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Vibrational Dispersion and Small-Polaron Motion: Enhanced Diffusion*

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The one-dimensional molecular-crystal model of Holstein is utilized in a preliminary investigation of the effects of the dispersion of the longitudinal optical frequencies on the hopping motion of small polarons. In particular, this work raises the question of whether the lattice relaxes sufficiently rapidly after a small-polaron hop so that a subsequent hop of the excess carrier may be considered independent of the initial hop. To this end, Holstein's perturbative approach is applied in calculating the probability of an initial small-polaron jump being followed by another small-polaron hop at a time t later. Furthermore, the small-polaron drift mobility is calculated assuming that the polaron's jump rate is only influenced by its immediately preceding hop. It is found that, for the circumstance in which the average time between jumps is small compared with the relaxation time of the lattice, the activation energy characterizing the small-polaron drift mobility is smaller than that found for completely independent jumps. In fact, for appropriate choices of the physical parameters, the drift mobility may display a very mild temperature dependence, decreasing with increasing temperature at sufficiently high temperatures.

I. INTRODUCTION

It has been recognized for a long time that the placing of a stationary excess carrier in a lattice would in general polarize the neighboring region about the carrier in such a way that a potential well is produced about the carrier which tends to trap it at its position in the lattice. In particular, if the potential well associated with the carrier-induced distortion is sufficiently deep that a bound state is formed, the carrier will be unable to move unless accompanied by its induced lattice deformation. The unit comprising the carrier and its associated lattice distortion is called a polaron. Furthermore, in the situation in which the carrier is localized about a given lattice site with a spatial extent of the order of a lattice spacing, the polaron is referred to as a *small polaron*.[1]

At sufficiently low temperatures the motion of a small polaron was shown to be describable in terms of motion in a small-polaron band, the width of which is a decreasing function of increasing temperature.[2] In addition, Holstein showed that above a temperature which is characterized by the energy uncertainty associated with the finite lifetime of a carrier in a band state being of the order of the width of the small-polaron band, it is no longer appropriate to view the motion of the small polaron in terms of the band picture. In this high-temperature regime, the small polaron is pictured as essentially localized, moving through the lattice via a succession of thermally activated hops. The remainder of this paper shall be concerned solely with small-polaron motion in this hopping regime.

A number of theoretical papers have been concerned with the hopping motion of small polarons. These calculations have been carried out within two complementary approximation schemes. In particular, in the perturbative approach developed by Holstein[2] it was assumed that the carrier responds sufficiently slowly to the vibrational motion of the lattice so that it is not generally able to "follow" the lattice motion. Within this approach (a) the drift mobility was found to be thermally activated,[2] (b) the Hall mobility in a hexagonal lattice was found to be thermally activated but with an activation energy roughly one-third that associated with the drift mobility,[3] and (c) the Hall mobility calculated for a square array (appropriate to cubic crystals) although being "thermally activated" possesses a sufficiently strong temperature dependence in the preexponential term (for reasonable choices of the physical parameters) to obscure the activated appearance of the Hall mobility.[4] In the complementary limit, the adiabatic approximation, in which the carrier is presumed to be able to adjust instantaneously to the vibrational motion, the drift mobility, and Hall mobility in a hexagonal lattice, have been calculated.[5] In this theory it is found that the drift mobility is also generally thermally activated while the Hall mobility possesses a much milder temperature dependence. In fact, in the adiabatic theory, the calculated Hall mobility in the hopping regime can be a decreasing function of temperature.

A basic assumption of all the prior studies of small-polaron hopping motion is that each hop may be treated as independent of the previous hops. In other words, the theories ask the question: If one places a small polaron on a site in the lattice, what rates (magnetic field dependent and magnetic field independent) characterize the motion of the small-polaron to a neighboring site? However, in general, a better question to ask in considering the diffusive small-polaron motion is: If the small polaron hops between two neighboring sites at time zero, what is the probability of making another hop at a time t later? If, in fact, there is no correlation between successive small-polaron hops, then both the above questions yield the same results. It is the purpose of this paper to investigate the effect of correlations between small-polaron hops on the drift mobility.

Fundamental to our discussion is the notion that each hop of a small polaron is associated with a "coincidence event."[2] Explicitly, for a carrier to hop, the local electronic energy level associated with an occupied site must momentarily coincide with the corresponding local electronic energy level of a neighboring unoccupied site,[6] where the local electronic energy levels are a function of the lattice-vibration coordinates. Furthermore, the previously calculated[2,3] drift-mobility activation energy ϵ_2 is simply the minimum potential energy (in excess of the polaron binding energy) required to establish a two-site coincidence event.[2,5] Thus, if a small-polaron hop is to be considered independent of its previous hop, one might expect that the distortion associated with the first hop must relax, dissipating the energy ϵ_2 to the remainder of the lattice, in a much shorter time than the mean time between small-polaron hops.

The relaxation of the lattice in the Holstein model[1,2] is associated solely with the dispersion of optical-vibration frequencies. In fact, this vibrational dispersion plays another crucial role in Holstein's nonadiabatic hopping theory.[2] In particular, it is assumed[2,7] that sufficient vibrational dispersion exists so that no correlation exists between the probabilities for a hop associated with possible successive coincidences at $t=0$ and at $t \simeq n(2\pi/\omega_0)$, n being an integer and ω_0 a typical longitudinal optical mode frequency. In other words, one asserts that the *carrier* loses all memory of a coincidence in less time that $2\pi/\omega_0$. The relevant condition for this to happen (in a lattice of two or more dimensions) is given by

$$\pi(2\omega_b/\omega_0)[(\epsilon_2 \kappa T)^{1/2}/\hbar\omega_0] \gg 1 \quad , \qquad (1)$$

where ω_b is the half-width of the band of longitudinal optical frequencies in the small-dispersion limit. It is noted from (1) that this electronic correlation effect is a quantum-mechanical effect, i.e., that condition (1) is automatically satisfied in the limit $\hbar \to 0$. This work will not consider the above-mentioned electronic correlation effect, but rather, for simplicity, it will be concerned with the essentially classical effects associated with the relaxation of the lattice from the highly distorted situation that characterizes a coincidence event.

The point of view taken here is that to begin to understand the role of lattice-relaxation effects on small-polaron hopping motion it is useful to investigate the simplest model which incorporates these effects. Thus we consider the one-dimensional molecular-crystal model introduced by Holstein.[1,2] In this model we assume that the carrier has hopped from one site $(n-1)$ to a neighboring site (n) at time zero and ask for the probability that a second hop occurs at a time t later. It is readily apparent that for sufficiently short times $(t \lesssim \pi/\omega_b)$ the probability of a return hop (to site $n-1$) is greater than that for a hop to a new site (to site $n+1$) since sites n and $n-1$ will not have completely relaxed from the distorted configuration they possessed at $t=0$, while site $n+1$ will in general not be substantially distorted. Furthermore, since at $t=0$ the occupied site n is generally compressed from its equilibrium position, we expect the probability of a hop to site $n+1$ to be greater than if both sites n and $n+1$ were near their equilibrium positions. In addition we expect the forward and return jump rates to be given by the previous calculated single value[2] only after the energy associated with the initial distortions is completely dissipated to the remainder of the lattice.

It is important to realize that these relaxation effects will be of little significance if the mean time between hops is much greater than the times characterizing the relaxation processes. Thus, in the limit of the electronic transfer integral J approaching zero or the optical phonon bandwidth $2\omega_b$ being arbitrarily large, the standard results are obtained. However, when the relaxation times are comparable to the hopping times, it will be demonstrated that relaxation effects greatly affect the magnitude and temperature dependence of the mobility.

The calculations of this paper demonstrate that for $t \lesssim \pi/\omega_b$ the return-jump rate is quite different from the forward-jump rate, and that for $t > \pi/\omega_b$ both rates merge, ultimately reducing to their relaxed values for $t \gg (2/\pi\omega_b)(2\epsilon_2/\kappa T)^2$. Furthermore, the forward-jump rate is not a monotonically decreasing function of time but increases with time for $t < \omega_b^{-1}$; this feature is the net result of the relaxation of site n and excitation of site $n+1$.[8]

It is found that for reasonable choices of the physical parameters, the relaxation effects may be important since the average jump rate is often comparable to $2\pi/\omega_b$. Furthermore, in such a situation, the resulting drift mobility is larger than that which results when these correlation effects are ignored. In addition, the temperature dependence of the drift mobility may be rather mild, even decreasing as a function of temperature at sufficiently high temperatures.

As a result of these preliminary considerations, it is seen that a nonactivated drift mobility may not in itself be interpreted as evidence of the absence of small-polaron hopping motion.

In Sec. II, we review the principal features of Holstein's molecular-crystal model. In Sec. III, the probability of a coincidence involving sites $n-1$ and n occurring between time 0 and dt_0 and a coincidence involving sites n and $n+1$ occurring between times t and $t+dt$ (computed in the Appendix) is related to the rate $R(t)$ which characterizes jumps from site n to site $n+1$ as a function of the time t. The time dependence of $R(t)$ is included in the function $G(t)$ which is calculated in Sec. IV. It is shown that $G(t)$ is a product of an oscillatory function characterized by the vibrational frequency ω_0 and a time-dependent amplitude characterized by the time ω_b^{-1}; for $\omega_b t \gg 1$ the amplitude of $G(t)$ varies as $(\omega_b t)^{-1/2}$. Furthermore, at long times, $R(t) \simeq w_2 e^{(2\epsilon_2/\kappa T)G(t)}$, w_2 being the uncorrelated jump rate.

We proceed in Sec. V to calculate the rate characterizing a return hop, that is, a hop from site n to site $n-1$. In Sec. VI, the time-dependent forward- and return-jump rates are related to the time-averaged forward-jump rate and thereby to the drift mobility via the Einstein relation.

We find it useful to eliminate the rapid variation of the time-dependent jump rates (characterized by the frequency ω_0) by averaging these rates over the time interval $2\pi/\omega_0$; this task is performed in Sec. VII.

Finally, the time-averaged jump rate is obtained and the associated mobility is plotted in Sec. VIII. The paper concludes with a discussion of the calculation and significance of the results. In particular in Sec. IX, a physical interpretation of the results of this calculation is presented, along with comments on the modification of the results that are expected to arise from a study of an analogous three-dimensional model.

II. REVIEW OF MOLECULAR-CRYSTAL MODEL

The molecular-crystal model is a theoretical model which was introduced by Holstein[1] to study the polaron problem. Explicitly, the lattice is taken to be a linear chain of N identical diatomic molecules whose orientations are fixed and whose internuclear separations are allowed to vary. In this model the optical mode vibrations are the harmonic oscillations of the internuclear separations of the diatomic molecules. The vibrational part of the Hamiltonian is simply

$$H_L = \sum_n \left[\frac{1}{2M} \left(\frac{\hbar}{i} \frac{\partial}{\partial x_n} \right)^2 + \tfrac{1}{2} M \omega_0^2 x_n^2 + \tfrac{1}{2} M \omega_1^2 x_n x_{n+1} \right] , \quad (2)$$

where x_n is the deviation of the internuclear separation of the nth diatomic molecule from its equilibrium value, M is the reduced mass of a diatomic molecule, and ω_0 is the harmonic oscillator frequency; the final term in the Hamiltonian couples neighboring oscillators and gives rise to dispersion of the vibrational frequencies. In particular, the dispersion relation gives the relationship between a normal mode wave vector and its associated frequency,

$$\omega_k^2 = \omega_0^2 + \omega_1^2 \cos k , \quad (3)$$

where $-\pi \leq k \leq \pi$.

