the free-energy change associated with the charge transfer.[10] The free-energy change can be created by external electric fields, so that a similar effect may be expected for the mobility. The decrease of mobility at extremely high electric fields was predicted a long time ago for polaron models.[17] However, the bell-shaped dependence of the mobility on the external electric field strength was observed only recently,[5–8]and the results were interpreted on the basis of the Marcus inverted region.[5–7]

The bell-shaped field dependence of the mobility supports the polaronic effect. On the other hand, the mobility normally does not obey an Arrhenius law. In many experiments the mobility scales with the reciprocal square of temperature, which suggests the importance of energetic disorder. Most experimental results in the last decade were interpreted using the Gaussian disorder model,[18] which describes the charge transport as a biased random walk among dopant molecules with Gaussian-distributed random site energies. Extensive numerical simulations based on the disorder model revealed that the phenomenological law of Gill's equation occurs in an intermediate region of the S-shaped field dependence of the mobility.[1,18] The bell-shaped field dependence of the mobility is also reported to arise due to the inclusion of positional disorder.[8] Furthermore, pure positional disorder results in mobilities that decrease with increasing field strength over the entire range of fields.[19] In the disorder model energetic disorder arises from charge-dipole or local van der Waals interactions.[19–30] Moreover, it is assumed that charge-carrier hopping to the adjacent sites is given by the Miller-Abrahams expression rather than the Marcus rate equation.[18,31] The Miller-Abrahams expression was originally proposed to describe impurity hopping in semiconductors.[31] On the other hand, the Marcus rate equation appeared in small polaron hopping theory, in which the hopping particle is a charge associated with molecular distortion which results from a charge-phonon interaction.[17] In this paper, we describe the hopping motion of charges in energetically disordered materials according to the Marcus rate equation. In most of experiments the mobilities depend on temperature T as $\log \mu \propto 1/T^2$, but in some measurements Arrhenius behavior is observed.[8,20] Both phenomena are inherent in our model where the polaron effect is combined with the disorder model. There are only a few examples of work done in this direction. In one example the mobilities are shown to obey Gill's law in the limit of large reorganization energy over a wide range of the field strength due to the long range nature of the charge-dipole interactions.[4] In another example, the origin of the compensation temperature at which the mobility becomes field independent is investigated by simulation with the Marcus rate equation.[32]

The mobility is obtained from the time-of-flight (TOF) measurements where photogenerated charge carriers cross a film of thickness L under an applied field E_0. The transit time $t_{\mathrm{tr.}}$ gives the mobility through $\mu = L/(E_0 t_{\mathrm{tr.}})$. In order to obtain analytical expressions, we consider the hopping motion of charge carriers on one-dimensional chains and calculate the mean first passage time. The mean first passage time corresponds to the transit time of the TOF experiments. Certainly, the one-dimensional model is an oversimplification at weak fields, due to the appearance of many loops which are energetically favorable compared to the direct short path. However, most of the analytical theories on transport through disordered media were restricted to one-dimensional systems.[33–37] Since predictions from the disorder model have been largely made by Monte Carlo simulations, analytical theories are still useful, especially to understand the roles of the polaron effect and the energetic disorder in determining the mobility.

The structure of the paper is as follows. In Sec. II the formulation of the theory is presented. In Sec. III the mobility is formulated in terms of the mean first passage time. In Sec. IV mobility in the absence of disorder is reviewed. In Sec. V an analytical expression of the mobility in the presence of energetic disorder is obtained in the limit of large reorganization energy. In Sec. VI the mobility, without any restrictions on the reorganization energy, is derived. Our theory is compared to the experimental results in Sec. VII. Section VIII is devoted to conclusions.

II. MARCUS RATE EQUATION AND ENERGETIC DISORDER

We consider charge transport across a sample of width $L = Nl$, where l is the mean interdopant spacing and $N+1$ is the number of sites. The charge transport from the site denoted by i to its adjacent site $i \pm 1$ is described by the Marcus theory (see Fig. 1). According to the Marcus rate equation, the transition probability is given by[10]

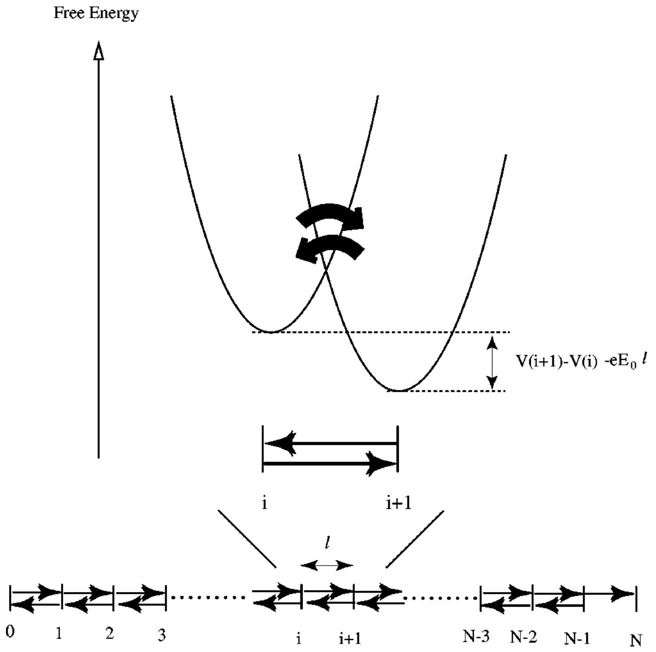

FIG. 1. Schematic representation of our theoretical model of one-dimensional charge transport among $N+1$ lattice sites. A perfectly reflecting boundary condition is imposed on site 0, and a perfectly absorbing boundary condition is imposed on site N. Each transition rate is described by the Marcus rate equation, for which a transition takes place at the intersection of the two parabolic free-energy curves.

$$W_{i \to i\pm 1} = \frac{2\pi}{\hbar} J^2 \frac{1}{\sqrt{4\pi E_r k_B T}} \times \exp\left[-\frac{[V(i\pm 1) - V(i) \mp eE_0 l + E_r]^2}{4E_r k_B T} \right], \tag{2.1}$$

where $\hbar$ represents the Planck constant divided by 2π, k_B is the Boltzmann constant, J is the transfer integral, $V(i)$ is the site energy in the absence of an external electric field, and E_r is the reorganization energy. The reorganization energy is twice the polaron binding energy. $E_r \sim 0.3$ eV is a rough estimate of the intramolecular relaxation in doped organic molecules. Since the site energy appears in the Marcus theory as an energy difference $V(i+1) - V(i)$, only the fluctuating component contributes to the transition rate when $\langle V(i+1) \rangle = \langle V(i) \rangle$. Thus, without loss of generality, $V(i)$ denotes the fluctuating component of a site energy whose sample average is zero: $\langle V(i) \rangle = 0$.

