Calculation of the temperature-dependent mobility transition
for small-polaron hopping in one dimension

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(Received 31 January 1991)

Exact expressions for the dc mobility of a small polaron hopping on a one-dimensional disordered lattice are derived. Several features are observed: (i) linear response is recovered in the limit of vanishing applied fields, in spite of the presence of random biases, (ii) the nondecaying part of the polaron memory function does not contribute to the dc mobility for a diagonally disordered system, and (iii) for a Gaussian distribution of site energies, the mobility vanishes below a transition temperature T_0. It is shown that at a temperature T near the transition point, the mobility scales as $\mu \sim (T - T_0)^{1/2}$.

I. INTRODUCTION

If electron-phonon interactions in a solid are strong enough to induce polaron formation, the resultant charge transport properties will be greatly affected by static disorder arising from lattice defects and impurities. This behavior is expected because polaron formation substantially reduces the electronic bandwidth. Consequently, the tendency of static disorder to localize electronic states may be enhanced. Nevertheless, after several decades of work on polaron-based theoretical explanations for low-mobility solids,[1-15] there have been few attempts to explicitly determine the role of static disorder on polaron transport.[3,11-15] In most applications, polaron transport is suitably described by the hopping of a single polaron on a lattice of regularly spaced sites. Observables are calculated from the solution to a master equation for the evolution of the site probabilities. Such studies have proved useful in analyzing experimental data on exciton mobility in molecular crystals.

However, there are numerous experimental systems, such as conducting polymers, in which strong electron-phonon coupling coexists with static disorder. In such a case, the predominant effect of the static disorder is to induce spatially random fluctuations in the hopping rates between adjacent lattice sites. In the most general case, however, the hopping rates will possess no special symmetry. The rate to hop between site m and site $m+1$, $R_{m,m+1}$, will not necessarily equal the backward rate $R_{m+1,m}$. The resultant master equation will correspond to the so-called random bias problem. While much theoretical effort has been expended to calculate the transport properties of the master equation in special cases such as the symmetric bond-disordered ($R_{m+1,m} = R_{m,m+1}$) or site-disordered ($R_{m,m-1} = R_{m,m+1}$) master equations,[16-19] few have investigated the random bias problem. Recently, progress has been made in the development of expansion methods in order to solve the ran-

dom bias problem.[20] Nevertheless, as with the bond-disordered and site-disordered master equations, exact expressions for the diffusion coefficient are only known in one dimension.[21] In the present application we explicitly include strong phonon interactions in the random bias problem. Our analysis of the transport properties is based on the exact method of Derrida.[21] From our analysis, we are able to show that there is a temperature-dependent transition beyond a critical value of the static site-diagonal disorder. In the vicinity of the transition, the mobility scales as $(T - T_0)^{1/2}$. These results are significant in light of recent experiments by Devreux and Lecavelier,[22] who have observed anomalous diffusion in the conducting polymer poly(pyrrole perchlorate) as a function of temperature. They attribute their observations to a crossover from two-dimensional (2D) dynamics as the temperature is lowered; interchain hopping processes diminish as the temperature decreases. Consequently, at sufficiently low temperatures, the conductivity is carried almost exclusively along single strands of the polymer. The vanishing of the mobility that we show exists in the one-dimensional disordered polaron problem as a function of temperature suggests that a two-dimensional treatment of this problem could be directly applicable to the vanishing of the mobility along a certain axis of the crystal as in the case of the Devreux-Lecavelier experiment.[22]

This paper is organized as follows. We review the basic site-disordered electron-phonon Hamiltonian in Sec. II and calculate the mobility in Sec. III. The polaron memory function is analyzed in Sec. IV, and the temperature dependence of the mobility is obtained in Sec. V.

II. POLARON HAMILTONIAN

The polaron Hamiltonian describes a single electron moving on a periodic lattice. The electron is linearly coupled to the lattice vibrations, such that

$$H = \sum_m \varepsilon_m a_m^\dagger a_m + \sum_m V_{m,m+1} a_m^\dagger a_{m+1} + V_{m+1,m} a_{m+1}^\dagger a_m$$
$$+ \sum_{q,m} g_q \omega_q e^{iqm}(b_{-q}^\dagger + b_q) a_m^\dagger a_m + \sum_q \omega_q(b_q^\dagger b_q + \tfrac{1}{2}) .$$

$$(2.1)$$

The operator $a_m^\dagger$ creates an electron at lattice site m with energy ε_m. The nearest-neighbor off-diagonal matrix element $V_{m,m+1}$ causes the electron to move from site to site. The operator $b_q^\dagger$ creates a phonon with wave number q and energy $\hbar\omega_q$. The electron-phonon coupling constant g_q determines how strongly an electron at site m is coupled to the displacement of a vibrational mode with frequency ω_q. We adopt units in which the constant $\hbar$ has been set equal to 1. If the time for the electron to move from one site to a neighboring site is long compared with to the time for vibrational relaxation, then electron transport may be envisioned as sequence of hops, each to be rapidly followed by a vibrational distortion of the local environment.[3] The transport of the polaron is the motion of the electron and this self-induced lattice distortion. In the limit of vanishing off-diagonal matrix elements $V_{m,m+1}$, the polaron is created by the operator $A_m^\dagger$, which is defined as[7]

$$A_m^\dagger = a_m^\dagger \exp\left[\sum_q g_q e^{iqm}(B_{-q}^\dagger - B_q)\right] .$$

$$(2.2)$$

The operator $B_q^\dagger$ creates phonons of a displaced harmonic oscillator with frequency ω_q. In terms of the operators $A_m^\dagger$ and $B_q^\dagger$, the Hamiltonian of expression (2.1) is[7]

$$H = H_0 + \mathcal{V} ,$$

$$H_0 = \sum_m (\varepsilon_m - E_p) A_m^\dagger A_m + \sum_q \omega_q(B_q^\dagger B_q + \tfrac{1}{2}) ,$$