The electronic portion of the Hamiltonian is given by

$$H_e = \frac{1}{2m} \left(\frac{\hbar}{i} \operatorname{grad} \vec{r} \right)^2 + \sum_n V(\vec{r} - n\vec{a}, x_n) , \quad (4)$$

where m is the electron mass, $\vec{a}$ is a unit lattice vector, and $V(\vec{r} - n\vec{a}, x_n)$ is the potential energy of the nth molecule. It is noted that this potential is dependent on the internuclear separation of the nth molecule, this feature being essentially the electron-lattice interaction.

The eigenfunction of the system whose Hamiltonian is $H_L + H_e$ is written as a linear superposition of local electronic wave functions, i.e.,

$$\Psi(\vec{r}, \ldots x_n \ldots) = \sum_n a_n(\cdots x_n \cdots) \phi_n(\vec{r}, x_n) , \quad (5)$$

where

$$\left[\frac{1}{2m} \left(\frac{\hbar}{i} \operatorname{grad} \vec{r} \right)^2 + V(\vec{r} - n\vec{a}, x_n) \right] \phi_n(\vec{r}, x_n) = E(x_n) \phi_n(\vec{r}, x_n) ; \quad (6)$$

$E(x_n)$ is the energy of an electron on an isolated diatomic molecule. The coefficients a_n are found, within the standard tight-binding approximations, to be given by the solutions of the coupled equations

$$i\hbar \frac{\partial a_n}{\partial t} = [H_L + W_n(\ldots x_n \ldots)]\, a_n - J(a_{n+1} + a_{n-1}) \ , \qquad (7)$$

where W_n is the electronic energy associated with the excess carrier being on site n, and J is an electronic transfer integral which for simplicity is taken to be independent of the x_n's. An additional simplification introduced by Holstein and employed here is to take

$$W_n = E(x_n) = \text{const} - Ax_n \quad , \qquad (8)$$

where A is a constant.

For sufficiently small J the above set of equations may be solved perturbatively in powers of J. In zeroth order a_n is the vibrational wave function associated with a carrier at site n, the corresponding vibrational Hamiltonian being simply $H_L + W_n(\ldots x_n \ldots)$.

Furthermore, at sufficiently high temperatures the vibrational motion may be treated classically. In this limit Holstein's occurrence-probability approach[2] becomes valid for treating small-polaron diffusion. This theory concludes that every time there is a momentary equality of the electronic energy level of the occupied site and its neighboring unoccupied site there is a finite probability of the carrier hopping to the neighboring site. Such an equality is termed a coincidence event and, within our approximations, is characterized by the equality $x_n = x_{n\pm 1}$. The probability that the carrier will avail itself of the opportunity to jump from site n to $n \pm 1$ given a coincidence between these sites is simply

$$2\pi J^2/\hbar A \,|\, v_n - v_{n\pm 1} \,| \ ,$$

where v_n and $v_{n\pm 1}$ are, respectively, the velocities associated with the internuclear separations of sites n and $n \pm 1$ evaluated at the time of coincidence.[9]

III. NONADIABATIC FORWARD-JUMP RATE $R(t)$

Let us now proceed to calculate the probability per unit time of a hop from site 1 to site 2 being followed by a hop from site 2 to site 3 at a later time t. Our approach is to note that associated with every coincidence event between initially occupied and unoccupied sites is a finite probability of a jump of the carrier from the occupied to unoccupied site. In the perturbative theory of Holstein[2] the probability of a jump from site p to site $p+1$ during a coincidence between these two sites, characterized by the relative vibrational velocity $v_{p,p+1} \equiv v_p - v_{p+1}$, is given by (cf. Sec. I.)

$$W_c(p \rightarrow p+1) = 2\pi J^2/\hbar A \,|\, v_{p,p+1} \,| \ , \qquad (9)$$

where J is the electronic transfer integral appropriate to a coincidence event. Restricting our attention to the regime of applicability of the above formula, we find that the probability of the hop $1 \rightarrow 2$ occurring between time zero and dt_0, and the hop $2 \rightarrow 3$ occurring between times t and $t + dt$, is $P_{12,23}(t)\,dt_0\,dt$, where

$$P_{12,23}(t) \equiv \int_{-\infty}^{\infty} dv_{12} \int_{-\infty}^{\infty} dv_{23} \left(\frac{2\pi J^2}{\hbar A\,|v_{12}|}\right)\left(\frac{2\pi J^2}{\hbar A\,|v_{23}|}\right) \times P(v_{12}, v_{23}, t) \ , \qquad (10)$$

$P(v_{12}, v_{23}, t)\, dv_{12}\, dv_{23}\, dt_0\, dt$ being the probability of (a) a coincidence between sites 1 and 2 occurring between time zero and time dt_0 with a relative vibrational velocity lying between v_{12} and $v_{12} + dv_{12}$, and (b) a coincidence between sites 2 and 3 occurring between times t and $t + dt$ with a relative vibrational velocity lying between v_{23} and $v_{23} + dv_{23}$; here, as in the previously cited works, we adopt the convention of writing $v_{1,2}$ as v_{12}, etc. The task of calculating $P(v_{12}, v_{23}, t)$ is carried out in the Appendix of this paper. Inserting the final result of this occurrence-probability calculation, Eq. (A24), into (10) and carrying out the indicated velocity integrations, we find

$$P_{12,23}(t) = \left(\frac{J^2}{\hbar A}\right)^2 \frac{\pi}{A_3 A_4 (1 + a^2/4A_2^2 A_3^2)^{1/2} (1 + a^2/4A_1^2 A_4^2)^{1/2}} \times \exp\left[-\frac{c_1^2}{2A_3^2}\left(\frac{1}{1 + a^2/4A_2^2 A_3^2}\right)\right] , \qquad (11)$$

where the previously undefined entities appearing above are defined in Eqs. (A16–A21) and Eqs. (A25). Furthermore, we may utilize the definitions (A25) to show that

$$P_{12,23}(t) = \left(\frac{J^2}{\hbar A}\right)^2 \frac{\pi}{c_2} \frac{1}{[1 - (c/2c_2)^2]^{1/2}} \times \exp\left[-\frac{2\epsilon_2}{kT}\left(\frac{1}{1 - c/2c_2}\right)\right] , \qquad (12)$$

where it has been noted that

$$\frac{c_1^2}{2c_2} = \frac{2}{\kappa T} \frac{1}{N} \sum_k \frac{A^2}{4M\omega_k^2}(1 - \cos k) = \frac{2\epsilon_2}{\kappa T} \ , \qquad (13)$$

ϵ_2 being the two-site activation energy introduced by Holstein. At this point it is noted that as the time between the two coincidence events becomes arbitrarily large, i.e., $t \rightarrow \infty$, the coincidence events become uncorrelated and $P_{12,23}(\infty)$ should become the square of the uncorrelated jump rate

$$w_2 = \frac{J^2}{\hbar}\left(\frac{\pi}{4\kappa T \epsilon_2}\right)^{1/2} e^{-\epsilon_2/\kappa T} . \qquad (14)$$

This, in fact, is easily verified by noting from (A21) that as $t \rightarrow \infty$, we have $c \rightarrow 0$, yielding the expected result

$$P_{12,23}(\infty) = \left[\frac{J^2}{\hbar}\left(\frac{\pi}{4\kappa T\epsilon_2}\right)^{1/2} e^{-\epsilon_2/\kappa T}\right]^2 = w_2^2 , \qquad (15)$$

where it has been noted that $c_2 = 4\kappa T \epsilon_2$.

It is now useful to define the jump rate for the *second* jump to be

$$R(t) \equiv P_{12,23}(t)/w_2 \equiv w_2 E(t), \tag{16}$$

where the time t is the time after the first hop, and $E(t)$, henceforth designated as the enhancement factor, is defined as

$$E(t) = \frac{1}{[1 - G^2(t)]^{1/2}} \exp\left[\frac{2\epsilon_2}{\kappa T}\left(\frac{G(t)}{1 + G(t)}\right)\right], \tag{17}$$

where

$$G(t) = \frac{-c}{2c_2} = -\sum_k \left(\frac{1}{\omega_k^2}\right)(1 - \cos k)\cos k \cos\omega_k t \Big/ \sum_k \left(\frac{1}{\omega_k^2}\right)(1 - \cos k), \tag{18}$$

$G(t)$ depending only on the frequency spectrum and the time t. It is now our task to calculate $G(t)$.

IV. CALCULATION OF $G(t)$

To begin, let us assume that the width of the band of optical frequencies is sufficiently small compared to a typical optical frequency so that we may write

$$\omega_k = (\omega_0^2 + \omega_1^2 \cos k)^{1/2} \simeq \omega_0 + \omega_b \cos k, \tag{19}$$

where $\omega_b = \omega_1^2/2\omega_0$; the optical bandwidth is $2\omega_b$. To lowest order in ω_b/ω_0 we may write

$$G(t) = -1 \int_0^\pi dk \left(\frac{1}{\omega_k^2}\right)(1 - \cos k)\cos k \cos\omega_k t \Big/ \int_0^\pi dk \left(\frac{1}{\omega_k^2}\right)(1 - \cos k) \simeq -\frac{1}{\pi}\int_0^\pi dk (1 - \cos k)\cos k \times \cos[(\omega_0 + \omega_b \cos k)t], \tag{20}$$

where, in the first line the sum over k is replaced by an integral and, in the second line, ω_k^2 is approximated[10] by ω_0^2. Rewriting the final cosine term we have

$$G(t) \equiv F_{\text{in}}(t)\cos\omega_0 t + F_{\text{out}}(t)\sin\omega_0 t, \tag{21}$$

$$F_{\text{in}}(t) \equiv -\frac{1}{\pi}\int_0^\pi dk (1 - \cos k)\cos k \cos[(\omega_b t)\cos k], \tag{22}$$

$$F_{\text{out}}(t) \equiv \frac{1}{\pi}\int_0^\pi dk (1 - \cos k)\cos k \sin[(\omega_b t)\cos k]. \tag{23}$$

The above integrals may now be evaluated in terms of Bessel functions by utilizing the identities[11]

$$\cos(\theta \cos k) = J_0(\theta) + 2\sum_{n=1}^{\infty}(-1)^n J_{2n}(\theta)\cos(2nk),$$

$$\sin(\theta \cos k) = 2\sum_{n=0}^{\infty}(-1)^n J_{2n+1}(\theta)\cos[(2n+1)k].$$

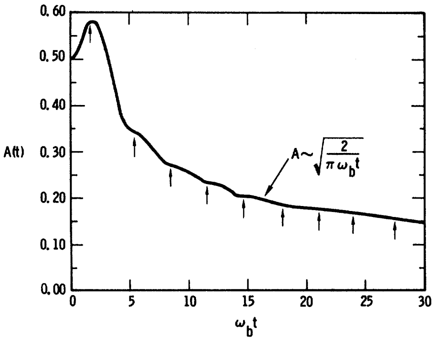

FIG. 1. Relaxation amplitude appropriate to a forward hop $A(t)$ defined in Eqs. (24)–(26), plotted as a function of t in units of ω_b^{-1}. It is significant that for short times $A(t)$ increases with time. The arrows denote points at which the first derivative of $A(t)$ with respect to time vanishes. Where the wiggles in the curve were extremely small they were smoothed over.