Charge carriers in disordered organic materials are believed to be highly localized at the site of doped molecules.[1] The site energy fluctuates statistically from site to site because the molecules are embedded in different environments. An inhomogeneous broadening of absorption and fluorescence spectra is a signature of such energy disorder.[1] A Gaussian distribution of the density of states is commonly assumed, because the energy fluctuation depends on large degrees of freedom, each varying randomly. One of the sources of the local energy difference, typically of the order ~ 0.1 eV, results from the electronic polarization. The localized charge causes a fast electronic polarization of surrounding molecules. The induced dipoles in the vicinity of the charged molecule create a local variation of the potential.[1] The local energy disorder of the Gaussian energy distribution can be characterized by

$$\langle V(i)V(j)\rangle = \sigma_L^2 \delta_{ij}, \tag{2.2}$$

where $\sigma_L^2 \sim 0.1$ eV and δ_{ij} is Kronecker's delta. In addition to the above local energy disorder, there is a considerable amount of evidence that the energy disorder depends on the permanent dipole moment of the dopant molecule as well as that of the host organic material.[25–29] The distribution of permanent dipoles generates fluctuations in the electrostatic potential due to the charge-dipole interactions,

$$V(i) = e\int_{EV} d\mathbf{r}\mathbf{P}(\mathbf{r})\cdot\frac{\mathbf{r}_i - \mathbf{r}}{|\mathbf{r}_i - \mathbf{r}|^3}, \tag{2.3}$$

where e is the charge of the carrier, $\mathbf{P}(\mathbf{r})$ is the dipole moment at the position $\mathbf{r}$, and $\mathbf{r}_i$ is the position of the charge. EV denotes that the region occupied by the charged dopant molecule which is assumed to be spherical with radius a_0 is excluded when calculating the spatial integration. Due to the long-range nature of the charge-dipole interactions, the site energy has spatial correlations. The spatial correlations of site energies due to the charge-dipole interactions can be calculated in the same way as in the calculation of the Marcus reorganization energy due to the charge-dipole interactions.[10] If ϵ denotes the dielectric constant of the doped organic materials, the fluctuation-dissipation theory in the mean-field approximation leads to

$$\langle \mathbf{P}_{\alpha}(\mathbf{r})\mathbf{P}_{\beta}(\mathbf{r}')\rangle = \frac{k_B T}{4\pi}\left(1-\frac{1}{\epsilon}\right)\delta_{\alpha\beta}\delta(\mathbf{r}-\mathbf{r}'), \tag{2.4}$$

where α and β is introduced to represent the Cartesian components of $\mathbf{P}$, and $\delta_{\alpha\beta}$ denotes Kronecker's delta, $\delta_{\alpha\beta}=1$ if $\alpha=\beta$ and $\delta_{\alpha\beta}=0$ if $\alpha\neq\beta$. Using the definition of $V(i)$ [Eq. (2.3)], together with Eq. (2.4), for the isotropic materials[10] we obtain

$$\langle V(i)V(j)\rangle = e^2 k_B T\left(1-\frac{1}{\epsilon}\right)\left(\frac{1}{a_0}\delta_{ij} + \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}(1-\delta_{ij})\right), \tag{2.5}$$

where $(1-\delta_{ij})$ should be regarded as zero if $i=j$, despite the multiplication of the divergent function. When the sample dielectric constant comes mainly from the permanent dipoles of the doped molecules, Debye's formula can be applied,[38] which in our case is written as

$$1-\frac{1}{\epsilon} = \frac{4\pi}{3}c\frac{p^2}{k_B T}, \tag{2.6}$$

where c is the molecular concentration (molecules/cm^3) of the doped molecules with the permanent dipole moment p. Then, the site energy correlation can be written as[4]

$$\langle V(i)V(j)\rangle = \frac{4\pi}{3}ce^2p^2\left(\frac{1}{a_0}\delta_{ij} + \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}(1-\delta_{ij})\right). \tag{2.7}$$

Some other models of energy disorder due to charge-dipole interactions were also proposed.[25–29] In general, both types of energetic disorder, the local disorder induced by the electronic polarization and the long-range disorder due to the permanent dipoles, are present. Hence the correlation of site energies can be written as

$$\langle V(i)V(j)\rangle = \sigma^2\left(\delta_{ij} + \frac{a}{|i-j|l}(1-\delta_{ij})\right), \tag{2.8}$$

where $a = a_0\sigma_d^2/\sigma^2, \sigma^2 = \sigma_L^2 + \sigma_d^2$, and $\sigma_d^2 = e^2 k_B T(1-1/\epsilon)/a_0$ in terms of the dielectric constant of doped materials, or $\sigma_d^2 = 4\pi c e^2 p^2/(3a_0)$ in terms of the dipole moment of the doped molecule. In the above treatment we adopt the continuum model to evaluate the electrostatic potential due to the permanent dipoles. Some deviation from the continuum model is observed for a molecular model of a solvent.[39] For simplicity any deviation due to short-range interactions is assumed to be completely local and isotropic, as shown in Eq. (2.2). The phenomenological parameter a includes the contribution of such local disorder relative to the long-range disorder derived from the continuum model.

III. MOBILITY: FORMAL EXPRESSION

We consider a segment of a linear chain with $N+1$ sites, which are numbered from 0 to N. The length of the chain is $L=Nl$. The hopping motion is described by a one-step process where charge transfer is allowed only between adjacent sites. We suppose that at site 0 there is a perfectly reflecting boundary and at site N a perfectly absorbing boundary is imposed (see Fig. 1).The drift mobility μ is defined by

$$\mu \equiv \frac{lN}{\tau_{\mathrm{mft}}E_0}, \tag{3.1}$$

where the mean first passage time τ_{mft} of carriers starting from the reflecting edge at site 0 should correspond to the transit time in TOF experiments. τ_{mft} is most easily derived through the adjoint equation to the master equation of the one step process.[40] The result is given by[40–42]

$$\tau_{\mathrm{mft}} = \sum_{i=0}^{N-1}\frac{1}{W_{i\to i+1}} + \sum_{i=1}^{N-1}\sum_{k=0}^{i-1}\prod_{j=k}^{i-1}\frac{W_{j+1\to j}}{W_{j\to j+1}}\frac{1}{W_{i\to i+1}}. \tag{3.2}$$

A similar factor appeared in the expression of the drift velocity and the diffusion constant of a periodic one-dimensional hopping model.[43] With the aid of a detailed balance condition,

$$\frac{W_{j+1\to j}}{W_{j\to j+1}}=\exp\left(-\frac{V(j)-V(j+1)+eE_0l}{k_BT}\right), \tag{3.3}$$

Eq. (3.2) is simplified to[40,42]

$$\tau_{\mathrm{mft}}=\sum_{i=0}^{N-1}\sum_{j=0}^{i}\exp\left(-\frac{eE_0jl}{k_BT}\right)\times\exp\left(-\frac{V(i-j)-V(i)}{k_BT}\right)\frac{1}{W_{i\to i+1}}. \tag{3.4}$$

For a system having a translational invariance for any correlations of site energies with a finite correlation length smaller than a system size of N sites, the summation with respect to each site is equivalent, and we can introduce the sample average $\langle\cdots\rangle$ for τ_{mft}/N:

$$\frac{\tau_{\mathrm{mft}}}{N}=\left\langle\sum_{j=0}^{N-1}\exp\left(-\frac{eE_0jl}{k_BT}\right)\times\exp\left(-\frac{V(N-1-j)-V(N-1)}{k_BT}\right)\frac{1}{W_{N-1\to N}}\right\rangle. \tag{3.5}$$

Recently, the ensemble average was exactly evaluated for a transition rate of Miller-Abrahams type and for the large reorganization energy limit of the Marcus rate equation, by assuming a certain model of site energy correlations.[44] The mobility is sensitive to the transition probability of the elementary hopping process. In this paper, we choose the physically most plausible form of the transition probability, namely, the Marcus rate equation [Eq. (2.1)]. After introducing dimensionless quantities

$$\overline{E}_0\equiv\frac{eE_0l}{k_BT},\quad \overline{V}(i)\equiv\frac{V(i)}{k_BT},$$

$$\overline{E}_r\equiv\frac{E_r}{k_BT},\quad \overline{\mu}=\frac{\hbar\sqrt{4\pi E_rk_BT}}{2\pi J^2}\frac{k_BT}{el^2}\mu,$$

$$\overline{\sigma^2}=\frac{\sigma^2}{(k_BT)^2},\quad \overline{a}=\frac{a}{l}, \tag{3.6}$$

we arrive at the fundamental equation for our later analysis:

$$\overline{\mu}=\frac{1}{\sum_{m=0}^{N-1}\overline{E}_0\exp(-\overline{E}_0m)\left\langle\exp\left[-\overline{V}(N-1-m)+\overline{V}(N-1)+\frac{\{\overline{V}(N)-\overline{V}(N-1)-\overline{E}_0+\overline{E}_r\}^2}{4\overline{E}_r}\right]\right\rangle}. \tag{3.7}$$

In order to calculate the mobility, the summation as well as the ensemble average should be taken. The ensemble average will be calculated analytically. The numerical calculation was also performed by generating a correlated Gaussian distribution with suitable correlation functions to the energies of 5000 sites, for which the square-root method was employed.[45] Subsequently, the average is taken for 50000 runs. The mobility thus calculated was used to confirm the accuracy of the analytical solutions.