$$\mathcal{V} = \sum_m V_{m,m+1}$$
$$\times \exp\left[\sum_q g_q e^{iqm}(1-e^{iq})(B_{-q}^\dagger - B_q)\right] A_m^\dagger A_{m+1}$$
$$+ V_{m+1,m} \exp\left[-\sum_q g_q e^{iqm}(1-e^{iq})(B_{-q}^\dagger - B_q)\right]$$
$$\times A_{m+1}^\dagger A_m ,$$

$$(2.3)$$

where E_p, the polaron binding energy, is equal to $\sum_q |g_q|^2 \omega_q$. In (2.3) we have deliberately separated the diagonal (H_0) and off-diagonal $(\mathcal{V})$ parts of the Hamiltonian for later reference. For most theories of transport via small polaron hopping, calculations of the mobility are effectively determined by the nearest-neighbor hopping rate $R_{m,m+1}$ in the site basis.[3] That is,

$$R_{m,m+1} = \lim_{t\to\infty} \int_0^t dt' W_{m,m+1}(t') .$$

$$(2.4)$$

The integration in (2.4) is over the memory function $W_{m,m+1}(t)$, where

$$W_{m,m+1}(t) = 2V_{m,m+1}^2 \exp\left[-\beta\frac{(\varepsilon_n - \varepsilon_m)}{2}\right] \exp\left[-4\sum_q |g_q|^2 \sin^2\left[\frac{\mathbf{q}\cdot\mathbf{a}}{2}\right] \coth\left[\beta\frac{\omega_q}{2}\right]\right]$$
$$\times \exp\left[4\sum_q |g_q|^2 \sin^2\left[\frac{\mathbf{q}\cdot\mathbf{a}}{2}\right] \operatorname{csch}\left[\beta\frac{\omega_q}{2}\right]\cos(\omega_q t)\right] \cos[(\varepsilon_{m+1} - \varepsilon_m)t] ,$$

$$(2.5)$$

β is $1/kT$, and a is the lattice constant. Expression (2.5) is the result of a second-order time-dependent perturbation in $\mathcal{V}$. The mobility may be determined from the solution to the master equation with nearest-neighbor hopping rates as given by (2.4):

$$\frac{d}{dt} P_m = -(R_{m+1,m} + R_{m-1,m}) P_m$$
$$+ R_{m,m+1} P_{m+1} + R_{m,m-1} P_{m-1} ,$$

$$(2.6)$$

where P_m is the probability of finding the polaron on site m. Because we are interested in dc quantities entirely, we use the Pauli master equation as opposed to the generalized master equation.[9] From (2.6) one may calculate the steady-state drift velocity v_d of an initially localized particle in the presence of a dc electric field E. The mobility is then determined from the ratio v_d/E in the limit that E tends to zero. If the system is ordered, the hopping rate is independent of the site label; $W_{m,m+1}(t) = W(t)$ and $R_{m,m+1} = R$, and the mobility is

$$\mu = \beta ea^2 R = \beta ea^2 \int_0^\infty dt\, W(t)$$

$$(2.7)$$

In utilizing expression (2.7) we are faced with a well-known dilemma. For the Hamiltonian (2.1) with linear electron-phonon interactions, the memory function $W(t)$ does not decay to zero at long times. Consequently, $W(\infty)\neq 0$, the integration in (2.7) diverges, and the dc mobility is infinite.[9] At this level of perturbation, the divergence may be associated with an unscattered contribution to transport from the polaron band.[2] Certainly it must be eliminated from (2.7) if a theory of polaron hopping is to be of any use. However, results vary considerably, depending upon the precise method in which the elimination is carried out. Several methods for dealing with this problem are more easily described if we introduce a modified memory function $W'(t)$, which is defined as the difference between $W(t)$ and $W(\infty)$. By definition then, $W'(t)$ decays to zero at long times. The memory function (2.5) can be written as the sum of two parts, a decaying part and a constant part,[9]

$$W(t) = W'(t) + W(\infty) .$$

$$(2.8)$$

In many theories of small-polaron hopping, $W(\infty)$ is discarded because the polaron band contribution to the mobility is smaller than the hopping contribution at temperatures of interest.[3,7,8] If the density of phonon states is three dimensional, the remaining integration of $W'(t)$ and the calculated mobility are finite.[3] A different treat-

ment is proposed in a theory by Silbey and Munn.[7] One contribution to the mobility is calculated from a perturbation in a site basis, which is carried out in a quantity that is the difference between $\mathcal{V}$ and its thermal average $\langle \mathcal{V} \rangle$. This procedure effectively extracts $W(\infty)$ from (2.7). A second contribution to the mobility is calculated from a perturbation in momentum space, and these two contributions are added together. In contrast, in a theory of Kenkre,[9] $W(\infty)$ is retained in the perturbation in $\mathcal{V}$ from a site basis. A finite mobility is obtained only by accounting for the memory-broadening effects of other processes. For example, it is possible that an effective broadening of the memory function is achieved in any system in which there is site-diagonal disorder. The analysis presented here will be based on the theory of Kenkre, where the perturbation is entirely from a site basis and $W(\infty)$ is explicitly retained. Our primary purpose is to determine, in the context of this theory, specifically how diagonal disorder influences the dc mobility.