We find, performing the standard trigonometric integrals, that

$$F_{\text{in}}(t) = \tfrac{1}{2}[J_0(\omega_b t) - J_2(\omega_b t)], \tag{24}$$

$$F_{\text{out}}(t) = J_1(\omega_b t). \tag{25}$$

Thus $G(t)$ is a sum of two terms oscillating with a frequency ω_0, the coefficients of which are relatively slowly varying functions of time characterized by the time ω_b^{-1}. At this point it is useful to rewrite $G(t)$ as

$$G(t) = A\cos(\omega_0 t - \phi), \tag{26}$$

where

$$A \equiv \{[F_{\text{in}}(t)^2] + [F_{\text{out}}(t)]^2\}^{1/2}, \tag{27}$$

$$\cos\phi = F_{\text{in}}(t)/A, \quad \sin\phi = F_{\text{out}}(t)/A; \tag{28}$$

$A(t)$ and $\phi(t)$ are functions of time. $A(t)$ is plotted vs $\omega_b t$ in Fig. 1. At "long" times, $\omega_b t \gtrsim 3$, $A(t) \simeq (2/\pi\omega_b t)^{1/2}$.

A discussion of the physical significance of $G(t)$ is deferred to Sec. IX.

V. RETURN-JUMP RATE $R_r(t)$

In this section we summarize the procedure that is involved in obtaining $R_r(t)$, the probability per unit time of a carrier returning to site 1 after having jumped from site 1 to site 2 at $t = 0$. The calculation proceeds in an analogous fashion to that utilized in finding $R(t)$. In particular we find that $P(v_{12}, v_{21}, t)$ is given by Eq. (A24) with the constants a, b, and c replaced by

$$a' \equiv \sum_k \left(\frac{\kappa T}{M\omega_k}\right) G_k^{12} G_k^{21} \sin\omega_k t = -\frac{1}{N}\sum_k \left(\frac{2\kappa T}{M\omega_k}\right)(1 - \cos k)\sin\omega_k t, \tag{29}$$

$$b' \equiv \sum_k \left(\frac{\kappa T}{M}\right) G_k^{12} G_k^{21} \cos\omega_k t$$

$$= -\frac{1}{N} \sum_k \left(\frac{2\kappa T}{M}\right)(1 - \cos k) \cos\omega_k t \,, \tag{30}$$

$$c' \equiv \sum_k \left(\frac{\kappa T}{M\omega_k^2}\right) G_k^{12} G_k^{21} \cos\omega_k t$$

$$= -\frac{1}{N} \sum_k \left(\frac{2\kappa T}{M\omega_k^2}\right)(1 - \cos k) \cos\omega_k t \,. \tag{31}$$

Proceeding as in Sec. III, we find that the enhancement factor associated with return hop is given by

$$E_r(t) = \frac{1}{[1 - G_r^2(t)]^{1/2}} \exp\left[\frac{2\epsilon_2}{\kappa T}\left(\frac{G_r(t)}{1 + G_r(t)}\right)\right] \,, \tag{32}$$

where

$$G_r(t) = \sum_k \left(\frac{1}{\omega_k^2}\right)(1 - \cos k) \cos\omega_k t \Big/ \sum_k \left(\frac{1}{\omega_k^2}\right)(1 - \cos k) \,. \tag{33}$$

In evaluating the above expression for $G_r(t)$ it is assumed that the band of vibrational frequencies is sufficiently narrow so that we may write $\omega_k = \omega_0 + \omega_b \cos k$. We find that by writing

$$G_r(t) = F_{\text{in}}^r(t) \cos\omega_0 t + F_{\text{out}}^r(t) \sin\omega_0 t \,, \tag{34}$$

we have, to lowest order in ω_b/ω_0,

$$F_{\text{in}}^r(t) = J_0(\omega_b t) \,, \tag{35}$$

$$F_{\text{out}}^r(t) = J_1(\omega_b t) \,. \tag{36}$$

At this point it is noted that the amplitude for the "out-of-phase" term $\sin\omega_0 t$ is identical in both the forward- and return-hop calculations,[12] i.e., $F_{\text{out}}^r(t) = F_{\text{out}}(t)$. It is also noted that at sufficiently long times (times for which the Bessel functions may be replaced by their asymptotic values $t \gg \omega_b^{-1}$), $J_2(\omega_b t)$ approaches $-J_0(\omega_b t)$ and hence $F_1^r(t)$ approaches $F_1(t)$.

To qualitatively understand the significance of these features we view the out-of-phase contributions to $G(t)$ and $G_r(t)$ as both being associated with the transfer of energy *to* the sites involved in the coincidence,[13] sites 2 and 3 and sites 2 and 1, respectively. Since at $t = 0$ in both situations each of the sites involved, i.e., site 1, 2, or 3, has one distorted neighbor and one undistorted neighbor, the transfer of energy to these sites is expected to be equivalent. The in-phase contributions are dependent on the initial distortion of the sites involved in the second hop, and therefore are quite different in the two calculations; at $t = 0$, sites 1 and 2 are distorted, while site 3 is generally not substantially deformed. The fact that the in-phase contributions to $G(t)$ and $G_r(t)$ approach equality for $t \gtrsim \pi/\omega_b$ demonstrates that a time $\sim \pi/\omega_b$ is required for the "initial" distortion to relax. The behavior of the system for $t \gg \omega_b^{-1}$ manifests the effects of the repeated transfer of vibrational energy between sites as the energy required to produce the first hop "diffuses" away from the vicinity of the initial hop.

Finally we write

$$G_r(t) = A_r \cos(\omega_0 t - \phi_r), \tag{37}$$

where

$$A_r \equiv \{[F_{\text{in}}^r(t)]^2 + [F_{\text{out}}^r(t)]^2\}^{1/2}, \tag{38}$$

$$\cos\phi_r = F_{\text{in}}^r(t)/A_r \,, \quad \sin\phi_r = F_{\text{out}}^r(t)/A_r \,, \tag{39}$$

ϕ_r and A_r being functions of time characterized by the time ω_b^{-1}. $A_r(t)$ is plotted vs $\omega_b t$ in Fig. 2.[14] It is noted that for $\omega_b t \gtrsim 3$, $A_r(t) \simeq (2/\pi\omega_b t)^{1/2}$, coinciding with $A(t)$. The relationship of $G(t)$ and $G_r(t)$ to the carrier-induced distortion of the lattice is one of the topics which is considered in Sec. IX; until then we shall focus attention on only the mathematical properties of these functions.

VI. AVERAGE HOPPING RATE w

Since we have derived the rates at which a small polaron, having made an initial hop at $t = 0$, makes a second hop or a return hop $R(t)$ and $R_r(t)$, respectively, we will now discuss the method by which we may relate these rates to w, the average hopping rate. It is w that is related to the diffusion constant

$$D = a^2 w \,, \tag{40}$$

a being the lattice spacing.

To begin let us note that having jumped from site 1 to site 2 at $t = 0$, the carrier may either return to site 1 or hop to site 3 with the respective

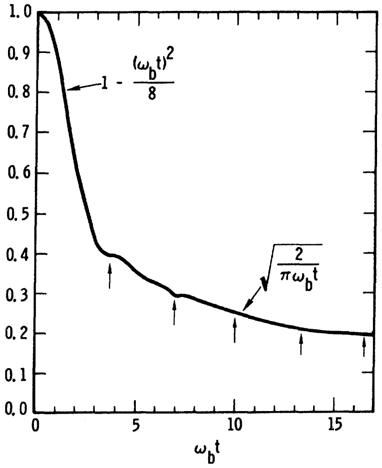

FIG. 2. Return-hop relaxation amplitude $A_r(t)$, defined in Eqs. (35), (36), and (38), plotted as a function of t in units of ω_b^{-1}. The arrows denote the critical points of the curve, some of which are not shown because they are associated with extremely small wiggles in the curve.

rates $R_r(t)$ and $R(t)$. It is now useful to write down the survival probability[15] $S(t)$; that is, the probability that the carrier will not have jumped from site 2 at a time t:

$$S(t)=\exp\{-\int_0^t[R(t')+R_r(t')]dt'\}\ . \tag{41}$$

The probability that the carrier remains on site 2 until time t and then jumps to site 3 in the time interval between t and $t+dt$ is then

$$P(t)dt=S(t)R(t)dt\ . \tag{42}$$

We note that the fact that $R_r(t)$ and $R(t)$ are not, in general, equal has an obvious effect on the carrier transport. In particular, if $R_r(t)\gg R(t)$ the carrier, after having jumped from site 2 to site 3, would tend to jump back and forth between sites 2 and 3 rather than move to another site. Clearly this would reduce the net charge transport.

The fraction of hops from site 3 which is associated with the enhanced return-jump rate is

$$f\equiv\int_0^\infty S(t)\Delta R(t)\,dt\ , \tag{43}$$

where

$$\Delta R(t)\equiv R_r(t)-R(t)\ . \tag{44}$$

Since after a hop there is a probability f that the carrier will, as a result of the enhanced return rate, be returned to its initial site, the probability of a hop resulting in the net transfer of the carrier is thus reduced by the factor

$$(1-f+f^2-f^3+\cdots)=1/(1+f)\ .$$

If the probability of an immediate return is very great, i.e., $f\to 1$, we see that having achieved the initial coincidence the carrier will jump back and forth between the initial and final sites ultimately effecting a forward hop in one-half of these instances[16]; in this circumstance $(1+f)^{-1}$ approaches $\frac{1}{2}$. Thus we may finally write

$$w\equiv\frac{1}{1+f}\int_0^\infty P(t)R(t)\,dt\Big/\int_0^\infty P(t)\,dt\ . \tag{45}$$

In the traditional situation where the jump rates $R(t)$ and $R_r(t)$ are equal and constant in time, i.e., $R_r(t)=R(t)=w_2$, we find the usual result

$$w=w_2\ .$$

We may now rewrite w as

$$w=\frac{1}{1+f}\int_0^\infty dr\,e^{-r}\{R[t(r)]\,e^{-g[t(r)]}\}\Big/\int_0^\infty dr\,e^{-r}(e^{-g[t(r)]})\ , \tag{46}$$

where

$$r\equiv r(t)\equiv 2\int_0^t R(t')\,dt'\ , \tag{47}$$

$$g(t)=\int_0^t[R_r(t')-R(t')]\,dt'\ . \tag{48}$$

It is this formula for w that will be the object of our subsequent attention.

At this point we may in principle calculate w by simply inserting the expressions for $R(t)$ and $R_r(t)$ into formulas (41) and (45). However, due to the complexity of the functions involved, this is a very formidable task. A major complicating feature of $R(t)$ and $R_r(t)$ is that their time dependences reflect not only the relaxation of the lattice but the relatively rapid oscillatory motion of the lattice. Hence, in order to simplify the calculation of the integrals involved in calculating w, we proceed to obtain relatively simple functions which describe only the effect of the lattice relaxation on the jump rate. In particular, in Sec. VII we average the rates $R(t)$ and $R_r(t)$ over the vibrational period $2\pi/\omega_0$ (the time dependence of these averaged rates is illustrated in Figs. 3 and 4). Finally, these averaged rates form the basis of the approximate evaluation of w which is carried out in Sec. VIII. Thus, the following two sections of this paper are strictly detailed computations. However, the salient features of the results of these sections are reviewed and discussed in Sec. IX.