IV. MOBILITY IN THE ABSENCE OF DISORDER

Before investigating charge transport under the influence of random potentials, mobility in the absence of random potentials is summarized in this section. In the absence of random potentials the summation in Eq. (3.7) is easily performed, yielding[17]

$$\overline{\mu}=\exp\left(-\frac{\overline{E}_r}{4}-\frac{\overline{E}_0^2}{4\overline{E}_r}\right)\frac{\sinh(\overline{E}_0/2)}{\overline{E}_0/2}. \tag{4.1}$$

For a large reorganization energy $\overline{E}_0<\overline{E}_r$, the above equation reduces to the well-known formula due to Bagley:[46]

$$\overline{\mu}=\exp\left(-\frac{\overline{E}_r}{4}\right)\frac{\sinh(\overline{E}_0/2)}{\overline{E}_0/2}. \tag{4.2}$$

The above expressions are nothing but the difference between the enhanced rate of hopping in the forward direction due to an electric-field reduction of the activation energy, and the decreased rate of transfer in the reverse direction. It should also be noted that the increase in mobility with field strength at high fields is more moderate in the result of the full Marcus model compared to Bagley's expression. This tendency of the result from the Marcus model is especially true for smaller reorganization energies (polaron binding energies). For very small reorganization energies even a negative field dependence can be predicted from the Marcus model. This phenomenon can be interpreted on the basis of the Marcus inverted region, where the charge-transfer rates for hops to lower energies decrease for sufficiently high fields. Incidentally, the external field dependence turns out to be weak compared with that in the presence of random potentials. In the following sections, we will show a strong field dependence due to the presence of random potentials in comparison with the above formulas.

V. MOBILITY FOR LARGE REORGANIZATION ENERGY

For a large reorganization energy, we approximate the transition probability as

$$W_{N-1\rightarrow N}\simeq\frac{2\pi}{\hbar}J^2\frac{1}{\sqrt{4\pi E_r k_B T}}\exp\left[-\frac{E_r}{4k_BT}-\frac{V(N)-V(N-1)-eE_0 l}{2k_BT}\right]. \tag{5.1}$$

When $V(i)$ is a Gaussian process, a linear combination of Gaussian processes is a Gaussian process, and after a cumulant expansion Eq. (3.7) can be written as

$$\bar{\mu}=\frac{\exp\left(-\frac{\bar{E}_r-2\bar{E}_0}{4}\right)}{\sum_{m=0}^{N-1}\bar{E}_0\exp\left[-\bar{E}_0 m+\frac{1}{2}\left\langle\left\{\frac{\bar{V}(N)+\bar{V}(N-1)}{2}-\bar{V}(N-1-m)\right\}^2\right\rangle\right]}. \tag{5.2}$$

The mobility is expressed in terms of correlations of the energy disorder. Now we evaluate Eq. (5.2) by introducing explicit forms of the correlations.

A. Local energy disorder

For local energy disorder,

$$\langle\bar{V}(i)\bar{V}(j)\rangle=\bar{\sigma}^2\delta_{ij}, \tag{5.3}$$

in the thermodynamic limit Eq. (5.2) is reduced to

$$\bar{\mu}=\frac{\exp\left(-\frac{\bar{E}_r+\bar{\sigma}^2-2\bar{E}_0}{4}\right)}{2\sinh(\bar{E}_0/2)+\exp\left(\frac{\bar{\sigma}^2-\bar{E}_0}{2}\right)}\frac{\sinh(\bar{E}_0/2)}{\bar{E}_0/2}. \tag{5.4}$$

The above equation coincides with the recent result of Cordes *et al.*[44] The zero-field mobility is derived from Eq. (5.4) as

$$\bar{\mu}|_{\bar{E}_0=0}=\exp\left(-\frac{\bar{E}_r+3\bar{\sigma}^2}{4}\right). \tag{5.5}$$

For a large reorganization energy the Arrhenius law should hold in addition to the algebraic weak-temperature dependence. However, even when the reorganization energy is dominant in the transition rate, $\bar{E}_r\gg\bar{\sigma}^2$, there exists a certain range of disorder $\bar{E}_r\geqslant\bar{\sigma}^2\geqslant\bar{E}_r/3$ where $\log\bar{\mu}\propto 1/T^2$ behavior dominates compared to $\log\bar{\mu}\propto 1/T$ behavior.

B. Long-range energy disorder

In the presence of charge-dipole interactions, the correlation of $\bar{V}(i)$ is obtained from Eq. (2.8) as

$$\langle\bar{V}(i)\bar{V}(j)\rangle=\bar{\sigma}^2\left(\delta_{ij}+\frac{\bar{a}}{|i-j|}(1-\delta_{ij})\right). \tag{5.6}$$

This model was first studied by Dunlap *et al.* by approximating $W_{N-1\rightarrow N}$ as a constant value in Eq. (3.5).[4] Therefore, our treatment in this section can be regarded as a refinement of their theory, taking into account all of the site energy correlations properly. In the thermodynamic limit Eq. (5.2) becomes

$$\bar{\mu}=\frac{\exp\left(-\frac{\bar{E}_r+\bar{\sigma}^2(1-\bar{a})-2\bar{E}_0}{4}\right)}{\bar{E}_0\left[1+\exp\left(\frac{\bar{\sigma}^2(1+\bar{a})}{2}-\bar{E}_0\right)\left\{\sum_{m=0}^{\infty}\exp\left(-\bar{E}_0 m-\bar{\sigma}^2\bar{a}\frac{2m+3}{2(m+1)(m+2)}\right)\right\}\right]}. \tag{5.7}$$

It should be noted that the exponential function in the summation appearing in the denominator can be approximated as $\exp(-\bar{E}_0 m)$ for $\bar{E}_0\gg 3\bar{\sigma}^2\bar{a}/4$. Therefore, for strong external fields we have the approximate expression

$$\bar{\mu}=\frac{\exp\left(-\frac{\bar{E}_r+\bar{\sigma}^2(1-\bar{a})-2\bar{E}_0}{4}\right)}{\bar{E}_0\left[1+\exp\left(\frac{\bar{\sigma}^2(1+\bar{a})-\bar{E}_0}{2}\right)\frac{1}{2\sinh(\bar{E}_0/2)}\right]}. \tag{5.8}$$

When the random potential has no spatial correlations, the above equation reduces to Eq. (5.4) in the limit of $a\rightarrow 0$. As the value of $\overline{\sigma}^2\overline{a}$ increases, the second term in $-\overline{E}_0 m-\overline{\sigma}^2\overline{a}(2m+3)/[2(m+1)(m+2)]$ cannot be neglected in Eq. (5.7). For $\overline{E}_0 \gg 5\overline{\sigma}^2\overline{a}/24$, we take the first term in the summation, and for the rest we again approximate $-\overline{E}_0 m-\overline{\sigma}^2\overline{a}(2m+3)/[2(m+1)(m+2)]$ as $-\overline{E}_0 m$. In this way, the next order approximation is obtained as

$$\overline{\mu}=\frac{\exp\left(-\dfrac{\overline{E}_r+\overline{\sigma}^2(1-\overline{a})-2\overline{E}_0}{4}\right)}{\overline{E}_0\left[1+\exp\left(\dfrac{\overline{\sigma}^2(1+\overline{a})}{2}-\overline{E}_0\right)\left\{\exp\left(-\dfrac{3\overline{\sigma}^2\overline{a}}{4}\right)+\dfrac{\exp(-\overline{E}_0/2)}{2\sinh(\overline{E}_0/2)}\right\}\right]}. \tag{5.9}$$