III. CALCULATION OF THE dc MOBILITY

In order to obtain the dc mobility in one-dimension, we first calculate the steady-state drift velocity of a particle in an applied electric field. Following Derrida,[21] we consider a ring of N sites. We define the probability current j_m between sites m and $m+1$ as

$$j_m = -R_{m,m+1}P_m + R_{m+1,m}P_{m+1} \ . \tag{3.1}$$

At steady state, the current between any two sites is a constant $j_m = j$. The steady-state drift velocity of an initially localized particle v_d is

$$v_d = \lim_{t \to \infty} \sum_m am \frac{d}{dt} P_m(t) = aNj \ , \tag{3.2}$$

where N is the number of sites in the ring. Combining (3.2) with (3.1), we obtain an equation that can be successively iterated around the ring

$$P_m = \frac{R_{m+1,m}}{R_{m,m+1}} P_{m+1} - \frac{v_d}{Na} \frac{1}{R_{m,m+1}} \tag{3.3}$$

in order to obtain an expression for P_m in terms of v_d and the hopping rates. Making use of the fact that $\sum_m P_m = 1$, we find that

$$1 - \prod_{m=1}^{N} \frac{R_{m+1,m}}{R_{m,m+1}} = \frac{v_d}{a} \left[\left\langle \frac{1}{R_{1,2}} \right\rangle + \left\langle \frac{R_{2,1}}{R_{1,2}R_{2,3}} \right\rangle \left\langle \frac{R_{2,1}R_{3,2}}{R_{1,2}R_{2,3}R_{3,4}} \right\rangle + \cdots + \left\langle \frac{R_{2,1}R_{3,2} \cdots R_{N,N-1}}{R_{1,2}R_{2,3}R_{3,4} \cdots R_{N-1,N}} \right\rangle \right] , \tag{3.4}$$

where the angular brackets denote a configurational average. We do not mean to single out specific sites by the subscripts on $R_{1,2}$, $R_{2,3}$, and $R_{3,4}$, etc. in the averages in (3.4), but rather to indicate that the average is over $R_{m,n}$, where n is greater than m by 1. For example,

$$\left\langle \frac{1}{R_{1,2}} \right\rangle = \left\langle \frac{1}{R_{2,3}} \right\rangle = \frac{1}{N} \sum_{m=1}^{N} \frac{1}{R_{m,m+1}} \ . \tag{3.5}$$

At this point it is important to specifically include a dc electric field E. We assume that the only effect of the field is to alter the site-energy difference between nearest neighbors by the amount Δ, where $\Delta = eEa$. Also, for convenience we write the hopping rate as a product of Boltzmann factors and a function G, which depends on the absolute value of the difference in site-energies:

$$R_{m,m+1} = \left[\exp\left[-\beta \frac{(\varepsilon_{m+1} - \varepsilon_m)}{2} \right] \exp\left[-\beta \frac{\Delta}{2} \right] \right]$$
$$\times G_{m,m+1}(\varepsilon_{m+1} - \varepsilon_m - \Delta) \ , \tag{3.6}$$

where

$$G_{m,m+1}(\varepsilon_{m+1} - \varepsilon_m - \Delta) = 2V^2 \exp\left[-4 \sum_q |g_q|^2 \sin^2\left[\frac{\mathbf{q \cdot a}}{2} \right] \coth\left[\beta \frac{\omega_q}{2} \right] \right]$$

$$\times \int_0^{\infty} dt \exp\left[4 \sum_q |g_q|^2 \sin^2\left[\frac{\mathbf{q \cdot a}}{2} \right] \operatorname{csch}\left[\beta \frac{\omega_q}{2} \right] \cos(\omega_q t) \right] \cos[(\varepsilon_{m+1} - \varepsilon_m - \Delta)t] \ . \tag{3.7}$$

After substituting (3.7) into (3.4), we see that the product on the left-hand side of (3.4) vanishes for an infinite system:

$$\lim_{N \to \infty} \prod_{m=1}^{N} \frac{R_{m+1,m}}{R_{m,m+1}} = \prod_{m=1}^{N} \frac{G_{m+1,m} \exp\left[-\beta \frac{\Delta}{2} \right] \exp\left[-\beta \frac{(\varepsilon_{m+1} - \varepsilon_m)}{2} \right]}{G_{m,m+1} \exp\left[\beta \frac{\Delta}{2} \right] \exp\left[\beta \frac{(\varepsilon_{m+1} - \varepsilon_m)}{2} \right]}$$

$$= [\exp(-\beta\Delta)]^N = 0 \ . \tag{3.8}$$

If we assume that there is no correlation between the site energies, the N terms on the right-hand side of (3.4) may be written as follows:

$$\left\langle \frac{1}{R_{1,2}} \right\rangle = \left\langle \frac{\exp\left[\frac{\beta(\varepsilon_2 - \varepsilon_1)}{2}\right]}{G_{1,2}} \right\rangle \exp\left[-\frac{\beta\Delta}{2}\right], \qquad (3.9)$$

$$\left\langle \frac{R_{2,1}}{R_{1,2}R_{2,3}} \right\rangle = \left\langle \frac{\exp\left[\frac{\beta(\varepsilon_2 + \varepsilon_3)}{2}\right]}{G_{2,3}} \right\rangle$$
$$\times \left\langle \exp\left[-\frac{\beta\varepsilon_1}{2}\right] \right\rangle \exp\left[-\frac{\beta\Delta}{2}\right] \exp(-\beta\Delta), \qquad (3.10)$$

$$\left\langle \frac{R_{2,1}R_{3,2}}{R_{1,2}R_{2,3}R_{3,4}} \right\rangle = \left\langle \frac{\exp\left[\frac{\beta(\varepsilon_3 + \varepsilon_4)}{2}\right]}{G_{3,4}} \right\rangle$$
$$\times \left\langle \exp\left[-\frac{\beta\varepsilon_1}{2}\right] \right\rangle$$
$$\times \exp\left[-\frac{\beta\Delta}{2}\right] \exp(-2\beta\Delta), \qquad (3.11)$$

etc. Because these terms are identical except for the factors $\langle \exp(-\beta\varepsilon_1/2) \rangle$ and powers of $\exp(-\beta\Delta)$, the right-hand side of (3.4) is simply the sum of a geometric series. In the limit of an infinite number of lattice sites,

$$\mu = ea^2\beta \left[\left[\int_{-\infty}^{\infty} d\varepsilon_1 \rho(\varepsilon_1) \exp(-\beta\varepsilon_1)\right]\left[\int_{-\infty}^{\infty} d\varepsilon_1 \int_{-\infty}^{\infty} d\varepsilon_2 \rho(\varepsilon_1)\rho(\varepsilon_2) \frac{\exp\left[\frac{\beta(\varepsilon_2 + \varepsilon_1)}{2}\right]}{G_{1,2}(\varepsilon_2 - \varepsilon_1)}\right]\right]^{-1}, \qquad (3.14)$$

where we have written the lattice averages as integrals over the density of site energies $\rho(\varepsilon)$.