VII. TIME-DEPENDENT JUMP RATES

Let us now consider the time dependence of the jump rates $R(t)$ and $R_r(t)$. To begin, let us recall that the time dependence of both these rates is contained in the respective functions $G(t)$ and $G_r(t)$. As is evident from Eqs. (26) and (37) and the associated comments, over a time interval $\sim\omega_0^{-1}$ both of these functions may be regarded as essentially simple oscillatory functions of time, characterized by the angular frequency ω_0. In particular, since the amplitudes and phases of these oscillatory functions are comparatively slowly varying, characterized by the time $\omega_b^{-1}\gg\omega_0^{-1}$, it is appropriate to treat them as constants over a time interval $\sim\omega_0^{-1}$. Thus, in considering the average value of $R(t)$ over the time interval $[t-\pi/\omega_0,\ t+\pi/\omega_0]$ – this average being denoted by $\langle R(t)\rangle$ – we treat the amplitude and phase angle $A(t)$ and $\phi(t)$ as constants,

$$\langle R(t)\rangle\equiv w_2\frac{\omega_0}{2\pi}\int_{t-\pi/\omega_0}^{t+\pi/\omega_0}dt'\frac{1}{\{1-A^2(t')\cos^2[\omega_0^2-\phi(t')]\}^{1/2}}\exp\left(\frac{2\epsilon_2}{\kappa T}\,\frac{A(t')\cos[\omega_0t'-\phi(t')]}{1+A(t')\cos[\omega_0t'-\phi(t')]}\right)$$

$$\simeq w_2\frac{\omega_0}{2\pi}\int_{t-\pi/\omega_0}^{t+\pi/\omega_0}dt'\frac{1}{\{1-A^2(t)\cos^2[\omega_0t'-\phi(t)]\}^{1/2}}\exp\left(\frac{2\epsilon_2}{\kappa T}\,\frac{A(t)\cos[\omega_0t'-\phi(t)]}{1+A(t)\cos[\omega_0t'-\phi(t)]}\right)$$

$$= w_2 \frac{1}{2\pi}\int_{-\pi}^{\pi} dx \frac{1}{(1-A^2\cos^2 x)^{1/2}} \exp\left(\frac{2\epsilon_2}{\kappa T}\frac{A\cos x}{1+A\cos x}\right), \tag{49}$$

where, in introducing the integration variable $x = \omega_0 t' - \phi(t)$, cognizance has been taken of the fact that since the integration extends over an entire period of the oscillatory function, the choice of a constant phase angle has no effect on the integral and hence may be ignored. In addition, we may now utilize the evenness of the cosine function to write

$$\langle R(t)\rangle = w_2 \frac{1}{\pi}\int_0^{\pi} dx \frac{1}{(1-A^2\cos^2 x)^{1/2}} \times \exp\left(\frac{2\epsilon_2}{\kappa T}\frac{A\cos x}{1+A\cos x}\right). \tag{50}$$

At this point we may simplify the above integral by transforming to a new variable θ where

$$\theta \equiv \cos^{-1}[(A+\cos x)/(1+A\cos x)]. \tag{51}$$

After some algebra we obtain

$$\langle R(t)\rangle = w_2 \exp\left(\frac{-2\epsilon_2}{\kappa T}\frac{A^2}{1-A^2}\right) \times\left[\frac{1}{\pi}\int_0^{\pi} d\theta \frac{1}{(1+A^2-2A\cos\theta)^{1/2}} \times \exp\left(\frac{2\epsilon_2}{\kappa T}\frac{A}{1-A^2}\cos\theta\right)\right]. \tag{52}$$

At this point we compare the relative θ variation of the exponential term,

$$\left|\frac{d}{d\theta}\ln\left[\exp\left(\frac{2\epsilon_2}{\kappa T}\frac{A}{1-A^2}\cos\theta\right)\right]\right| = \frac{2\epsilon_2}{\kappa T}\frac{A}{1-A^2}\sin\theta,$$

with the relative θ variation of the remaining term in the integrand,

$$\left|\frac{d}{d\theta}\ln\frac{1}{(1+A^2-2A\cos\theta)^{1/2}}\right| = \frac{A\sin\theta}{1+A^2-2A\cos\theta}.$$

We see that the θ variation of the exponential term is much more rapid provided that

$$\frac{2\epsilon_2}{\kappa T} \gg \frac{1-A^2}{(1+A^2-2A\cos\theta)^{1/2}}. \tag{53}$$

Since we shall take $2\epsilon_2/\kappa T \gg 1$ and (as is evident from Fig. 1) $A \lesssim 0.6$, we see that this condition is fulfilled. Thus we may approximate the integral in Eq. (52) by taking the nonexponential portion of the integrand to be a constant equal to its value when the integrand is a maximum. This procedure yields

$$\langle R(t)\rangle = w_2 \exp\left(-\frac{2\epsilon_2}{\kappa T}\frac{A^2}{1-A^2}\right)\frac{I_0[(2\epsilon_2/\kappa T)A/(1-A^2)]}{1-A}, \tag{54}$$

where $I_0(z)$ is the zeroth-order modified Bessel function.[17] Furthermore, noting that $I_0(z)$ may be written as $e^z g(z)$ where $g(z)$ is a decreasing function of z which has the properties that for $z \ll 1$, $g(z) \simeq 1 - z + \frac{1}{2}z^2$, and for $z \gg 1$, $g(z) \simeq (2\pi z)^{-1/2}$, we have

$$\langle R(t)\rangle = w_2 \exp\left(\frac{2\epsilon_2}{\kappa T}\frac{A}{1+A}\right)\frac{g[(2\epsilon_2/\kappa T)A/(1-A^2)]}{1-A}. \tag{55}$$

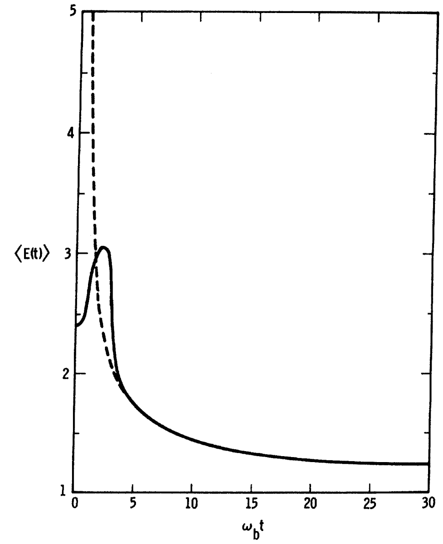

Fig. 3. Enhancement factors associated with a forward hop $\langle R(t)\rangle/w_2$ (solid line) and with a return hop $\langle R_r(t)\rangle/w_2$ (dashed line) derived from Eqs. (55) and (59), respectively plotted as a function of time, in units of ω_b^{-1}, for $\epsilon_2 = 2.5\ \kappa T$. Where only one curve is shown the two curves are effectively superimposed on one another.

We now recall that the validity of the approximation scheme used above hinged on A not being sufficiently close to unity so that the right-hand side of (53) is much greater than unity. While this condition is satisfied in the calculation of $\langle R(t)\rangle$, the analogous condition which arises if one attempts to apply this scheme to the calculation of $\langle R_r(t)\rangle$ is not satisfied since $A_r(t)$ tends to unity as $t \to 0$. Hence we now present an alternative evaluation of $\langle R(t)\rangle$ and $\langle R_r(t)\rangle$ which is valid for sufficiently short times.

Explicitly, we note that at sufficiently short times such that

$$\frac{2\epsilon_2}{\kappa T}\frac{A(t)}{1-A^2(t)} \gg 1,$$

the chief contribution to the integral of Eq. (52) comes from the immediate vicinity of $\theta = 0$. Thus it is appropriate to replace $\cos\theta$ by $1-\frac{1}{2}\theta^2$ in the integral and write

$$\langle R(t)\rangle \simeq w_2\left[\exp\left(\frac{2\epsilon_2}{\kappa T}\,\frac{A}{1+A}\right)\right] \times\left(\frac{1}{\pi}\int_0^\infty d\theta\,\frac{\exp[-(\epsilon_2/\kappa T)A/(1-A^2)\theta^2]}{[(1-A^2)+A\theta^2]^{1/2}}\right) . \tag{56}$$

Performing the integration we find

$$\langle R(t)\rangle = w_2\left[\exp\left(\frac{2\epsilon_2}{\kappa T}\,\frac{A}{1+A}\right)\right] \times\left[\frac{1}{2\pi\sqrt{A}}\,K_0\left(\frac{\epsilon_2}{2\kappa T}\,\frac{1-A}{1+A}\right)\exp\left(\frac{\epsilon_2}{2\kappa T}\,\frac{1-A}{1+A}\right)\right] , \tag{57}$$

where $K_0(z)$ is a modified zeroth-order Bessel function. It may be noted that in the limit in which the argument of the Bessel function is large compared with unity we may write

$$\langle R(t)\rangle = w_2\left[\exp\left(\frac{2\epsilon_2}{\kappa T}\,\frac{A}{1+A}\right)\right] \times\left[\left(\frac{1}{4\pi\epsilon_2/\kappa T}\right)^{1/2}\left(\frac{1+A}{A(1-A)}\right)^{1/2}\right] . \tag{58}$$

As expected, this result is identical with that obtained from Eq. (55) in the limit where $g(z)$ may be replaced by $(2\pi z)^{-1/2}$, i.e., at sufficiently short times.

Applying formula (57) to the calculation of $\langle R_r(t)\rangle$ and utilizing the result that for $\omega_b t \ll 2\pi$, $A_r(t) \simeq 1-\frac{1}{8}(\omega_b t)^2$, we have that for short times $\omega_b t \ll 2\pi$

$$\langle R_r(t)\rangle = w_2\left[\exp\left(\frac{\epsilon_2}{\kappa T}\left(1-\tfrac{1}{8}\omega_b^2 t^2\right)\right)\right] \times\left[\frac{1+\frac{1}{16}\omega_b^2 t^2}{2\pi}\,K_0\left(\frac{\epsilon_2}{32\kappa T}(\omega_b t)^2\right) \times\exp\left(\frac{\epsilon_2(\omega_b t)^2}{32\kappa T}\right)\right] . \tag{59}$$

In Figs. 3 and 4, $\langle E(t)\rangle = \langle R(t)\rangle/w_2$ is plotted vs $\omega_b t$ for $\epsilon_2/\kappa T = 2.5$ and $\epsilon_2/\kappa T = 5$, respectively. The interesting characteristics of these curves are that they rise to a peak at $t \sim \pi/\omega_b$ and that they approach unity very slowly; that is, $\langle R(t)\rangle \sim w_2$ when $(2\epsilon_2/\kappa T)A \simeq (2\epsilon_2/\kappa T)(2/\pi\omega_b t)^{1/2} \lesssim 1$. The dashed curve of Fig. 3 is a plot of $\langle E_r(t)\rangle = \langle R_r(t)\rangle/w_2$. It is noted that as $t\to 0$, $\langle E_r(t)\rangle \propto -\ln t$, while for $\omega_b t \gtrsim \pi$ it merges with the $\langle E(t)\rangle$ curve. These curves illustrate the general features of the enhancement factors $\langle E(t)\rangle$ and $\langle E_r(t)\rangle$.