A completely different approximate formula is possible when $\overline{E}_0\sim\overline{\sigma}^2\overline{a}$.We approximate the sum by the integral

$$\sum_{m=0}^{\infty}\exp\left(-\overline{E}_0 m-\overline{\sigma}^2\overline{a}\frac{2m+3}{2(m+1)(m+2)}\right)\sim\int_0^{\infty}\exp\left(-\overline{E}_0 x-\frac{\overline{\sigma}^2\overline{a}}{x+1}\right)dx. \tag{5.10}$$

Then, by further approximating the integrand by the Gaussian function, we obtain

$$\overline{\mu}=\frac{\exp\left(-\dfrac{\overline{E}_r+\overline{\sigma}^2(1-\overline{a})-2\overline{E}_0}{4}\right)}{\overline{E}_0\left[1+\sqrt{\dfrac{\pi}{\overline{E}_0}\sqrt{\dfrac{\overline{\sigma}^2\overline{a}}{\overline{E}_0}}}\exp\left(-2\sqrt{\overline{E}_0\overline{\sigma}^2\overline{a}}+\dfrac{\overline{\sigma}^2(1+\overline{a})}{2}\right)\right]}. \tag{5.11}$$

The same zero-field mobility is obtained from Eqs. (5.8) and (5.9) as

$$\overline{\mu}|_{\overline{E}_0=0}=\exp\left(-\frac{\overline{E}_r+\overline{\sigma}^2(3+\overline{a})}{4}\right). \tag{5.12}$$

In general, the summation appearing in the denominator of Eq. (5.7) can be divided into a finite summation and a remainder which can be approximated as $\Sigma\exp(-\overline{E}_0 m)$; the finite summation part does not contribute in the zero-field limit. As a result Eq. (5.12) should be regarded as the exact zero-field limit of Eq. (5.7).

Now we compare our expressions with those of Dunlap *et al.*[4] They obtained $\overline{\mu}\propto\exp(-\overline{\sigma}^2)$ in the low-field limit.[4] The slightly different coefficient of 3/4 appeared in our expression, [Eq. (5.12)] instead of their value of 1. It should also be noted that our expressions for the field dependence are much more complicated than the simple analytical expressions of Dunlap *et al.*, which clearly predicted Gill's law mathematically. The difference arises simply because Dunlap *et al.* neglected some energy correlations when $W_{N-1\rightarrow N}$ in Eq. (3.5) was assumed to be a constant.[4] Note that the assumption of the constant forward rate in the ensemble average is appropriate for a transition rate of Miller-Abrahams type in the strong external field, because under such conditions most forward transitions are toward energetically lower sites and the corresponding transition rates are a constant according to the Miller-Abrahams expression. The mobility expression depends on the form of the transition rate assumed, and the elegant theory of Dunlap *et al.* may be better applied for a transition rate of Miller-Abrahams type.

VI. MOBILITY: EXACT RESULT

When the transition probability is described by the full Marcus rate equation, [Eq. (2.1)], the cumulant expansion introduced in Sec. V is not an efficient method to calculate the sample average. It is more convenient to rewrite Eq. (3.7) in terms of variables $\overline{V}_d\equiv\overline{V}(N)-\overline{V}(N-1)$ and $\overline{V}_m\equiv\overline{V}(N-1-m)-\overline{V}(N-1)$, and introduce the distribution function explicitly,

$$P(\overline{V}_d,\overline{V}_m)=\begin{cases}\dfrac{1}{2\pi\sqrt{|\Sigma|}}\exp\left(-\dfrac{\overline{V}_d^2\Sigma_{\{1,1\}}^{-1}+2\overline{V}_d\overline{V}_m\Sigma_{\{1,2\}}^{-1}+\overline{V}_m^2\Sigma_{\{2,2\}}^{-1}}{2}\right) & \text{for } (m\neq 0)\\[2ex] \dfrac{1}{\sqrt{2\pi\langle\overline{V}_d^2\rangle}}\exp\left(-\dfrac{\overline{V}_d^2}{2\langle\overline{V}_d^2\rangle}\right) & \text{for } (m=0),\end{cases} \tag{6.1}$$

where $\Sigma^{-1}_{\{i,j\}}$ is the $\{i,j\}$ component of the inverse matrix of

$$\Sigma=\begin{pmatrix} \langle \overline{V}_d^2\rangle & \langle \overline{V}_d\overline{V}_m\rangle \\ \langle \overline{V}_d\overline{V}_m\rangle & \langle \overline{V}_m^2\rangle \end{pmatrix}, \tag{6.2}$$

and $|\Sigma|$ denotes the determinant of the matrix Σ. Then the mobility is given by the Gaussian integral which is solvable analytically,

$$\overline{\mu}=\frac{\exp\left[-\frac{\overline{E}_r}{4}\left(1-\frac{\overline{E}_0}{\overline{E}_r}\right)^2\right]}{\sum_{m=0}^{N-1}\overline{E}_0\exp(-\overline{E}_0 m)f_m}, \tag{6.3}$$

where

$$f_m=\int_{-\infty}^{\infty}d\overline{V}_d\int_{-\infty}^{\infty}d\overline{V}_m P(\overline{V}_d,\overline{V}_m)$$

$$\times\exp\left[-\overline{V}_m+\frac{1}{2}\left(1-\frac{\overline{E}_0}{\overline{E}_r}\right)\overline{V}_d+\frac{\overline{V}_d^2}{4\overline{E}_r}\right]. \tag{6.4}$$

After performing the Gaussian integration, we find that the variance is renormalized by the factor $1-\Sigma_{\{1,1\}}/(2\overline{E}_r)$ due to the interplay between the distribution of potentials and the potential shape:

$$f_m=\frac{1}{\sqrt{1-\frac{\Sigma_{\{1,1\}}}{2\overline{E}_r}}}\exp\left\{\frac{1}{2}\frac{1}{1-\frac{\Sigma_{\{1,1\}}}{2\overline{E}_r}}\left[\frac{\Sigma_{\{1,1\}}}{4}\left(1-\frac{\overline{E}_0}{\overline{E}_r}\right)^2 -\Sigma_{\{1,2\}}\left(1-\frac{\overline{E}_0}{\overline{E}_r}\right)+\Sigma_{\{2,2\}}-\frac{|\Sigma|}{2\overline{E}_r}\right]\right\}. \tag{6.5}$$

As long as we know the correlation matrix of the energy disorder, we can calculate the mobility by substituting Eq. (6.5) into Eq. (6.3). It is interesting to note that the mobility is proportional to the renormalization factor $\overline{\mu} \propto\sqrt{1-\Sigma_{\{1,1\}}/(2\overline{E}_r)}$. The mobility decreases as the ratio of the variance of the random energy difference to the reorganization energy, $\langle\overline{V}_d^2\rangle/(2\overline{E}_r)$, increases. When the variance of the disorder is comparable to the reorganization energy, $\langle\overline{V}_d^2\rangle\sim 2\overline{E}_r$, the mobility tends to zero. This is due to the fact that we consider an infinite length of the one-dimensional chain. Specifically, the mobility is inversely proportional to the ensemble average of the waiting time needed for the hopping transition. Due to the detailed balance condition, only a single waiting time is involved in each sequence of the random work accomplished by the absorption at the edge—as we can see from Eq. (3.5), where the summation is divided by a single transition rate. The condition that the width of the site energy distribution is the same as the reorganization energy, i.e., the width of the parabolic free energy curve, implies that the sample average of the waiting time appearing for each sequence of the random work tends to infinity. The sample average by the Gaussian distribution assumes an infinite number of site energies resulting from the migration of charge carriers between an infinite number of sites in the chain. For a finite chain length the mobility decreases monotonically to a limiting value of zero as the disorder strength increases.