IV. THE NONDECAYING PART OF THE POLARON MEMORY FUNCTION

The symmetric function $G_{1,2}$ is sufficiently complex that the evaluation of (3.14) for arbitrary coupling and temperature is not straightforward. Many of the essential features, however, are easily explored in a high-temperature and/or high-coupling limit. In this limit, the decaying part of the memory function may be approximated by a Gaussian.[2] The nearest-neighbor memory function is of the form

$$W_{1,2}(t) = 2V^2 \exp\left[-\beta\frac{(\varepsilon_2 - \varepsilon_1)}{2}\right]$$
$$\times \exp(-\Gamma_1)[A \exp(\Gamma_2)\exp(-\alpha^2 t^2) + 1]$$
$$\times \cos[(\varepsilon_2 - \varepsilon_1)t], \qquad (4.1)$$

where A, Γ_1, Γ_2, and α are functions of temperature. In-

the expression for the drift velocity is

$$v_d = a \exp\left[\frac{\beta\Delta}{2}\right]\left[\left\langle \frac{\exp\left[\frac{\beta(\varepsilon_2 - \varepsilon_1)}{2}\right]}{G_{1,2}} \right\rangle\right.$$
$$+ \langle \exp(-\beta\varepsilon_1) \rangle \left\langle \frac{\exp\left[\frac{\beta(\varepsilon_2 + \varepsilon_1)}{2}\right]}{G_{1,2}} \right\rangle$$
$$\left. \times \frac{1}{\exp(\beta\Delta) - 1}\right]^{-1}. \qquad (3.12)$$

In the limit of small Δ, only the second term on the right-hand side of (3.12) is important. If we expand $\exp(\beta\Delta) - 1$ to linear order in Δ, we find that the drift velocity in a 1-D system for small electric fields is proportional to the field strength

$$v_d = a\beta\Delta \left[\langle \exp(-\beta\varepsilon_1) \rangle \left\langle \frac{\exp\left[\frac{\beta(\varepsilon_2 + \varepsilon_1)}{2}\right]}{G_{1,2}} \right\rangle\right]^{-1}. \qquad (3.13)$$

The linearity of the drift velocity with the electric field stands in stark contrast to Derrida's prediction of a velocity cutoff at low fields, a discrepancy which will be discussed further in Sec. V. Dividing both sides of (3.13) by E, and taking the limit as E approaches zero, we obtain an expression for the zero-field dc mobility,

tegrating (4.1), we obtain

$$G(\Omega) = V^2 \exp(-\Gamma_1)\left[A \exp(\Gamma_2)\frac{\sqrt{\pi}}{\alpha}\right.$$
$$\left. \times \exp\left[-\frac{\Omega^2}{4\alpha^2}\right] + 2\pi\delta(\Omega)\right], \qquad (4.2)$$

where $\Omega = \varepsilon_2 - \varepsilon_1$. The decaying and nondecaying parts of (4.1) give rise to the Gaussian $\exp(-\Omega^2/4\alpha^2)$ and the delta function $\delta(\Omega)$ in (4.2), respectively. In calculating the mobility from (3.14), however, we must integrate over the reciprocal of (4.2), $[G(\Omega)]^{-1}$. We note that $[G(\Omega)]^{-1}$ is proportional to an inverted Gaussian $\exp(\Omega^2/4\alpha^2)$, except for an abrupt deviation from this form in the shape of a downward-pointing spike at $\Omega = 0$. This is shown in Fig. 1. The spike is the reciprocal of a δ function $1/\delta(\Omega)$, and thus has an area of zero. It does not contribute to the integration in (3.14) for any well-behaved density of energies $\rho(\varepsilon)$. We see therefore that for any amount of site-energetic disorder in a one-
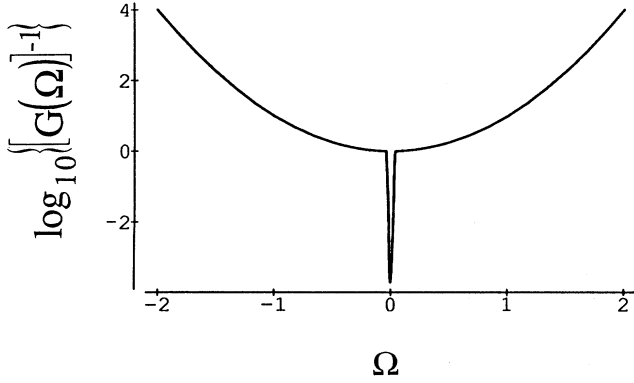
FIG. 1. Plot of $[G(\Omega)]^{-1}$ as a function of Ω for the case that $G(\Omega)$ is given by the form of expression (4.2). The contribution from $\delta(\Omega)$ is approximated in the figure by a narrow Gaussian. $\delta(\Omega)$ plays the role of a downward-pointing spike at $\Omega=0$ but does not contribute to the integration of $[G(\Omega)]^{-1}$ in (3.14). The units are arbitrary.