VIII. APPROXIMATE EVALUATION OF *w*

At this point we shall proceed to calculate the average jump rate w. As is clear from the formula for w [Eq. (46)] and the discussion of the time dependence of $R(t)$ and $R_r(t)$, this is, in general, a formidable task. Furthermore, since the point of view taken in pursuing this study is to elucidate the essential physical effects of the herein described lattice-relaxation processes rather than to perform a detailed calculation which would be strictly applicable to a specific material, it is appropriate to direct our attention to an approximate evaluation of w.

To begin, for simplicity, let us ignore the effects associated with the feature that for short times $t \ll \omega_b^{-1}$ we have $\langle R_r(t)\rangle \gg \langle R(t)\rangle$, and take $R_r(t) = R(t)$. In this situation we have

$$w = \int_0^\infty dr\, e^{-r} R(t(r)) . \tag{60}$$

Thus we shall now proceed to calculate $R(t(r))$.

To begin we write, without loss of generality,

$$R(t(r)) \equiv \langle R(t)\rangle \equiv F e^{Y(t)}; \tag{61}$$

then we note [using Eq. (47)] that

$$\frac{dR}{dr} = \frac{dR}{dt}\Big/\frac{dR}{dt} = \frac{dR}{dt}\Big/ 2R = \frac{1}{2}\frac{d}{dt}Y(t) . \tag{62}$$

At this point we approximate $R(t)$ by replacing $R(t)$ with $\langle R(t)\rangle$ and writing

$$F = R(0) \quad\text{and}\quad Y(t) = C\,\frac{2\epsilon_2}{\kappa T}\,\omega_b t \quad\text{for } \omega_b t \le 2, \tag{63}$$

$$F = w_2 \quad\text{and}\quad Y(t) = \frac{2\epsilon_2}{\kappa T}\left(\frac{2}{\pi}\right)^{1/2}(d+\omega_b t)^{-1/2} \quad\text{for } \omega_b t \ge 2, \tag{64}$$

where d and C are simply numerical factors (C

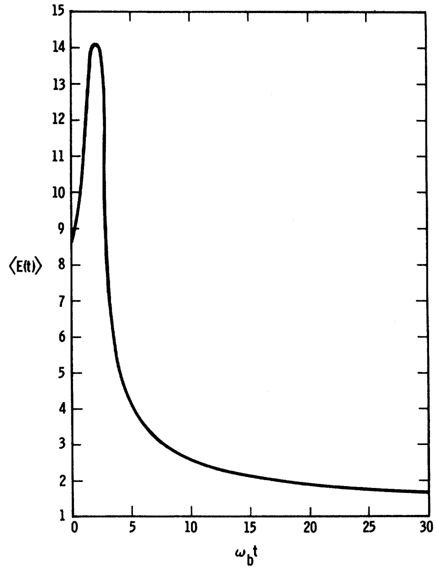

FIG. 4. Forward-hop enhancement factor $\langle R(t)\rangle/w_2$ associated with Eq. (55) plotted vs time, measured in units of the longitudinal optical band half-width, for $\epsilon_2 = 5\kappa T$.

~ 0.02). It should be noted that as $t \rightarrow \infty$ the above expression for $R(t)$ becomes exact. Inserting these expressions for $Y(t)$ into Eq. (62) we find that

$$\frac{dR}{dr} = \frac{1}{2} C \frac{2\epsilon_2}{\kappa T} \omega_b \quad \text{for } \omega_b t \leq 2, \tag{65}$$

$$\frac{dR}{dr} = \frac{1}{2} \frac{2\epsilon_2}{\kappa T} \left(\frac{2}{\pi}\right)^{1/2} \left(-\tfrac{1}{2}\right) (d + \omega_b t)^{-3/2} \omega_b$$

$$= -A w_2 Y^3 = -A w_2 \ln^3 (R/w_2) \quad \text{for } \omega_b t > 2\,, \tag{66}$$

where

$$A \equiv \tfrac{1}{16}\pi\, (\kappa T/\epsilon_2)^2 (\omega_b/w_2)\ .$$

We now solve the above differential equations to find $R(r)$. The first of these equations is readily solved yielding

$$R(r) = R(0)(1 + Br), \quad r < r_0 \equiv r(t = 2\omega_b^{-1}) \tag{67}$$

where

$$B \equiv C(\epsilon_2/\kappa T)[\omega_b/R(0)]\ , \tag{68}$$

$$R(0) = (J^2/\epsilon_2 \hbar)\sqrt{\tfrac{3}{8}}\, e^{-\epsilon_2/3\kappa T}\,. \tag{69}$$

The second of the differential equations is also readily solved by direct integration. However, such a procedure yields $r(R)$ rather than the inverse function $R(r)$, i.e., $R(r)$ is obtained implicitly rather than explicitly. An alternative procedure which becomes exact in the limit of long times ($r \rightarrow \infty$ and $R/w_2 \rightarrow 1$) is to replace Eq. (66) by

$$\frac{d(R/w_2)}{dr} = -A(R/w_2 - 1)^3\ , \tag{70}$$

where, as is appropriate at long times, we have expanded the logarithm about unity. This approach overestimates the rate of decline of R/w_2 with r and hence leads to an underestimate of $R(r)$. However, it yields the correct dependence of R on r as r approaches infinity. Hence, adopting this approximation we find

$$R(r) = w_2 + \frac{w_2[R(r_0) - w_2]}{\{w_2^2 + 2A[R(r_0) - w_2]^2 (r - r_0)\}^{1/2}} \quad \text{for } r > r_0. \tag{71}$$

Finally, an explicit expression for r_0 is given by

$$r_0 = 2 \int_0^{2/\omega_b} dt\, R(t) = \frac{4R(0)}{\omega_b} \frac{e^{4C\epsilon_2/\kappa T} - 1}{4C\epsilon_2/\kappa T}\ . \tag{72}$$

Inserting expressions (67) and (71) into Eq. (60) we find

$$w = R(0) \int_0^{r_0} dr\, e^{-r} (1 + Br) + w_2 \int_{r_0}^{\infty} dr\, e^{-r}$$

$$\times \left(1 + \frac{R(r_0) - w_2}{\{w_2^2 + 2A[R(r_0) - w_2]^2 (r - r_0)\}^{1/2}}\right). \tag{73}$$

Performing the indicated integrations, we find

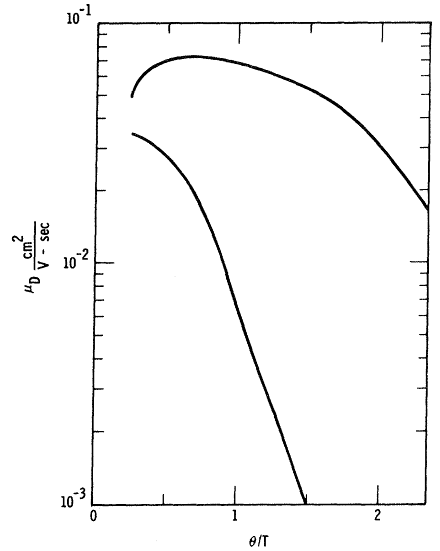

FIG. 5. The top drift mobility vs θ/T curve, where $\theta \equiv \hbar\omega_0/\kappa$, is the result of the present calculation. Below it lies the steeper mobility curve found by Holstein, i.e., ignoring lattice-relaxation effects. Both curves are plotted for $J = \hbar\omega_0 = \frac{1}{5}\epsilon_2$. In the top curve the optical band half-width ω_b is taken to be $\frac{1}{10}\omega_0$.

$$w = R(0)\{[1 - e^{-r_0}] + B[1 - e^{-r_0}(1 + r_0)]\}$$

$$+ w_2 e^{-r_0}\left[1 + \left(\frac{2}{A}\right)^{1/2} I\left(\frac{w_2}{\{2A[R(r_0) - w_2]^2\}^{1/2}}\right)\right]\ , \tag{74}$$

where

$$I(x) \equiv e^{x^2} \int_x^{\infty} dz\, e^{-z^2}\ , \tag{75}$$

and $I(0) = \frac{1}{2}\pi^{1/2}$, $I(x \rightarrow \infty) \simeq 1/2x \rightarrow 0$. The first term of Eq. (74) results from the short-time ($\omega_b t \leq 2$) enhancement effects, while the second term contains the contribution to w from longer times. In the limit of arbitrarily large vibrational dispersion ($\omega_b \rightarrow \infty$), arbitrarily small J($w_2 \rightarrow 0$), or arbitrarily low temperatures, the first term vanishes and the second yields Holstein's result $w = w_2$. (Explicitly, in this limit $r_0 \rightarrow 0$, $A \rightarrow \infty$, and $r_0^2 B \rightarrow 0$.) However, choosing a modest amount of vibrational dispersion ($\omega_b = \frac{1}{10}\omega_0$) we find that for the representative choice of the physical parameters originally chosen by Holstein (namely, $J = \hbar\omega_0 = \frac{1}{5}\epsilon_2$) the first term dominates except at very low temperatures. In Fig. 5 the resulting mobility (related to D via the Einstein relation) is plotted along with that obtained with $w = w_2$; the increased magnitude and milder temperature dependence of the present result is stressed. Furthermore, it should be noted that although the inclusion of the fact that for short times $R_r(t) > R(t)$ would increase the influence of the short-time behavior of $R(t)$ on w, it does not qualitatively alter our results.

IX. DISCUSSION

This work constitutes an exploratory study into the classical effects of finite vibrational dispersion on small-polaron hopping motion. Specifically, Holstein's one-dimensional molecular-crystal model, concerned with an excess carrier in a linear chain of coupled diatomic molecules, has been investigated. While prior considerations[2,7] of the role of the intermolecular coupling in Holstein's model (associated with the dispersion of the optical mode frequencies) have been solely concerned with correlation between a carrier's response to successive coincidences between the occupied site and a neighboring site, the present work has focused attention on the correlations in space and time of coincidence events themselves. In particular, it is found that at a time after an initial coincidence that is less than that associated with the relaxation of the concomitant distortion, the rates characterizing the occurrence of another coincidence involving one or both of the initially coincident sites are generally quite different from the uncorrelated occurrence rate for a coincidence. Furthermore, the corresponding carrier-jump rates also differ considerably from the single-jump rate found from Holstein's uncorrelated diffusion theory,[2] all rates reducing to the uncorrelated rate at times much greater than the relaxation time; $\tau_{\mathrm{relax}} \equiv (2\epsilon_2/\kappa T)^2 \times (2/\pi\omega_b)$. In addition it is found that, in the narrow-band limit, the time-dependent jump rates are characterized by the two vibration-related times: $2\pi/\omega_0$ and $2\pi/\omega_b$. The first of these times, the vibrational period, arises simply because the vibrational state of the system will, in the absence of dispersion, repeat its configuration with the characteristic vibrational frequency. Hence in studying the relaxation phenomena it is useful (but not necessary) to average the jump rates over a vibrational period and study the averaged rates $\langle R(t)\rangle$ and $\langle R_r(t)\rangle$, these averaged rates possessing time dependences which are associated only with the parameters ω_b, κT, and ϵ_2. While $\langle R_r(t)\rangle$ falls monotonically from a maximum value at the time characterizing the first chance of a return hop, $t \simeq 2\pi/\omega_0$, the forward rate $\langle R(t)\rangle$ does not behave so simply.