A. Local energy disorder

For local energy disorder, described by Eq. (5.3), the mobility in the thermodynamic limit follows from Eqs. (6.3) and (6.5),

$$\overline{\mu}=\sqrt{\frac{\overline{\sigma}^2}{\overline{\sigma}_r^2}}\frac{\exp\left[-\frac{\overline{E}_r+\overline{\sigma}_r^2}{4}\left(1-\frac{\overline{E}_0}{\overline{E}_r}\right)^2\right]}{2\sinh(\overline{E}_0/2)+\exp\left[\overline{\sigma}_r^2\left(\frac{2+\overline{E}_0/\overline{E}_r-3\overline{\sigma}^2/\overline{E}_r}{4}\right)-\frac{\overline{E}_0}{2}\right]}\frac{\sinh(\overline{E}_0/2)}{\overline{E}_0/2}, \tag{6.6}$$

where the renormalized variance is defined by $\overline{\sigma}_r^2\equiv\overline{\sigma}^2/(1-\overline{\sigma}^2/\overline{E}_r)$. The zero-field mobility is obtained as

$$\overline{\mu}|_{\overline{E}_0=0}=\sqrt{\frac{\overline{\sigma}^2}{\overline{\sigma}_r^2}}\exp\left(-\frac{\overline{E}_r+3\overline{\sigma}^2}{4}\right). \tag{6.7}$$

The dominant temperature dependence comes from the exponential function. When $3\overline{\sigma}^2$ is larger than $\overline{E}_r$, a better straight line is obtained if one plots the logarithm of the mobility against $1/T^2$ instead of $1/T$. It is also clear that the distinction becomes difficult as $\overline{\sigma}^2$ becomes smaller. Moreover, the normalization factor of the mobility adds an additional temperature factor to the real mobility: $\mu\propto\overline{\mu}/(k_BT)^{3/2}$. Because of this algebraic factor, even though a straight line is found for the semilogarithmic plot of the dimensionless mobility $\overline{\mu}$ versus $1/T$, the line is bent when the logarithm of the real mobility μ is plotted against $1/T$, and the semilogarithmic plot of μ versus $1/T^2$ tends to look straight.

B. Long-range energy disorder

In terms of the long-range correlations due to the charge-dipole interactions [Eq. (5.6)], the renormalized variance can be defined as

$$\overline{\sigma_r^2} \equiv \frac{\overline{\sigma^2}}{1-\dfrac{\overline{\sigma^2}(1-\bar{a})}{\bar{E}_r}}, \tag{6.8}$$

and the mobility in the thermodynamic limit is expressed as

$$\bar{\mu} = \frac{\sqrt{\dfrac{\overline{\sigma^2}}{\overline{\sigma_r^2}}}}{\bar{E}_0} \frac{\exp\left[-\dfrac{\bar{E}_r+\overline{\sigma_r^2}(1-\bar{a})}{4}\left(1-\dfrac{\bar{E}_0}{\bar{E}_r}\right)^2\right]}{1+\exp\left[\overline{\sigma_r^2}\left\{1-(1-\bar{a})\dfrac{2(1-\bar{E}_0/\bar{E}_r)+(3+\bar{a})\overline{\sigma^2}/\bar{E}_r}{4}\right\}-\bar{E}_0\right]f}, \tag{6.9}$$

where

$$f \equiv \sum_{m=0}^{\infty} \exp\left[-\bar{E}_0 m - \frac{\overline{\sigma_r^2}\,\bar{a}}{2(m+1)(m+2)}\left\{(2m+3)\frac{\overline{\sigma^2}}{\overline{\sigma_r^2}}+\frac{\bar{E}_0}{\bar{E}_r}-\frac{\overline{\sigma^2}}{2\bar{E}_r}\frac{\bar{a}}{(m+1)(m+2)}\right\}\right]. \tag{6.10}$$

As before, the summation is easily performed for the lowest order approximation, $f \sim \Sigma \exp(-\bar{E}_0 m)$,

$$\bar{\mu} = \frac{\sqrt{\dfrac{\overline{\sigma^2}}{\overline{\sigma_r^2}}}}{\bar{E}_0} \frac{\exp\left[-\dfrac{\bar{E}_r+\overline{\sigma_r^2}(1-\bar{a})}{4}\left(1-\dfrac{\bar{E}_0}{\bar{E}_r}\right)^2\right]}{1+\exp\left[\overline{\sigma_r^2}\left\{1-(1-\bar{a})\dfrac{2(1-\bar{E}_0/\bar{E}_r)+(3+\bar{a})\overline{\sigma^2}/\bar{E}_r}{4}\right\}-\bar{E}_0/2\right]\dfrac{1}{2\sinh(\bar{E}_0/2)}}, \tag{6.11}$$

which goes to Eq. (6.6) in the limit of no spatial correlations, $\bar{a}\rightarrow 0$. As in Sec. V the next-order approximation is given by

$$f \sim \exp\left[-\frac{\overline{\sigma_r^2}\,\bar{a}}{4}\left(3\frac{\overline{\sigma^2}}{\overline{\sigma_r^2}}+\frac{\bar{E}_0}{\bar{E}_r}-\frac{\overline{\sigma^2}\,\bar{a}}{4\bar{E}_r}\right)\right]+\frac{\exp(-\bar{E}_0/2)}{2\sinh(\bar{E}_0/2)}, \tag{6.12}$$

together with Eq. (6.9). In the zero-field limit Eqs. (6.11) and (6.12) reduce to the same expression. The approximation can be improved by increasing the number of terms in the finite summation in *f*. Moreover, it is obvious that the approximate expression gives the same mobility in the zero-field limit regardless of the number of terms in the finite summation. Thus the zero-field mobility should be given by

$$\bar{\mu}|_{\bar{E}_0=0} = \sqrt{\frac{\overline{\sigma^2}}{\overline{\sigma_r^2}}}\exp\left[-\frac{\bar{E}_r+\overline{\sigma_r^2}(3+\bar{a})\{1-(1-\bar{a})\overline{\sigma^2}/\bar{E}_r\}}{4}\right]. \tag{6.13}$$

The zero-field mobility has a remarkably simple form even in the presence of long-range disorder.

VII. RESULTS AND DISCUSSION

In this section, we study some aspects of the analytical expressions of the mobility. The most general expression, Eq. (6.9) with Eq. (6.10), was derived in Sec. VI and its zero-field limit was obtained in Eq. (6.13). In Fig. 2 we compare the analytical expressions with the numerical evaluation of Eq. (3.7). When the dimensionless field strength is equal to 1, $\bar{E}_0=1$, the real field strength is $E_0 \sim 3\times 10^5$ V/cm for the lattice separation $l=10$ Å at room temperature. A numerical evaluation is performed according to two procedures; one uses the Marcus expression for its elementary process, and the other is based on a limiting form valid for a large reorganization energy [Eq. (5.1)]. In both cases the agreement between the analytical expressions and the numerical evaluation is excellent; our analytical expressions are fully reliable. In the same figure, we also present the results in the absence of disorder [Eqs. (4.1) and (4.2)]. The mobility is smaller in the presence of disorder compared to that in its absence, because the mobility is limited by the small transition rates or equivalently the large barriers created by the energetic disorder. At weak fields charge transport is more influenced by energetic disorder than at higher fields, so that as the field strength decreases the mobility is considerably lowered from that in the absence of disorder. The field dependence of the mobility is very weak in the absence of energetic disorder, while the mobility increases considerably with field strength in the presence of disorder. The plot of $\log \bar{\mu}$ against $\sqrt{\bar{E}_0}$ exhibits a linear dependence over a wide range in the intermediate region of the field strength, even though the correlation length is small: $\bar{a}=0.1$. Nevertheless, our expression is well approximated by Gill's law. As shown in Fig. 3, the linear region shifts toward a lower field strength by increasing $\bar{a}$, which is the charac-

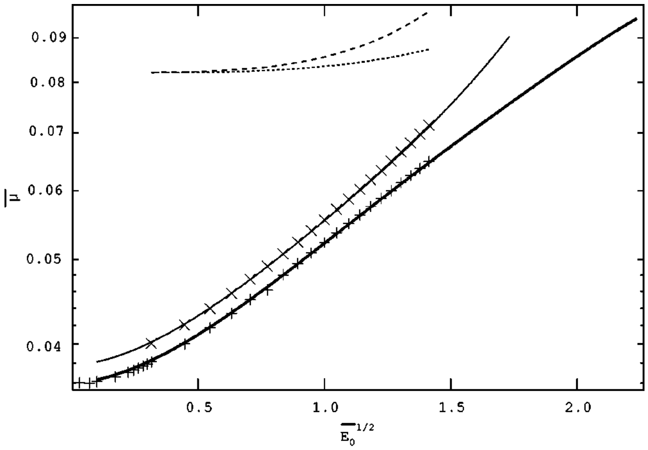

FIG. 2. Semilogarithmic plot of the dimensionless mobility against the square root of the dimensionless electric-field strength. The parameters are $\bar{E}_r=10.0$,$\bar{\sigma}=1.0$, and $\bar{a}=0.1$. The lower thick solid line is the analytical result of Eq. (6.9) with Eq. (6.10). The + symbols on the line are the numerical evaluation of Eq. (3.7). The upper thin solid line is the analytical result of Eq. (5.7), and the × symbols on the line are the corresponding numerical results. The short dashed line is the mobility from the Marcus rate equation without energetic disorder [Eq. (4.1)]. The long dashed line is Bagley's mobility [Eq. (4.2)].