dimensional chain, the nondecaying part of the memory function, $W(\infty)$, makes no contribution to the mobility. This result is true, independent of our choice of a Gaussian form for (2.5). In order to further evaluate (3.14), we take $\rho(\varepsilon)$ to be a Gaussian distribution with variance σ^2. After performing the integrations in (3.14) with (4.2) and a Gaussian density of site energies, we find that the mobility is

$$\mu = \begin{cases} e^2 a^2 \beta V^2 \dfrac{\sqrt{\pi}}{\alpha^2} A \sqrt{\alpha^2 - \sigma^2} \exp(-\tfrac{3}{4}\beta^2\sigma^2) \\ \times \exp(\Gamma_2 - \Gamma_1), \quad \alpha \geq \sigma \\ 0, \quad \alpha < \sigma , \end{cases} \quad (4.3)$$

The disorder specifically enters expression (4.3) through σ in two places: under the radical, $\sqrt{\alpha^2 - \sigma^2}$ and in an exponential factor $\exp(-\tfrac{3}{4}\beta^2\sigma^2)$. The exponential factor suppresses the mobility at low temperatures, and arises simply from detailed balance. The Boltzmann factor in (2.5) reduces hopping rates from low energy to high energy, and enhances hopping rates in the opposite direction. Due to the sequential nature of transport in a one-dimensional chain, however, the smaller hopping rates dominate the mobility. Consequently, the mobility decreases as temperature is lowered because the smaller rates are reduced still further. The radical $\sqrt{\alpha^2 - \sigma^2}$ gives rise to a transition to zero mobility. If the disorder is increased so that σ approaches α, the mobility will vanish as $\sqrt{\alpha^2 - \sigma^2}$ tends to zero. This can be understood from the requirement of energy conservation. The width of the Gaussian function $\exp(-\Omega^2/4\alpha^2)$ is a measure of the availability of the phonon absorptions and emissions that can make up for the differences in site energies Ω. If the half-width $\sqrt{2}\sigma$ of the distribution of site energy differences is larger than the width of the Gaussian $\sqrt{2}\alpha$, some of the hopping rates will be suppressed be-

cause energy cannot be conserved through an exchange of phonons. A fraction of the bonds in the lattice will be effectively broken, which results in a vanishing of the dc mobility for a one-dimensional system. Thus the observed mobility transition is similar to one-dimensional percolation. We shall see below that because α decreases with decreasing temperature, there exists a temperature below which the dc mobility in a 1D lattice will be frozen out.

V. TEMPERATURE DEPENDENCE OF THE MOBILITY

In the case of electron-phonon coupling to a single optical-phonon branch, the functions A, Γ_1, Γ_2, and α in (4.1) have been determined elsewhere.[2,3] Therefore we will simply list the results and the assumptions on which the calculations are based. The optical-phonon frequency ω_q is centered at a frequency ω_0 with a bandwidth δ, which is narrow compared with kT. For a narrow phonon band, it is reasonable to assume a frequency-independent electron-phonon coupling constant g. The Gaussian approximation (4.1) applies when $2g^2 \operatorname{csch}(\beta\omega_0/2) \gg 1$. If the conditions $2g^2 \operatorname{csch}(\beta\omega_0/2)\delta^2 \ll \omega_0^2$, $\sigma/\omega_0 \ll 1$, and $\beta\delta \ll 1$ are also met, then the hopping rates will be dominated by processes in which the phonon number is conserved, and all other multiphonon transitions may be neglected. In such a case, $\alpha^2 = g^2 \operatorname{csch}(\beta\omega_0/2)\Theta\delta^2$, where the factor Θ is a dimensionless number of order unity which arises from the integration of the function $\sin^2(\mathbf{q}\cdot\mathbf{a}/2)$ over the density of phonon states. We take $\Theta=1$ in what follows. In addition,

$$A = \left[4\pi g^2 \operatorname{csch}\left[\beta\frac{\omega_0}{2}\right] \right]^{1/2} ,$$

$$\Gamma_1 = 2g^2 \coth\left[\beta\frac{\omega_0}{2}\right], \quad \Gamma_2 = 2g^2 \operatorname{csch}\left[\beta\frac{\omega_0}{2}\right] .$$

The difference

$$\Gamma_2 - \Gamma_1 = -2g^2 \tanh\left[\beta\frac{\omega_0}{4}\right] .$$

Substituting these expressions into (4.3) yields the mobility

$$\mu = e^2 a^2 \beta \frac{V^2}{2\delta^2} \left[\frac{g^2 \operatorname{csch}\left[\beta\dfrac{\omega_0}{2}\right]\delta^2 - \sigma^2}{\left[g^2 \operatorname{csch}\left[\beta\dfrac{\omega_0}{2}\right]\right]^3} \right]^{1/2}$$

$$\times \exp(-\tfrac{3}{4}\beta^2\sigma^2)\exp\left[-2g^2 \tanh\left[\frac{\beta\omega_0}{4}\right]\right] . \quad (5.1)$$

The usual Arrhenius temperature dependence of the polaron mobility arises from the factor

$$\exp\left[-2g^2 \tanh\left[\frac{\beta\omega_0}{4}\right]\right] .$$

The significant new feature in (5.1) is, however, the emergence of a threshold temperature for the transition to zero mobility. Even when $2g^2 \operatorname{csch}(\beta\omega_0/2) \gg 1$, the quantity $2g^2 \operatorname{csch}(\beta\omega_0/2)\delta^2$ may be greater than or less than σ^2, depending on the width of the optical-phonon band. Expanding

$$\left[g^2 \operatorname{csch}\left[\beta\frac{\omega_0}{2} \right]\delta^2 - \sigma^2 \right]^{1/2}$$

in a Taylor series about zero, we find near the transition point that

$$\mu \sim (T - T_1)^{1/2} \tag{5.2}$$

for $T > T_1$, where the transition temperature T_1 is given by

$$T_1 = \frac{\omega_0}{2k \ln\left[\dfrac{1 + \left[1 + \left[\dfrac{\sigma}{\sqrt{2}g\delta} \right]^4 \right]^{1/2}}{\left[\dfrac{\sigma}{\sqrt{2}g\delta} \right]^2} \right]} . \tag{5.3}$$