For short times $t \ll \omega_b^{-1}$, $\langle R(t)\rangle$ is characterized by an activation energy which is one-third the activation energy associated with a hop in a relaxed lattice. This feature may be understood by noting that for such times the initial distortion has relaxed very little and thus the activation energy characterizing the producing of the additional coincidence required for the forward hop is simply the difference between the activation energies associated with creating a three-site coincidence and a two-site coincidence:

$$\epsilon_3 - \epsilon_2 \simeq A^2/3M\omega_0^2 - A^2/4M\omega_0^2 = \tfrac{1}{3}\epsilon_2 .$$

An interesting aspect of the time dependence of $\langle R(t)\rangle$ is its increase with increasing time, with its maximum value occurring at $t \simeq 2/\omega_b$. This phenomenon arises as a result of the fact that as the initially distorted sites relax, the neighboring sites receive energy from the initially distorted sites and become somewhat distorted themselves. The net result is that the additional vibrational energy required to form a coincidence decreases with time until the energy propagates away from the region of the initial coincidence, at $t \sim 2/\omega_b$. Actually a complete discussion of this property of $\langle R(t)\rangle$ involves the detailed consideration of the relative phases of the oscillations at the initially distorted site and the relevant unoccupied neighbor. The classical calculation of the vibrational motion of the lattice for $t < \pi/\omega_b$ is carried out in a forthcoming paper by the present author[8]; it includes a detailed consideration of the relative-phase issue, and hence the question will not be discussed here.

For $t > 2\pi\omega_b$ the rates $\langle R(t)\rangle$ and $\langle R_r(t)\rangle$ merge and decline with time, achieving the time-independent value w_2 for $t \gg \tau_{\mathrm{relax}}$. The denoting of a time as the relaxation time results from the situation that $\langle R(t)\rangle$ and $\langle R_r(t)\rangle$ reach the single value w_2 when

$$(2\epsilon_2/\kappa T)(2/\pi\omega_b t)^{1/2} \ll 1. \tag{76}$$

Hence it is appropriate to define the relaxation time τ_{relax} by

$$\tau_{\mathrm{relax}} \equiv (2/\pi\omega_b)(2\epsilon_2/\kappa T)^2 . \tag{77}$$

In order to understand the origin of condition (76) it should be first noted that one expects the effects of a residual distortion to be significant only when the difference between the activation energies required for a two-site coincidence with and without the residual distortion is greater than the energy associated with a thermally produced distortion. Furthermore, recalling[3] that the two-site activation energy is the minimum potential energy, in excess of the small-polaron binding energy, which is required to produce the two-site-coincidence configuration, one may generally write (ignoring dispersion in this formula for simplicity) that, at a time t after an initial coincidence, the two-site activation energy E_A characterizing a subsequent coincidence is

$$E_A = \tfrac{1}{4}M\omega_0^2(x_a - x_b)^2 , \tag{78}$$

where x_a and x_b are the time-dependent residual displacements of the two relevant diatomic molecules.[18] In particular, taking site a to be the occupied site, one obtains Holstein's result[2] when the residual distortions are neglected; that is, when $x_a = A/M\omega_0^2$ and $x_b = 0$, $E_A = A^2/4M\omega_0^2 \equiv \epsilon_2$. Thus, if one writes $x_a \equiv A/M\omega_0^2 + \Delta x_a$ and $x_b \equiv \Delta x_b$, where Δx_a and Δx_b are the residual distortions of sites a and b at time t, then the difference in activation energies between the relaxed and unrelaxed situations (at sufficiently long times such that $|\Delta x_a|, |\Delta x_b| \ll A/M\omega_0^2$) is

$$\Delta E_A \approx 2\epsilon_2 \left|(M\omega_0^2/A)\,(\Delta x_a - \Delta x_b)\right| . \tag{79}$$

In order to evaluate the time dependence of $(\Delta x_a - \Delta x_b)$ let us view the localized distortion associated with the initial coincidence at $t = 0$ as being composed of a linear superposition of the optical mode states. Assuming the vibrational-dispersion relation (19), it then follows that at sufficiently long times $\omega_b\, t > 2\pi$, the *amplitude* of the relative distortion of the adjacent sites a and b $(\Delta x_a - \Delta x_b)$ decreases with time as

$$|\,\Delta x_a - \Delta x_b\,| \approx (A/M\omega_0^2)(2/\pi\omega_b t)^{1/2} , \tag{80}$$

corresponding to the decline of the center of the wave packet which describes the initial distortion[19]; this result hold regardless of whether site b is taken to be the previously occupied neighboring site or the previously unoccupied neighboring site. Thus, upon combining Eq. (80) with (79), we find that

$$\Delta E_A \approx 2\epsilon_2\,(2/\pi\omega_b t)^{1/2} . \tag{81}$$

Finally, imposing the relaxation condition $\Delta E_A \ll kT$, we obtain inequality (76) for both forward and return hops.

A physical interpretation of the quantities $G(t)$, $G_r(t)$, $A(t)$, and $A_r(t)$, heretofore treated only as mathematical entities, arises readily from the abovementioned wave packet analysis. In particular, if one assumes that a coincidence event, requiring the minimum coincidence energy ϵ_2 occurs between the occupied site (site a) and a neighboring site at $t = 0$, it can be shown that the relative displacement between site a and the "forward" site (site b) is

$$x_a(t) - x_b(t) = \Delta x(\infty)[1 - G(t)], \tag{82}$$

where $G(t)$ is defined by Eq. (18) and

$$\Delta x(\infty) \equiv \frac{1}{N}\sum_k \left(\frac{A}{M\omega_k^2}\right)(1 - \cos k). \tag{83}$$

Furthermore, if site b is taken to be the site that is involved in the initial coincidence, we find that

$$x_a(t) - x_b(t) = \Delta x(\infty)[1 - G_r(t)] , \tag{84}$$

$G_r(t)$ having been defined in Eq. (33). Thus the functions $G(t)$ and $G_r(t)$ are simply related to the "time-dependent" relative displacements $x_a(t) - x_b(t)$. Let us now recall [from Eqs. (26) and (37)] that $A(t)$ and $A_r(t)$ are the time-dependent amplitudes of the oscillatory functions $G(t)$ and $G_r(t)$, respectively. Thus we observe that (in the narrow-band limit $\omega_b/\omega_0 \to 0$) the minima of the relative displacements of the sites involved in a forward and return hop are given by

$$x_a(t) - x_b(t) = \Delta x(\infty)[1 - A(t)], \tag{85}$$

$$x_a(t) - x_b(t) = \Delta x(\infty)[1 - A_r(t)], \tag{86}$$

respectively. It is therefore evident that the quantities $A(t)$ and $A_r(t)$ which appear in the expressions for the jump rates found in Sec. VII are physical quantities related to the residual distortion of the lattice following a coincidence event.[20]

At this point it is useful to stress that in situations where the jump rate is greater than ω_b/π the activation energy characterizing the drift mobility is essentially $\sim\frac{1}{3}\epsilon_2$ rather than ϵ_2. Thus, while the small-polaron condition[1,21]

$$J \ll A^2/M\omega_0^2 \simeq 4\epsilon_2 \tag{87}$$

and the condition for the validity of the nonadiabatic theory[2,5]

$$J^2 < (\epsilon_2\kappa T/\pi)^{1/2}(\hbar\omega_0/\pi) \tag{88}$$

generally set a lower limit on ϵ_2, the activation energy *may* be sufficiently small compared with κT so that the drift mobility may not manifest a simple exponential dependence on reciprocal temperature. Such a situation is illustrated in Fig. 5.

It is now appropriate to investigate the relationship of the model studied here to the situation existing in a real crystal. A major question which immediately arises is that of the relationship of our one-dimensional model to a similar three-dimensional model. In discussing this question let us recall that the enhancement effect at short times $t \lesssim \omega_b^{-1}$ is due to the circumstance that the occupied site is substantially distorted from its equilibrium configuration as a result of the preceding hop. As this effect is not related to the crystal structure it may be anticipated that this feature will not be affected by going to a three-dimensional model. However, since the rise with time of $\langle R(t)\rangle$ to a peak at $t \sim 2/\omega_b$ is associated with the transfer of energy from the initially distorted sites to sites adjacent to them, it is expected that this effect will be somewhat reduced in a three-dimensional lattice because of the increased number of neighbors. Finally, we may modify our estimate of τ_{relax} to take into account the fact that the relaxation of the distortion is associated with the decrease of the central peak of a three-dimensional wave packet rather than a one-dimensional wave packet. These considerations yield, at long times $\omega_b t \gg 1$,

$$|\,\Delta x_a - \Delta x_b\,| \approx (A/M\omega_0^2)(2\times 3/\pi\omega_b t)^{3/2} . \tag{89}$$

The concomitant estimate of the relaxation time being

$$\tau_{\text{relax}} \approx (6/\pi\omega_b)(2\epsilon_2/\kappa T)^{2/3} , \tag{90}$$

this time is usually somewhat shorter than that characterizing our one-dimensional model. Thus, we conclude that while the relaxation in a three-dimensional model may occur more rapidly than that of this initial one-dimensional investigation, the result that the drift mobility associated with a hopping time of the order of ω_b^{-1} may not manifest a clear activation-type temperature dependence is essentially unaffected by going to a three-dimensional model.

It should also be noted that for crystals which possess a sufficiently anisotropic optical phonon dispersion curve $\omega(\vec{k})$ and a similarly anisotropic mobility, the results of a one-dimensional calculation may find direct applicability.

In the present work our considerations have been based on the tacit assumption that one need only consider the effect of a small-polaron hop on the rate characterizing the immediately succeeding hop. In other words, hops of the small polaron other than the jump of the small polaron immediately previous to the hop being considered are taken to have no influence on the small polaron's motion. This ansatz is based on the generally increasing temporal and spatial separation between a hop and its nth predecessor as n increases. Although this assumption has not been studied in detail, it is felt to be a reasonable one for an initial study of correlation effects between small-polaron hops.

As stated earlier we have ignored the result[7] that in the absence of sufficient vibrational dispersion, as defined by Eq. (1), the probability of a hop (without the vibrational-relaxation effects considered here) is not w_2 but a larger quantity. Furthermore, the temperature dependence of the jump rate found by deWit[7] associated with this enhanced rate is milder than that of w_2. We expect, therefore, that the inclusion of the effect of correlation between the carrier's response to successive coincidence events will lead to an even milder temperature dependence of the drift mobility than that calculated here. It should be added that in the limit of a *sufficiently* large electron-lattice interaction strength the small-polaron jump rate is simply w_2 as found by Holstein.[2]

Finally, it should be commented that the Hall mobility is also expected to be affected by lattice-relaxation effects. In particular, in the regime where the mean time between hops is $\lesssim w_b^{-1}$, we might expect the Hall mobility activation energy of the nonadiabatic theory of the triangular lattice[3] to be given by the difference between the activation energies required to form a quadruple coincidence ϵ_4 and a triple coincidence ϵ_3, rather than by the difference $\epsilon_3 - \epsilon_2 \approx \frac{1}{3}\epsilon_2$ appropriate for a relaxed lattice. Thus, since $\epsilon_4 - \epsilon_3 \approx \frac{1}{6}\epsilon_2$ is less than the drift-mobility activation energy in the same regime $E_D \approx \frac{1}{3}\epsilon_2$ we see that the Hall mobility will, as in the prior studies,[3-5] possess a smaller activation energy than the drift mobility. Furthermore it is important to recall[3-5] that the ratio of the Hall to drift mobilities is proportional to $\exp[(E_{\text{drift}} - E_{\text{Hall}})/\kappa T]$, this quantity generally being sufficiently large in the preceding triangular-lattice studies[3,5] ($\approx e^{2\epsilon_2/3\kappa T}$) so that in most instances the calculated Hall mobility is greater than the drift mobility.[22] However, in the situation being discussed here this factor is considerably smaller[23] ($\approx e^{\epsilon_2/6\kappa T}$); thus it is possible for the small-polaron Hall and drift mobilities to be comparable. In fact, applying these arguments to the adiabatic theory of the triangular-lattice Hall effect one sees [cf. Eq. (9.8) of Ref. 5] that the Hall mobility may be considerably smaller than the drift mobility; in addition both the Hall and drift-mobility activation energies are expected to be considerably smaller than their counterparts in the nonadiabatic theory.