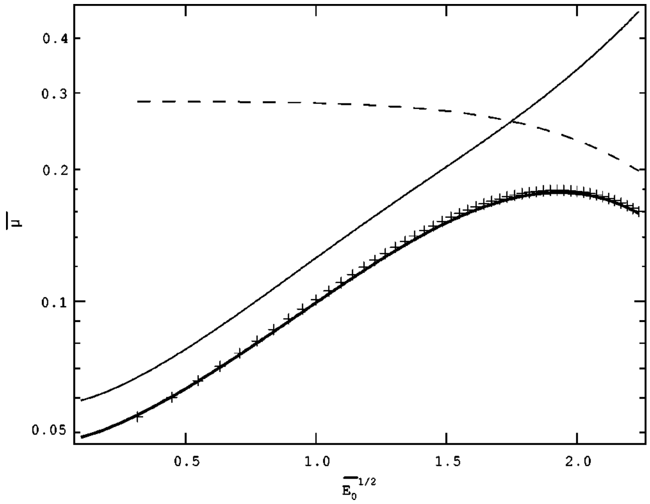

FIG. 4. Semilogarithmic plot of the dimensionless mobility against the square root of the dimensionless electric-field strength. The parameters are $\bar{E}_r=5.0$,$\bar{\sigma}=2.0$, and $\bar{a}=0.2$. The lower thick solid line is the analytical result of Eq. (6.9) with Eq. (6.10). The + symbols on the line are the numerical evaluation of Eq. (3.7). The upper thin solid line is the analytical result of Eq. (5.7). The dashed line is the mobility from the Marcus rate equation without energetic disorder [Eq. (4.1)].

teristic length of the long-range spatial correlations. The straight line of log $\bar{\mu}$ against $\sqrt{\bar{E}_0}$ is apparently the signature of the influence of energetic disorder on hopping motion described by the Marcus rate equation. The further introduction of spatial correlations moves the region described by the straight line. Here the long-range correlation due to the interaction of the charge with the permanent dipole moments is not essential for a linear relation between log $\bar{\mu}$ and $\sqrt{\bar{E}_0}$. In our expressions $\bar{\mu}$ is a complicated function of $\bar{E}_0$, which can be approximated by Gill's law in a wide range of field strengths. Note that Dunlap *et al.* derived the mathematical relation log $\bar{\mu}\propto\sqrt{\bar{E}_0}$, which arises purely from the interaction of the charge with randomly distributed permanent dipoles.[4] Since the forward transition rate in the ensemble average is simplified as a constant in their theory,[4] their mechanism is appropriate for a rate of Miller-Abrahams type, as mentioned in Sec. V B.

At high electric fields the mobility obtained from the Marcus rate equation saturates, in sharp contrast to the result obtained from its limiting form valid for large reorganization energy. In general, a plot of the mobility against the electric-field strength is S shaped when the hopping motion is described by the Marcus rate equation under the influence of energetic disorder; upon increasing the applied field, the mobility initially increases, and then a region of log $\bar{\mu}\approx\sqrt{\bar{E}_0}$ appears, which is followed by saturation. For a small reorganization energy the mobility even decreases after saturation, as shown in Fig. 4. If we approximate the Marcus rate equation by its limiting form valid for a large reorganization energy, such a decrease of the mobility with field strength is never observed. In the absence of disorder the mobility based on the Marcus rate equation depends weakly on the field strength, and then drops with increasing field strength. The decrease of the mobility with field strength is the signature of the Marcus inverted region, where the activation energy increases with a decreasing free-energy change. On the other hand, the increase of the mobility with field strength in a

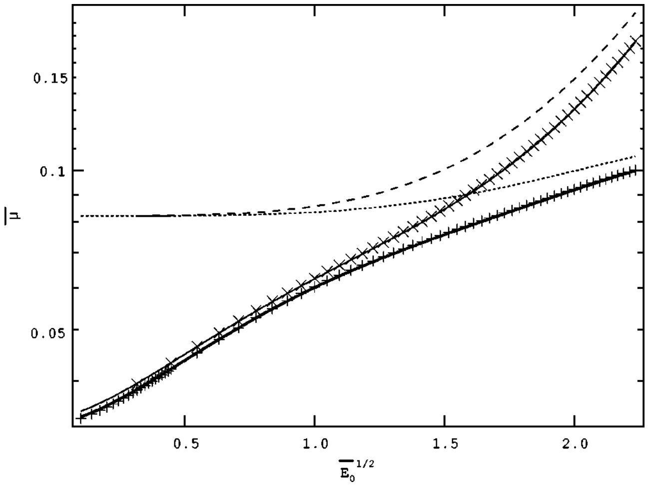

FIG. 3. Semilogarithmic plot of the dimensionless mobility against the square root of the dimensionless electric-field strength. The parameters are $\bar{E}_r=10.0$,$\bar{\sigma}=1.0$, and $\bar{a}=0.5$. The lower thick solid line is the analytical result of Eq. (6.9) with Eq. (6.10). The + symbols on the line are the numerical evaluation of Eq. (3.7). The upper thin solid line is the analytical result of Eq. (5.7), and the × symbols on the line are the corresponding numerical results. The short dashed line is the mobility from the Marcus rate equation without energetic disorder [Eq. (4.1)]. The long dashed line is Bagley's mobility [Eq. (4.2)].

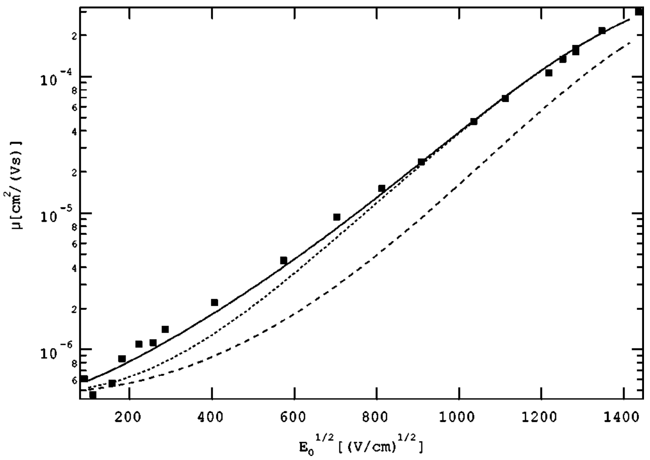

FIG. 5. Semilogarithmic plot of the mobility $[\mathrm{cm}^2/(\mathrm{V\,s})]$ against the square root of the electric-field strength $[(\mathrm{V/cm})^{1/2}]$. Points are the measured data of the mobility for 50 mol %DEH-doped polycarbonate at 298 K taken from Ref. 30. The solid line is the analytical result of Eq. (6.9) with Eq. (6.10) with $E_r=0.3$ eV, $\sigma=0.072$ eV, $a_0=4$ Å, $l=10$ Å, and $\mu_0=0.0067$ $\mathrm{cm}^2/(\mathrm{V\,s})$. The long dashed line is the first approximate expression [Eq. (6.11)]. The short dashed line is the second approximate expression [Eq. (6.9)] with Eq. (6.12).

relatively low-field region originates from energetic disorder. The mobility increases faster with field strength for large energetic disorder, while a prominent decrease of the mobility with field strength is found for small reorganization energy.