Although the mobility should still exhibit Arrhenius behavior at high temperatures, it will be predominantly determined by (5.2) as the temperature approaches T_1. An example of this behavior is shown in Fig. 2, where we have plotted the mobility as a function of inverse temperature when $\delta = 0.2\omega_0$ for the two cases: $\sigma = 0$ and ω_0. We see that when the disorder is large, the mobility quickly drops to zero around $T = \omega_0/2k$. We remind the reader, however, that the behavior at the transition point has been calculated under the assumption that the site-energy distribution is a Gaussian. If $\rho(\varepsilon)$ falls off faster than a Gaussian, the transition to zero mobility will never occur. By the same argument, if $\rho(\varepsilon)$ falls off more slowly than a Gaussian, the mobility will always be zero. Furthermore, only terms in which the total phonon number is conserved have been retained in deriving (5.1). By discarding terms in which the phonon number changes, we have effectively forbidden multiphonon transitions which allow energy conservation for a still larger amount of disorder. Hence the mobility will be substantially reduced at temperatures below T_1; however, it will not be
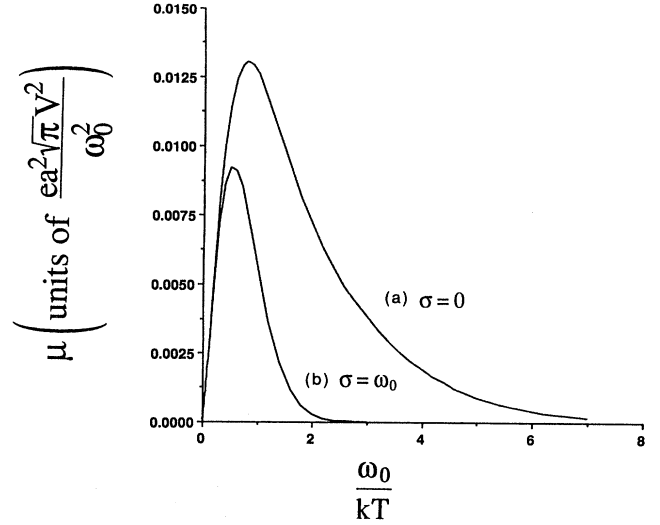
FIG. 2. Graph of the normalized mobility $\mu\omega_0^2/ea^2\sqrt{\pi}V^2$ as a function of the inverse temperature ω_0/kT. The optical-phonon density of states has been taken to be a Gaussian for simplicity, with a standard deviation $\delta = 0.2\omega_0$. The coupling constant is $g = 1$. The curves (a) and (b) were obtained from the numerical integration of (3.14) for small and large disorder, $\sigma = 0$ and ω_0, respectively. We see in the case of (b) that the mobility becomes considerably smaller below a temperature of about $kT = \omega_0/2$.

identically zero because a certain amount of residual hopping will still be allowed via higher multiphonon exchanges. We now show, however, that a true transition to zero mobility does occur, but at a lower temperature $T_0 < T_1$.

As we have seen above, the characterization of the transition to zero mobility is determined by the overlap of the tails of the Fourier transform of the polaron memory function and the distribution of site-energy differences. In order to determine the behavior at the transition point, it is therefore necessary that we know only the very large Ω dependence of $G(\Omega)$. But this in turn depends on only the short-time behavior of the decaying part of the memory, $W''(t)$. At short times, $W''(t)$ is a Gaussian,

$$W''(t) = 2V^2 \exp\left[-\beta\frac{\Omega}{2} \right] \exp\left[-4\sum_q |g_q|^2 \sin^2\left[\frac{\mathbf{q}\cdot\mathbf{a}}{2} \right] \tanh\left[\beta\frac{\omega_q}{4} \right] \right]$$

$$\times \exp\left\{ -\left[2\sum_q |g_q|^2 \sin^2\left[\frac{\mathbf{q}\cdot\mathbf{a}}{2} \right] \operatorname{csch}\left[\beta\frac{\omega_q}{2} \right]\omega_q^2 \right] t^2 \right\} \cos(\Omega t) . \tag{5.4}$$

Equation (5.4) is obtained from (2.5) by replacing $\cos(\omega_q t)$ by $1 - \omega_q^2 t^2/2$, the first two terms of an expansion about $t = 0$. The integral of (5.4) gives rise to a Gaussian function $G(\Omega)$, provided that the phonon density of states and the coupling constant are sufficiently well behaved that the sum over q exists. We see therefore that the tail of the function $G(\Omega)$ is always a Gaussian of the form $\exp(-\Omega^2/4\alpha^2)$, where α^2 is given by

$$\alpha^2 = 2 \sum_q |g_q|^2 \sin^2 \left[\frac{\mathbf{q} \cdot \mathbf{a}}{2} \right] \mathrm{csch} \left[\beta \frac{\omega_q}{2} \right] \omega_q^2 . \qquad (5.5)$$

The transition occurs when the tail of $G(\Omega)$ falls off faster than the tail of the distribution of site-energy differences. The behavior near the mobility transition is therefore

$$\mu \sim (T - T_0)^{1/2} , \qquad (5.6)$$

where T_0 is determined from the integral equation

$$2 \sum_q |g_q|^2 \sin^2 \left[\frac{\mathbf{q} \cdot \mathbf{a}}{2} \right] \mathrm{csch} \left[\frac{\omega_q}{2kT_0} \right] \omega_q^2 = \sigma^2 . \qquad (5.7)$$

For the case of coupling to a narrow optical-phonon band, T_0 is given by Eq. (5.3), but with the substitution of ω_0 for δ:

$$T_0 = \frac{\omega_0}{2k \ln \left[\dfrac{1 + \left[1 + \left[\dfrac{\sigma}{\sqrt{2}g\omega_0} \right]^4 \right]^{1/2}}{\left[\dfrac{\sigma}{\sqrt{2}g\omega_0} \right]^2} \right]} . \qquad (5.8)$$

In contrast to (5.3), which applies only in a specific parameter regime, expression (5.8) is exact for all values of g, ω_0, and σ. In Fig. 3, expression (5.8) for T_0 is plotted as a function of $\sigma / \sqrt{2}g\omega_0$. We observe that for small disorder, T_0 approaches zero as $(\ln|\sigma/\sqrt{2}g\omega_0|)^{-1}$, whereas for large disorder, T_0 is proportional to $(\sigma/\sqrt{2}g\omega_0)^2$. This is one of the principal results of this paper.