Thus it is concluded that it is within the domain of the small-polaron for both Hall and drift mobilities to possess sufficiently small activation energies so that the preexponential temperature dependence of the mobility expressions plays an important role in determining the temperature dependence of the mobilities. Such a situation is characterized by mobilities which (a) do not display a simple activation-type temperature dependence (they may even decrease with increasing temperature) and which (b) are associated with hopping times less than or of the order of the reciprocal of the longitudinal optical bandwidth.

APPENDIX: OCCURRENCE PROBABILITY

Let us now consider the occurrence probability appropriate to a coincidence event involving sites $n=1$ and $n=2$ occurring at an initial time defined as zero and another coincidence event involving sites $n=2$ and $n=3$ occurring at a later time t. Applying the occurrence-probability approach developed by Holstein[2] and Friedman and Holstein[3] to the problem of two subsequent coincidence events in a linear chain, we find the following expression for the probability of (a) a coincidence between sites 1 and 2 occurring between time zero and time dt_0 with a relative vibrational velocity lying between v_{12} and $v_{12}+dv_{12}$ and (b) a coincidence between sites 2 and 3 occurring between times t and $t+dt$ with a relative vibrational velocity lying between v_{23} and $v_{23}+dv_{23}$:

$$P(v_{12}, v_{23}, t)dt_0 dt\, dv_{12}\, dv_{23} = \frac{1}{Z}\int \cdots dv_n \cdots \int \cdots dx_n \cdots \int e^{-E/\kappa T}$$

$$\times\{\delta[x_1(0)-x_2(0)]|v_{12}|\,dt_0\,\delta[v_1(0)-v_2(0)-v_{12}]dv_{12}\}$$
$$\times\{\delta[x_2(t)-x_3(t)]|v_{23}|\,dt\,\delta[v_2(t)-v_3(t)-v_{23}]dv_{23}\}, \tag{A1}$$

where E in the energy of the system when the carrier occupies site 2,[24]

$$E=\textstyle\sum_n(\frac{1}{2}Mv_n^2+\frac{1}{2}M\omega_0^2x_n^2+\frac{1}{2}M\omega_1^2x_nx_{n+1})-Ax_2, \tag{A2}$$

$$Z\equiv\int\cdots dv_n\cdots\int\cdots dx_n\cdots\int e^{-E/\kappa T}. \tag{A3}$$

Proceeding to introduce the Fourier-integral formula for the δ functions, i.e.,

$$\delta(z)=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\alpha\, e^{-iz\alpha},$$

we may rewrite $P(v_{12}, v_{23}, t)$ as

$$P(v_{12},v_{23},t)=\frac{|v_{12}|\,|v_{23}|}{Z(2\pi)^4}\int\cdots dv_n\cdots\int\cdots dx_n\cdots\int_{-\infty}^{\infty}d\alpha\int_{-\infty}^{\infty}d\beta\int_{-\infty}^{\infty}d\gamma\int_{-\infty}^{\infty}d\delta\, e^{-E/\kappa T}$$
$$\times\exp(-i\{\alpha[x_1(0)-x_2(0)]+\beta[v_1(0)-v_2(0)-v_{12}]+\gamma[x_2(t)-x_3(t)]+\delta[v_2(t)-v_3(t)-v_{23}]\}). \tag{A4}$$

At this point we may introduce the normal mode coordinates via the transformation

$$x_n(t)=(2/N)^{1/2}\textstyle\sum_k\sin(kn+\frac{1}{4}\pi)\,q_k(t). \tag{A5}$$

We find that

$$P(v_{12},v_{23},t)=\frac{|v_{12}|\,|v_{23}|}{Z(2\pi)^4}\int\cdots d\dot{q}_k\cdots\int\cdots dq_k\cdots\int d\alpha\int d\beta\int d\gamma\int d\delta\, e^{-E/\kappa T}e^{\,i(\beta v_{12}+\delta v_{23})}$$
$$\times\prod_k\exp\{-i[\alpha G_k^{12}q_k(0)+\beta G_k^{12}\dot{q}_k(0)+\gamma G_k^{23}q_k(t)+\delta G_k^{23}\dot{q}_k(t)]\}, \tag{A6}$$

where

$$G_k^{p,p+1}\equiv(2/N)^{1/2}[\sin(kp+\tfrac{1}{4}\pi)-\sin(kp+\tfrac{1}{4}\pi+k)]. \tag{A7}$$

Furthermore, in terms of the normal mode coordinates the energy of the system becomes

$$E=\textstyle\sum_k\frac{1}{2}M\dot{q}_k^2+\frac{1}{2}M\omega_k^2(q_k-q_k^{(2)})^2-E_b, \tag{A8}$$

where the following three quantities have been defined:

$$q_k^{(p)}\equiv(2/N)^{1/2}(A/2M\omega_k^2)\,\sin(kp+\tfrac{1}{4}\pi), \tag{A9}$$

$$E_b\equiv(1/N)\textstyle\sum_kA^2/2M\omega_k^2, \tag{A10}$$

$$\omega_k^2\equiv\omega_0^2+\omega_1^2\cos k. \tag{A11}$$

At this point it is expedient to transform to a new set of variables which explicitly displays the harmonic time dependence of the normal modes. We write

$$q_k=q_k^{(2)}+Q_k\cos(\omega_kt+\delta_k), \tag{A12}$$

$$\dot{q}_k=-\,\omega_kQ_k\sin(\omega_kt+\delta_k), \tag{A13}$$

where Q_k and δ_k, the amplitude and phase factor for the kth mode, are taken as the new variables, the Jacobian for this transformation being $|-\omega_kQ_k|$. Performing the elementary integrations which are required in evaluating Z we find

$$P(v_{12},v_{23},t)=\frac{|v_{12}|\,|v_{23}|}{(2\pi)^4}\int d\alpha\int d\beta\int d\gamma\int d\delta\prod_k\int_0^{\infty}dQ_k e^{-M\omega_k^2Q_k^2/2\kappa T}\,\frac{M\omega_k^2Q_k}{\kappa T}\,e^{i\beta v_{12}}\,e^{i\delta v_{23}}$$
$$\times\frac{1}{2\pi}\int_0^{2\pi}d\delta_k\exp(-i\{\alpha G_k^{12}[q_k^{(2)}+Q_k\cos\delta_k]+\beta G_k^{12}[-\,\omega_kQ_k\sin\delta_k]$$
$$+\gamma G_k^{23}[q_k^{(2)}+Q_k\cos(\omega_kt+\delta_k)]+\delta G_k^{23}[-\,\omega_kQ_k\sin(\omega_kt+\delta_k)]\}). \tag{A14}$$

At this point it is recalled that $G_k^{p,p+1}\sim N^{-1/2}$ and that $q_k^{(2)}\sim N^{-1/2}$, so that (taking N arbitrarily large) we may evaluate the above integrals by expanding the exponents to second order in $N^{-1/2}$, obtaining

$$[1-i\alpha G_k^{12}(q_k^{(2)}+Q_k\cos\delta_k)-\tfrac{1}{2}\alpha^2(G_k^{12}Q_k\cos\delta_k)^2]\quad[1-i\beta G_k^{12}(-\,\omega_kQ_k\sin\delta_k)-\tfrac{1}{2}\beta^2(G_k^{12}\omega_kQ_k\sin\delta_k)^2]$$
$$\times\{1-i\gamma G_k^{23}[q_k^{(2)}+Q_k\cos(\omega_kt+\delta_k)]-\tfrac{1}{2}\gamma^2[G_k^{23}Q_k\cos(\omega_kt+\delta_k)]^2\}$$

$$\times \{1 - i\delta G_k^{23}[-\omega_k Q_k \sin(\omega_k t + \delta_k)] - \tfrac{1}{2}\delta^2[G_k^{23}\omega_k Q_k \sin(\omega_k t + \delta_k)]^2\}.$$

The integrals over the phase factor δ_k are now readily performed, yielding (again discarding higher-order terms)

$$\begin{aligned} P(v_{12}, v_{23}, t) &= \frac{|v_{12}|\,|v_{23}|}{(2\pi)^4} \int d\alpha \int d\beta \int d\gamma \int d\delta \prod_k \int_0^\infty dQ_k \frac{M\omega_k^2 Q_k}{\kappa T} e^{-M\omega_k^2 Q_k^2/2\kappa T} e^{i\beta v_{12}} e^{i\delta v_{23}} \\ &\quad \times \{1 - i[\alpha G_k^{12} q_k^{(2)} + \gamma G_k^{23} q_k^{(2)}] - \tfrac{1}{4} Q_k^2[(\alpha G_k^{12})^2 + (\beta G_k^{12}\omega_k)^2 + (\gamma G_k^{23})^2 + (\delta G_k^{23}\omega_k)^2] \\ &\quad - \tfrac{1}{2} Q_k^2 G_k^{12} G_k^{23}[\alpha\gamma \cos\omega_k t - \alpha\delta\omega_k \sin\omega_k t + \beta\gamma\omega_k \sin\omega_k t + \beta\delta\omega_k^2 \cos\omega_k t]\} \\ &= \frac{|v_{12}|\,|v_{23}|}{(2\pi)^4} \int d\alpha \int d\beta \int d\gamma \int d\delta\; e^{i\beta v_{12} + i\delta v_{23}} \\ &\quad \times \prod_k \Big[1 - i[\alpha G_k^{12} q_k^{(2)} + \gamma G_k^{23} q_k^{(2)}] - \frac{\kappa T}{2M\omega_k^2}[(\alpha G_k^{12})^2 + (\beta G_k^{12}\omega_k)^2 + (\gamma G_k^{23})^2 + (\delta G_k^{23}\omega_k)^2] \\ &\quad - \Big(\frac{\kappa T}{M\omega_k^2} G_k^{12} G_k^{23}(\alpha\gamma\cos\omega_k t - \alpha\delta\omega_k \sin\omega_k t + \beta\gamma\omega_k \sin\omega_k t + \beta\delta\omega_k^2 \cos\omega_k t)\Big)\Big] \\ &= \frac{|v_{12}|\,|v_{23}|}{(2\pi)^4} \int d\alpha \int d\beta \int d\gamma \int d\delta\; \exp[i(\alpha - \gamma)c_1 + \beta v_{12} + i\delta v_{23} \\ &\quad - c_2(\alpha^2 + \gamma^2) - c_3(\beta^2 + \delta^2) - a(\beta\gamma - \alpha\delta) - b\beta\delta - c\alpha\gamma], \end{aligned} \tag{A15}$$