So far we have examined the general feature of the field dependence of the mobility. We now investigate whether our analytical expression of the mobility can fit the experimental data by the reasonable choice of parameter values. In Fig. 5 the measured mobility for 50-mol % DEH (hydrazone)-doped polycarbonate, taken from the paper by Schein *et al.*[30] is fitted by Eq. (6.9) with Eq. (6.10). The parameters are $E_r=0.3$ eV, $\sigma=0.072$ eV, $a_0=4$ Å, $l=10$ Å, and $\mu_0=0.0067$ $\mathrm{cm}^2/(\mathrm{Vs})$, where $\mu_0\equiv 2\pi J^2 e l^2/(\hbar\sqrt{4\pi E_r k_B T_r}\, k_B T_r)$ with the room temperature $T_r=300$ K. Since the ratio of the energy disorder by the electronic polarization to that by the charge-dipole interactions is ambiguous, we assume that both contributions are comparable, $\sigma_d^2/\sigma^2=1/2$. Our theoretical curve is consistent with the data throughout the whole field range. The long dashed line represents the first approximate expression [Eq. (6.11)], which has the same functional form as that of the local energy disorder. Roughly speaking, the long dashed line shows a good correlation with experimental data. The linear relation between $\log\mu$ and $\sqrt{E_0}$ arises because of the complicated combination of exponential functions of E_0. When Dunlap *et al.* analyzed the same experimental data, an excellent fit was obtained from the expression which reduces mathematically to Gill's law.[4] In their derivation, the interaction of the charge carrier and the randomly distributed permanent dipoles is a necessary ingredient for the field dependence.[4] The role of such correlations is diminished in our analysis because we use the full Marcus equation for the forward transition rate in the ensemble average needed to obtain the mobility [Eq. (3.5)]. On the other hand, in their theory[4] it was approximated as a constant independent of random site energy. The E_r value chosen for the fitting is reasonable for the reorganization energy due to vibronic relaxation. By using the method commonly used in this field the distance between adjacent dopant molecules can be estimated by assuming a cubic lattice, $l=(1/c)^{1/3}\sim 9.9$ Å, where c is the number density of DEH molecules,[47] and $c=9.6\times10^{20}$ molecules/cm^3. A similar distance can be obtained from the mean nearest-neighbor distance for the uniform distribution of dopant molecules outside the region of spherical volume whose radius is the contact distance $2a_0$. Since the nearest-neighbor distribution is given by[48] $P(r)=cv'(r)\exp[-cv(r)]$, where $v(r)\equiv 4\pi r^3/3$ and $v'(r)\equiv 4\pi r^2$ is its derivative, the mean nearest-neighbor distance, $\int_{2a_0}^{\infty} rP(r)dr$ becomes $[3/(4\pi c)^{1/3}]\exp[cv(2a_0)]\Gamma[1/3,cv(2a_0)]\sim 14.5$ Å, where $\Gamma(a,z)$ is the incomplete gamma function. The value of l thus estimated is a little larger than that for the cubic lattice. We may conclude that the distance of $l\sim(10\text{–}15)$Å is reasonable. From the definition, $\sigma_d^2=4\pi c e^2 p^2/(3a_0)$ and the dipole moment of DEH,[20] $p\sim 3$ D, we estimate $\sigma_d\sim 0.05$ eV. The other expression $\sigma_d^2=e^2 k_B T(1-1/\epsilon)/a_0$ with $\epsilon\sim 3$ gives the larger value $\sigma_d\sim 0.24$ eV. The value for the fitting $\sigma=0.072$ eV is close to the lower bound. $J=0.42\times10^{-3}$ eV is obtained from $\mu_0=0.0067$ $\mathrm{cm}^2/(\mathrm{V\,s})$. By assuming a typical form of the transfer integral $J^2=J_0^2\exp[-\beta(l-2a_0)]$ with the values $J_0=50$ cm^{-1} and $\beta=1$ 1/Å, we find a slightly larger value $J=2.3\times10^{-3}$ eV, but the difference is within a range of error which arises from the uncertainties in the values of J_0 and β. Therefore, our parameter values for the fitting are in agreement with those estimated. In the same figure, the approximate expressions [Eqs. (6.11) and (6.9), with Eq. (6.12)], are also presented. They do not deviate significantly from the exact expression, which implies that the summation in the exact expression converges rather quickly.

As we already mentioned, a bell-shaped field dependence of the mobility has been reported.[5–8] We examine one of the recent results on this issue.[8] In Fig. 6 the measured mobility from the paper[8] by Hartenstein *et al.* is presented for 17-wt % EFTP doped polycarbonate at 298 K. The theoretical curve is calculated by Eq. (6.9) with Eq. (6.10), with the parameters $E_r=0.1$ eV, $\sigma=0.03$ eV, $a_0=5$ Å, $l=18$ Å, and $\mu_0=1.4\times10^{-4}$ $\mathrm{cm}^2/(\mathrm{V\,s})$. The curves from the approximated expressions are also presented in the same figure. The theoretical curves are consistent with the measured data. The result suggests that the decrease of the mobility with increasing field strength is in analogy to the Marcus inverted region.

In order to investigate more about the bell-shaped field dependence of the mobility, the temperature dependence of the mobility is presented in Fig. 7. The experimental data for temperatures of 357 and 268 K are taken from Ref. 8. Since the sample is the same as that in Fig. 6, the measured data at 298 K in Fig. 6 are also included in Fig. 7. The theoretical curves are calculated by Eq. (6.9) with Eq. (6.10) with the same parameters as those used to calculate the theoretical curves in Fig. 6 except for μ_0. By assuming $J^2=J_0^2\exp[-\beta(l-2a_0)]$ with the values $J_0=50$ cm^{-1} and $\beta=1 1/$Å we estimate $J=1.14\times10^{-4}$ eV, which is larger

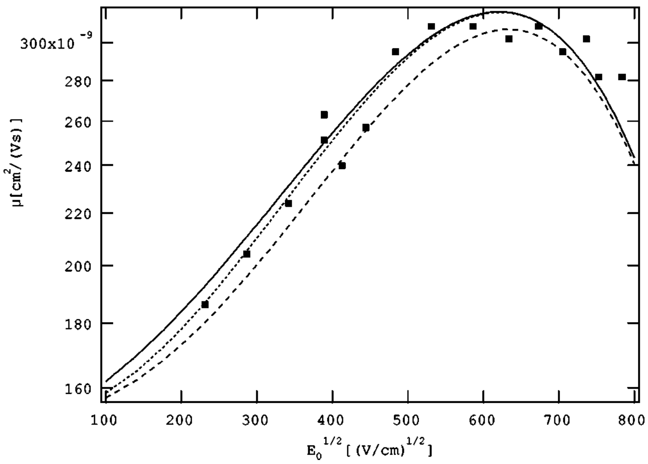

FIG. 6. Semilogarithmic plot of the mobility $[\mathrm{cm}^2/(\mathrm{V\,s})]$ against the square root of the electric-field strength $[(\mathrm{V/cm})^{1/2}]$. Points are the measured data of the mobility for 17 wt%EFTP-doped polycarbonate at 298 K taken from Ref. 8. The solid line is the analytical result of Eq. (6.9) with Eq. (6.10), with $E_r = 0.1$ eV,$\sigma = 0.03$ eV,$a_0 = 5$ Å,$l = 18$ Å, and $\mu_0 = 1.4 \times 10^{-6}$ cm^2/(V s). The long dashed line is the first approximate expression, [Eq. (6.11)]. The short dashed line is the second approximate expression [Eq. (6.9)], with Eq. (6.12).