In a system with electron-phonon coupling to both optical- and acoustic-phonon branches, the temperature dependence of the mobility near the transition temperature is still determined from Eq. (5.6). Expression (5.8)
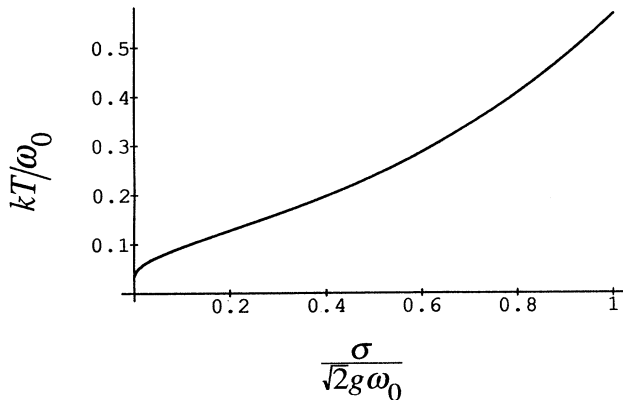

FIG. 3. Transition temperature T_0 as a function of the width σ of the disorder, from expression (5.8). For small disorder, T_0 approaches zero logarithmically with σ. For large disorder, T_0 is proportional to σ^2.

may even be applicable if the coupling to optical vibrations is sufficiently strong. As we have observed above, however, when the width of the disorder is small, the transition temperature will be low. At low enough temperatures with respect to ω_0/k, the terms in (5.6) corresponding to optical-phonon coupling will be exponentially suppressed by the factor $\mathrm{csch}(\beta\omega_0/2)$, and the transition temperature will be determined primarily by the size of the acoustic-phonon coupling. To calculate the transition temperature T_0 for acoustic-phonon coupling, we use the deformation potential form for the coupling constant and the phonon density of states in the Debye approximation. Expression (5.7) becomes

$$\frac{2}{\frac{4}{3}\pi\Omega_d^3} \int_0^\pi 2\pi\, d\theta \int_0^{\Omega_D} d\omega \left[\frac{g^2\Omega_D}{\omega} \right] \sin^2 \left[\frac{\omega\pi\cos\theta}{2\Omega_D} \right]$$

$$\times \mathrm{csch} \left[\frac{\beta\omega}{2} \right] \omega^4 \sin(\theta) = \sigma^2 , \qquad (5.9)$$

where ω is the phonon frequency, Ω_D is the Debye frequency, and here β is $1/kT_0$. The coupling constant $|g_q|^2$ in (5.7) has been replaced by $g^2\Omega_D/\omega$ in (5.9) in the deformation potential approximation so that the polaron binding energy is simply $E_p = g^2\Omega_D$. The factor $\sin^2(\mathbf{q}\cdot\mathbf{a}/2)$ in (5.7) has been replaced by

$$\sin^2 \left[\frac{\omega\pi\cos\theta}{2\Omega_D} \right]$$

in (5.9). At temperatures much below the Debye temperature, the hyperbolic function $\mathrm{csch}(\beta\omega/2)$ in the integrand of (5.9) falls off exponentially at small frequencies so that the upper limit on the frequency integration may be extended to infinity and the factor

$$\sin \left[\frac{\omega\pi\cos\theta}{2\Omega_D} \right]$$

may be replaced by its argument. The integration over the azimuthal angle θ supplies a factor of $\frac{1}{6}$. If we transform the frequency integration to a dimensionless form, (5.9) becomes

$$\frac{g^2\Omega_D^2\pi^2}{2(\beta\Omega_D)^6} \int_0^\infty dx\, x^5 \mathrm{csch} \left[\frac{x}{2} \right] = \sigma^2 . \qquad (5.10)$$

Numerically integrating (5.10) gives a factor of 15×10^3. Inverting (5.10), we find an expression for the transition temperature:

$$T_0 = 0.15 \frac{\Omega_D}{k} \left[\frac{\sigma}{g\Omega_D} \right]^{1/3} . \qquad (5.11)$$

We observe that for acoustic-phonon coupling, the transition temperature scales as the cube root of σ for small enough disorder.