where we have defined

$$c_1 \equiv -\sum_k G_k^{12} q_k^{(2)} = \sum_k G_k^{23} q_k^{(2)} = \frac{1}{N}\sum_k \frac{A}{M\omega_k^2}(1 - \cos k), \tag{A16}$$

$$c_2 \equiv \sum_k \frac{\kappa T}{2M\omega_k^2}(G_k^{12})^2 = \sum_k \frac{\kappa T}{2M\omega_k^2}(G_k^{23})^2 = \frac{1}{N}\sum_k \frac{\kappa T}{M\omega_k^2}(1 - \cos k), \tag{A17}$$

$$c_3 \equiv \sum_k \frac{\kappa T}{2M}(G_k^{12})^2 = \sum_k \frac{\kappa T}{2M}(G_k^{23})^2 = \frac{\kappa T}{M}, \tag{A18}$$

and the time-dependent quantities

$$a \equiv \sum_k \frac{\kappa T}{M\omega_k} G_k^{12} G_k^{23} \sin\omega_k t = \frac{1}{N}\sum_k \frac{2\kappa T}{M\omega_k} \cos k(1 - \cos k)\sin\omega_k t, \tag{A19}$$

$$b \equiv \sum_k \frac{\kappa T}{M} G_k^{12} G_k^{23} \cos\omega_k t = \frac{1}{N}\sum_k \frac{2\kappa T}{M} \cos k(1 - \cos k)\cos\omega_k t, \tag{A20}$$

$$c \equiv \sum_k \frac{\kappa T}{M\omega_k^2} G_k^{12} G_k^{23} \cos\omega_k t = \frac{1}{N}\sum_k \frac{2\kappa T}{M\omega_k^2} \cos k(1 - \cos k)\cos\omega_k t. \tag{A21}$$

The above expressions are readily derived by utilizing well-known trigonometric identities.

It is now our task to perform the integrals over α, β, γ, and δ. To do this it is convenient to introduce the quantities

$$\begin{aligned} x &\equiv (\alpha - \gamma)/\sqrt{2}, \quad y \equiv (\alpha + \gamma)/\sqrt{2}, \\ u &\equiv (\beta - \delta)/\sqrt{2}, \quad v \equiv (\beta + \delta)/\sqrt{2}. \end{aligned} \tag{A22}$$

We find that

$$\begin{aligned} P(v_{12}; v_{23}, t) = \frac{|v_{12}|\,|v_{23}|}{(2\pi)^4} \Big\{ &\int dx \exp\Big[-\Big(c_2 - \tfrac{1}{2}c\Big)x^2 + i\sqrt{2}\, c_1 x\Big] \int dv \exp\Big[-\Big(c_3 + \frac{b}{2}\Big)v^2 + \frac{i(v_{12} + v_{23})}{\sqrt{2}} v + axv \\ &\times \int dy \exp\Big[-\Big(c_2 + \frac{c}{2}\Big)y^2\Big] \int du \exp -\Big(c_3 - \tfrac{1}{2}b\Big) u^2 + \frac{i(v_{12} - v_{23})u}{\sqrt{2}} - ayu\Big]\Big\}. \end{aligned} \tag{A23}$$

Performing the indicated integrations, we finally find

$$\begin{aligned} P(v_{12}, v_{23}, t) &= \frac{|v_{12}|\,|v_{23}|}{(2\pi)^4} \left(\frac{\pi^2}{A_1 A_2 A_3 A_4}\right) \\ &\quad \times \exp\Big\{-\Big[\frac{(v_{12} - v_{23})^2}{8A_1^2}\Big(1 + \frac{a^2}{4A_1^2 A_4^2}\Big) + \frac{(v_{12} + v_{23})^2}{8A_2^2}\Big(1 + \frac{a^2}{4A_2^2 A_3^2}\Big) + \frac{(v_{12} + v_{23})ac_1}{4A_2^2 A_3^2} + \frac{c_1^2}{2A_3^2}\Big]\Big\}, \end{aligned} \tag{A24}$$

where we have defined the following coefficients:

$$A_1 \equiv (c_3 - \tfrac{1}{2} b)^{1/2}, \quad A_2 \equiv (c_3 + \tfrac{1}{2} b)^{1/2},$$

$$A_3 \equiv \left(c_2 - \tfrac{1}{2} c - \frac{a^2}{4(c_3 + \frac{1}{2} b)}\right)^{1/2}, \quad A_4 \equiv \left(c_2 + \tfrac{1}{2} c - \frac{a^2}{4(c_3 - \frac{1}{2} b)}\right)^{1/2}. \qquad \text{(A25)}$$

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[1] T. Holstein, Ann. Phys. (N. Y.) 8, 325 (1959).

[2] T. Holstein, Ann. Phys. (N. Y.) 8, 343 (1959).

[3] L. Friedman and T. Holstein, Ann. Phys. (N. Y.) 21, 494 (1963).

[4] D. Emin, Ann. Phys. (N. Y.) (to be published).

[5] D. Emin and T. Holstein, Ann. Phys. (N. Y.) 53, 439 (1969).

[6] Except in the classical limit $\hbar \to 0$ the energetic coincidence is viewed as taking a finite time. In particular, since the change in electronic energy due to lattice motion in the time interval Δt_c is $\Delta E \sim Av\Delta t_c$ (in the model adopted here – see Sec. II), where A is essentially an electron-lattice coupling constant and v is a relative velocity associated with ionic motion, we find, noting that the spread in energies is related to the spread in time via the uncertainty relation $\Delta t_c \sim \hbar/\Delta E$, that $\Delta t_c \sim (\hbar/Av)^{1/2}$. This estimate of the duration of a coincidence Δt_c is found in the more detailed arguments of Refs. 1–4.

[7] H. J. deWit, Philips Res. Rept. 23, 449 (1968).

[8] To understand this effect in detail one must consider the phase relationships between the lattice vibrations of the occupied site n and the site $n+1$. Such a study has been carried out and will be reported in a future publication by the present author.

[9] This formula is based on the assumption that adequate vibrational dispersion exists so that the carrier views each coincidence event as an independent event, i. e., there is no phase correlation between the electronic jump amplitudes of successive coincidence events. This situation will be assumed to prevail for the remainder of this work. The specific criterion for the validity of this assumption is discussed in Refs. 2 and 7 and in a forthcoming publication of the present author.

[10] It is a straightforward matter to include higher-order terms in the expansion of ω_k in powers of ω_b/ω_0. However, these terms are found to be of little significance and therefore are discarded at this point to simplify the subsequent calculations.

[11] M. Abromowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1965), specifically formulas 9. 1. 44 and 9. 1. 45.

[12] The inclusion of higher-order terms in ω_b/ω_0 in general destroys this equality. This result may be understood in terms of the discussion of the next paragraph in light of the fact that the inclusion of higher powers of ω_b/ω_0 is associated with the transfer of energy between non-nearest-neighbor sites.

[13] The different roles of the in-phase and out-of-phase components of the vibrational oscillations is studied in the work mentioned in Ref. 8.

[14] The arrows in Figs. 1 and 2 are directed at the points where the slopes $A(t)$ and $A_r(t)$ are zero. In that these slight wiggles in the curves have a negligible effect on our argument, they will not be discussed. They are merely pointed out for completeness.

[15] The calculation of $S(t)$ is a straightforward generalization of the analogous calculation for a single process. Such a calculation is found in F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965), pp. 463-464.

[16] It should be stressed that although the carrier oscillates between the two sites as a result of this enhanced return effect, the quantum-mechanical amplitudes (the a_n' s) are such that the carrier generally remains localized at one site or another at a particular instant. This situation is distinct from the regime of the intermediate polaron in which the electronic wave function simultaneously has a significant amplitude at a number of sites.

[17] The integral in Eq. (52) may, in fact, be solved exactly by expanding the exponential expression in the integrand in terms of the Bessel functions $I_n(z)$. The coefficients of the expansion may then be readily evaluated and are found to be of order A^n. The approximation utilized here provides generally good agreement with the series expression, the agreement becoming exact in the limit of long times $\omega_b t \gg 1$.

[18] Formula (78) may be obtained by the arguments of Appendix B of Ref. 3 when one makes the replacements $x_1 - A/M\omega_0^2 \to x_1 - x_a$ and $x_3 \to x_3 - x_b$ in Eq. (B1) of that paper.

[19] An anlogous situation is found in studying the decay of the center of a spreading Gaussian wave packet, namely [see Sec. 3. 5 of D. Bohm, *Quantum Theory* (Prentice-Hall, New York, 1951)], the center of a stationary wave packet falls at long times as $(\Delta\omega\, t)^{-1/2}$, where $\Delta\omega$ is the spread of frequencies which are involved in producing the wave packet.

[20] The above derivations and the physical significance of $A(t)$ and $A_r(t)$ are discussed further in the work of Ref. 8.

[21] The small-polaron condition is not expressed in terms of the small-polaron binding energy since a study of a model in which the electron is affected by distortions on sites other than the occupied site (unpublished work) indicates that the relevent small-polaron condition is not in general $J \ll E_b$ but is a more complicated expression. While the condition $J \ll 4\epsilon_2$ is not strictly correct either, it has the virtues of being much closer to the exact expression and of relating the small-poloran condition to quantities which can be inferred from measurements of the temperature dependence of the drift and Hall mobilities.

[22] In the nonadiabatic theory of the Hall effect in a square lattice (Ref. 4), it is shown that (at sufficiently low temperatures, $\kappa T < \epsilon_4 - \epsilon_3 \approx \frac{1}{6}\epsilon_2$) the temperature dependence of the Hall mobility is essentially the same as that calculated for a triangular lattice (Ref. 3). However, at higher temperatures the Hall mobility is multiplied by an additional factor of $1/\kappa T$ and the activation energy is slightly increased by the amount of $\epsilon_4 - \epsilon_3$. This leads to a some-

what smaller ratio factor ($\approx e^{\epsilon_2/2\kappa T}$) than the triangular-lattice value.

[23] In the correlated regime, it is expected that the transition between the high-temperature and low-temperature regime of the square-lattice Hall mobility (Cf. Ref. 22) will occur at $\kappa T \approx \epsilon_5 - \epsilon_4 \approx \frac{1}{10}\epsilon_2$. In the high-temperature correlated regime. we have $E_{\mathrm{Hall}} \approx (\epsilon_5 - \epsilon_2) - (\epsilon_3 - \epsilon_2) \approx \frac{1}{4}\epsilon_2$, while $E_{\mathrm{drift}} \approx \epsilon_3 - \epsilon_2 \approx \frac{1}{3}\epsilon_2$, thereby yielding an even smaller ratio factor ($e^{\epsilon_2/12\kappa T}$) than that for a triangular lattice quoted in the text.

[24] It has been stressed previously (cf. footnotes 33 of Ref. 2 and 5 of Ref. 3) that, within the domain of validity of the herein utilized semiclassical approach, it is irrelevant to the calculation of the rate characterizing a single small-polaron hop whether one assumes the initial or final site to be occupied in writing the energy of the system. Furthermore, in that we are concerned with the behavior of the lattice in the time interval between the two hops, the proper choice of Hamiltonian should manifest the situation in which the intermediate site is occupied. Thus the appropriate Hamiltonian for the consideration of two successive hops is seen to be that in which the intermediately occupied site is taken to be occupied, i.e., the electronic-energy term of (A2) is taken to be $-Ax_2$.