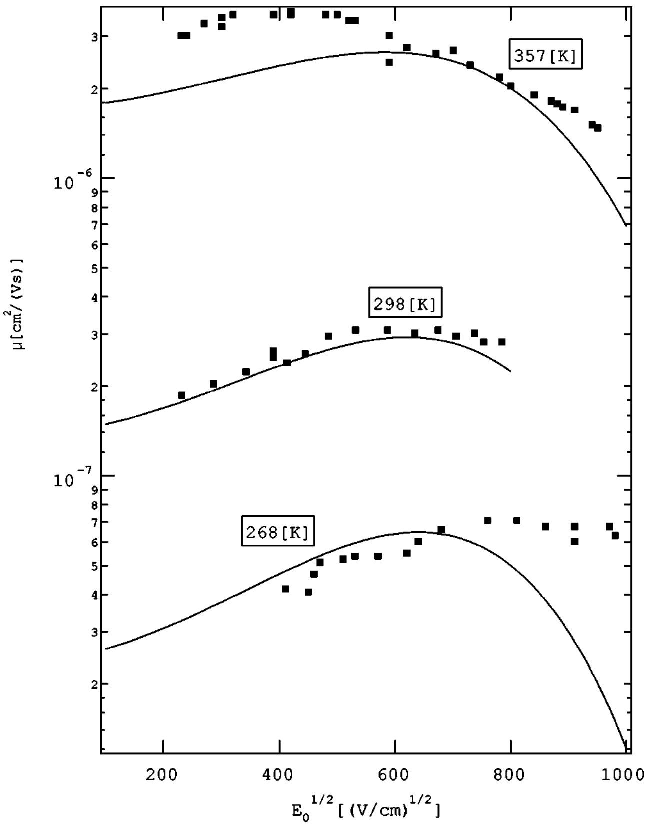

FIG. 7. Semilogarithmic plot of the mobility $[\mathrm{cm}^2/(\mathrm{V\,s})]$ against the square root of the electric-field strength $[(\mathrm{V/cm})^{1/2}]$. Points are the measured data of the mobility for 17 wt% EFTP-doped polycarbonate at various temperatures taken from Ref. 8. The solid line is the analytical result of Eq. (6.9) with Eq. (6.10). For details on the parameters, see the text. The temperature is 357,298, and 268 K from top to bottom.

than $J = 4.6 \times 10^{-6}$ eV obtained from $\mu_0 = 1.4 \times 10^{-6}$ cm^2/(V s), the parameter value used in Fig. 6. The smaller parameter value suggests that the charge transfer is limited by the vibronic relaxation; the corresponding concept for reactions in liquid is referred to as the dynamical solvent control, where solvent fluctuation is the limiting step.[49,50] By assuming an Arrhenius-type temperature dependence for the vibronic relaxation rate, $\mu_0 = 1.1 \exp[-E_a/(k_B T)] \times [\mathrm{cm}^2/(\mathrm{V\,s})]$, with an activation energy $E_a = 0.35$ eV, the theoretical curves are calculated by Eq. (6.9), with Eq. (6.10), and compared to the measured field-dependent mobility at different temperatures in Fig. 7. The theoretical curves are in overall accordance with the measured data at each temperature except at high-field strength, where our theoretical curve drops faster with the field strength compared to the measured data. The reason for this may be due to the neglect of high-frequency quantum modes of vibrational states in the Marcus rate equation, which tend to maintain an activationless situation even in an inverted region.[11,51] In the normal region, specifically given by the condition $eE_0 l < E_r$, where the mobility increases with the field strength, the contribution of high-frequency modes is negligibly small in practice.[11,51] The charge-transfer rate increases if high-frequency quantum modes are excited in the reactant state because in this case tunneling barriers become lower; however, the thermal population of excited vibrational states decreases strongly with increasing quanta involved in those states.[11,51] The situation is different in the inverted region, $eE_0 l > E_r$. The particular high-frequency modes in the product state ensures that the transition remains approximately activationless; the mobility is underestimated in the inverted region when the large quantum intramolecular vibrations are ignored.[11,51] Therefore, it is important to take such high-frequency modes into account in the inverted region. Research in this direction is in progress. The activation energy of 0.35 eV corresponds to 8.1 kcal/mol; this value is close to the activation energy of the dielectric relaxation rate of monoalcohols with long chain lengths in the pure state, such as[52] octanol-1: ~8.4 kcal/mol. The value is a little smaller than the activation energy for the isomerization reaction of stilbenes: ~15 kcal/mol.[53] The origin of the activation process may be the torsional motion of the dopant molecule associated with charge transfer; the activation barrier of 0.35 eV found by our fitting procedure is reasonable for such a process. Our theory agrees well with not only the field dependence but also with the temperature dependence of the measured mobility, which indicates that the polaron model with energetic disorder may be realistic and the appearance of a maximum in the mobility at high fields can be considered as evidence of a transition to an inverted region.

VIII. CONCLUSION

In this paper we have theoretically investigated the applicability of the Marcus rate equation to describe charge transport in disordered molecular solids. In the solid state the reorganization energy, due to the reorientation of dipole molecules in the environment, is absent. Under such circumstances, the Marcus rate equation is equivalent to the small polaron model, where the reorganization energy is twice the polaron binding energy. In a one-dimensional analysis an exact analytical expression of the field-dependent mobility is derived for charge transport by using the Marcus rate equation under the influence of energetic disorder. The most general expression for the Gaussian energetic disorder is given by Eq. (6.3) with Eq. (6.5). For the problem of charge transport in molecularly doped polymers, two types of Gaussian disorder are considered. One is the local energy disorder due to the electronic polarization, for which the mobility is given by Eq. (6.6). The other is the long-range energy disorder due to the charge-dipole interactions. In the presence of charge-dipole interactions the mobility is obtained as Eq. (6.9) with Eq. (6.10). The phenomenological Gill's relation occurs in the intermediate region of the S-shaped field dependence of the mobility. The slope of $\ln \mu$ against $\sqrt{E_0}$ is mainly governed by the reorganization energy and the variance of the energetic disorder. On the other hand, the region of $\ln \mu \propto \sqrt{E_0}$ shifts by changing the characteristic length of the long-range correlations. Therefore, Gill's law does not necessarily imply long-range correlations, and such correlations are needed for a qualitative fit to the experimental data. In the presence of energetic disorder the mobility is limited by the escape from energetically deep traps. As the energy disorder relative to the potential gradient due to the external field decreases, the mobility increases toward values without energetic disorder whose field dependence is much weaker. The way mobility increases with field strength is not trivial, and it depends on the transition rate. The mobility derived on the basis of the Marcus rate equation is well approximated by Gill's law in a wide range of field strengths. Within reasonable values of the parameters, our theoretical expressions are consistent with the experimental data, which exhibit Gill's relation over a wide range of field strengths, $10^4 \sim 10^6$ V/cm. Our theoretical expressions are also in accordance with the measured data on the field dependence of the mobility, which show that the mobility increases with increasing field strength at low fields, passes through a maximum, and then decreases with increasing field strength. Such a decrease of the mobility with increasing field strength is never observed if it is derived on the basis of an approximate rate expression valid in the limit of the large reorganization energy, as done by Dunlap *et al.*,[4] since the transition rate is an increasing function of the field strength. The increase of the mobility with field strength is mainly due to energetic disorder, whereas the appearance of a maximum in the mobility at high fields can be regarded as an evidence for a transition to the Marcus inverted region.

ACKNOWLEDGMENTS

We would like to thank Dr. T. Kato for useful discussions in the early stages of the present work. We are indebted to Dr. A. V. Barzykin for critical comments and for useful discussions on the mobility derived on the basis of the Miller-Abrahams rate expression in the presence of energetic disorder. It is our pleasure to acknowledge Professor S. D. Baranovskii for discussions on the occasion of the PCPM01 conference (Tsukuba, March 14–16 2001), and for providing us with his reprints.

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