VI. DISCUSSION

The primary result of Sec. III is Eq. (3.14), an expression for the zero-field dc mobility on a one-dimensional disordered chain with random hopping rates. In addition to their dependence on the absolute value of the site-energy differences, the hopping rates are nonsymmetrically biased in a random fashion due to the Boltzmann factor. Although there exist several methods for exactly calculating the expectation values of dc quantities, only the method of Derrida,[21] which we followed here, is applicable in the presence of random biases. However, as we have already pointed out, our result for the steady-state drift velocity is markedly distinct from the result of Derrida.[21] It is shown by Derrida that the drift velocity drops to zero below a particular value of the applied dc electric field, and thus the zero-field dc mobility always vanishes. In contrast, we find here that as the electric field approaches zero, the drift velocity is linearly proportional to the dc field. The difference in these results, we believe, lies in the choice of the independent random variable. In Derrida's calculation, the difference in energy between adjacent sites is the random variable, which is taken to be independent from one pair of sites to the next. This assumption, though surely made for convenience, is not supported by the underlying microscopics in the polaron model. The difference in site energies between sites 1 and 2 is certainly correlated with the difference in site energies between sites 2 and 3, for the two pairs are connected through the common energy of site 2. For this reason, we choose to retain the individual site energies as independent random variables. Because the hopping rates depend only on the site-energy differences, it appears that the correlation should produce a minor effect. We point out, however, that if the site-energy differences are treated as independent random variables, there may exist in an infinite lattice arbitrarily large clusters of positive site-energy differences across which a particle must hop "upward" in energy many times in succession. If the correlations between site-energy differences are correctly accounted for, on the other hand, the total energy difference of successive upward hops across a large cluster is limited by the width of the site-energy distribution. This may be the key distinction which accounts for the velocity cutoff seen by Derrida,[21] but not seen here.

In Sec. IV we have used Eq. (3.14) together with a Gaussian memory function and a Gaussian distribution of site energies to illustrate two features of this analysis. The first is that for large enough disorder the mobility will vanish. As we have discussed, the vanishing of the mobility with large disorder can be understood from energy conservation arguments and "percolation" in one-dimension. The second feature is that only the decaying part of the memory function contributes to the mobility for nonvanishing disorder, a result which is not entirely unexpected for a one-dimensional system. After all, in a one-dimensional lattice with disordered site energies the eigenstates are localized,[23] and so hopping transport can only occur with phonon assistance. Because the phonon-assisted and phonon-unassisted processes have a one-to-one correspondence with the decaying and nonde-

caying parts of the memory function, respectively, it is not surprising that transport should depend on only the decaying part of the memory function. By these arguments, one expects that the nondecaying part of the memory function should contribute to transport only amongst the delocalized states in three-dimensions. For completeness we should point out that the above interpretation of our one-dimensional result is not without its counter examples. For instance, if the site energies are arranged in a regular periodic fashion, the eigenstates of the noninteracting system are clearly delocalized, and by the above arguments one would expect that the nondecaying part of the memory function should contribute. However, if the perturbation is made from the same site basis, the nondecaying part of the memory function again has no effect on the mobility. In another counter example, if instead of diagonal disorder, off-diagonal disorder is introduced via random interaction matrix elements, the eigenstates are again completely localized in one-dimension. In this case, however, the nondecaying part of the memory function causes the mobility to diverge.

Except for the second-order perturbation in $\mathcal{V}$, which is made in obtaining a closed form for the memory function, (3.14) represents an exact result for the zero-field dc mobility in one-dimension. However, an expression for the zero-field mobility may also be obtained from the Kubo theory of linear response. If a second-order perturbation in $\mathcal{V}$ is made in order to evaluate the Kubo response function, one obtains a different expression for the mobility,[3]

$$\mu = e^2 a^2 \beta \int_{-\infty}^{\infty} d\varepsilon_1 \int_{-\infty}^{\infty} d\varepsilon_2 \rho(\varepsilon_1)\rho(\varepsilon_2)\exp(-\beta\varepsilon_1)$$
$$\times \exp\left[-\beta\frac{(\varepsilon_2-\varepsilon_1)}{2}\right]$$
$$\times G_{1,2}(\varepsilon_2-\varepsilon_1). \quad (6.1)$$

If we substitute (4.2) in (4.1) and use again a Gaussian distribution of site energies, we find that

$$\mu = e^2 a^2 \beta\sqrt{\pi}V^2\exp(-\Gamma_1)\exp\left[-\frac{\beta^2\sigma^2}{4}\right]$$
$$\times\left[\frac{1}{\sigma}+\frac{A}{\sqrt{\alpha^2+\sigma^2}}\exp(\Gamma_2)\right]. \quad (6.2)$$

An important difference between (3.14) and (6.2) is that in (6.2) the mobility is the sum of two terms,[9] the first of which arises from $W(\infty)$ and the second arises from the integration of $W'(t)$, whereas we have already shown that (3.14) depends only on $W'(t)$. In addition, the transition to zero mobility for large disorder is not predicted by (6.2). In order to predict proper one-dimensional percolation, one would therefore tend to favor (3.14), but at the price of losing any effects which should be associated with $W(\infty)$. Nevertheless, expression (6.2) may be quite appropriate for small disorder in three-dimensions. As we have discussed above, one would expect some contribution from $W(\infty)$ when the states are not fully localized. We note, for example, that Eq. (6.2) has been successfully utilized in explaining the observed temperature

dependence of the mobilities of photoinjected charges in naphthalene.[24]

The most dramatic effect of disorder on transport that emerges from this analysis is the mobility transition, characterized by a temperature T_0 below which the mobility vanishes. At a temperature T just above T_0, the mobility scales as the square root of the difference $T - T_0$. As we have already remarked, the transition behavior depends crucially on the fact that we have chosen the site energies from a Gaussian density of states. Complete transitions to zero mobility will not occur for any density with non-Gaussian tails. We should, nevertheless, observe large changes in the temperature dependence of the Arrhenius prefactors as the width of the memory function passes below the width of the density of states.

On a final note, we remark that the results presented here apply only to transport in one dimension. While it is clearly of broader interest to examine the temperature dependence of the percolation transition in higher dimensions, we have focused on only the one-dimensional case for the following reasons. Only in one-dimension have the effects of disorder on certain dc quantities been determined exactly, albeit starting with approximate memory functions. Any conclusions in higher dimensions, on the other hand, are necessarily affected by further approximations in the form of effective-medium or mean-field solutions of the master equation.[25] Furthermore, as we have seen, it is a requirement of detailed balance that hopping rates in an energetically disordered solid should be randomly biased and correlated. However, we know of no approximation schemes for random walks with correlated random biases in dimensions higher than 1.

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