PHYSICAL REVIEW B VOLUME 26, NUMBER 12 15 DECEMBER 1982

Transition between coherent and stochastic motion of light interstitials

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(Received 6 November 1981; revised manuscript received 16 August 1982)

We consider first the application of a linear-coupling small-polaron theory to the motion of light interstitials such as hydrogen isotopes and the positive muon in solids. We carry out a microscopic quantum calculation of the density-density correlation function for a diffusing particle that passes smoothly as a function of temperature between the low-temperature limit of coherent bandlike motion and the high-temperature limit of stochastic hopping. A numerical calculation of the mean time of stay of the particle on a given interstitial site shows a maximum at the transition temperature T^*. For a Debye phonon spectrum $0.3 \leq T^*/\Theta \leq 0.7$ for reasonable estimates of the lattice distortion energy and rigid-lattice bandwidth appropriate for positive muons. Higher-order phonon interactions are then introduced and treated within the same formalism. They give rise to a kind of "motional narrowing" of the coherent portion of the density-density correlation function, that depresses T^* substantially. Numerical calculations of the mean time of stay for a range of linear- and quadratic-phonon-coupling strengths indicate a substantial depression of the transition temperature between "coherent" and stochastic diffusion, while the transition to true bandlike motion occurs at a still lower temperature.

I. INTRODUCTION

The small polaron was originally introduced to treat the motion of an excess electron or hole in a (polar) deformable lattice.[1] For the case of electronic propagation in metals, the large Fermi velocity and screening of the ion cores greatly reduce the Coulomb coupling to the lattice, so that the effects of phonons can be handled in the context of perturbation theory about a basically bandlike motion. However, for polar insulators the motion of carriers is so strongly coupled to the ions that such a perturbative treatment breaks down. This led to a theory in which the bandlike behavior expected of a particle in a rigid lattice disappears entirely at high temperatures. Instead, the particle motion becomes a stochastic jumping, mediated by multiphonon emission and absorption processes. In essence the mean free path of the particle becomes short compared to a lattice constant, in which case the idea of propagation in band states becomes meaningless.

In more recent years the original polaron theory, with suitable modifications, has been applied to a domain not originally envisaged—the diffusion of light interstitial particles such as the isotopes of hydrogen and the positive muon.[2-4] The basic observations motivating such a treatment are (1) the occurrence of relatively large lattice distortions around these interstitials,[5] (2) the relatively small mass of these particles leading to an appreciable ground-state tunneling between neighboring interstitial sites, and (3) the still relatively narrow bandwidths $W \ll \hbar\omega_D$ that make phonons a large perturbation of the rigid-lattice band structure. We refer the reader to the recent review article by Kehr[6] for an overview of much of this work.

The basic outlines of the theory are fairly well developed. At high temperatures the interstitial motion is dominated by uncorrelated jumping between neighboring sites. A stochastic jump rate between these sites is calculated in the second order of time-dependent perturbation theory applied to the tunneling matrix element (but to infinite order in particle-lattice coupling). The resulting diffusion constant is then predicted to have an approximate Arrhenius-law temperature dependence, but the activation energy is associated not with classical over-the-barrier hops but with the lattice relaxation energy. The random walk of the particle is characterized by multiphonon absorption and emission processes, which become increasingly probable as the temperature increases.

At low temperature the stochastic transport mode disappears and is replaced by coherent tunneling. In a pure crystal the particle then exists in Bloch eigenstates labeled by a wave vector $\vec{k}$ in the first

Brillouin zone. Since phonons of different wave vectors are only rarely emitted or absorbed, external momentum is only infrequently imparted to the particle (scattering), and $\vec{k}$ remains a relatively good quantum number. One difference between ordinary band transport and this coherent polaron motion derives from the fact that the polaron bandwidth is temperature dependent. The particle must drag its lattice deformation along as it moves. This results in its "bare" rigid-lattice bandwidth being narrowed by a Debye-Waller factor that is a monotonically decreasing function of increasing temperature.

While both the low- and high-temperature limits of a polaronic model for light interstitial diffusion are reasonably understood, a theory that interpolates smoothly between these limits has not yet been presented. It is the purpose of this work to provide such a theory through a microscopic quantum calculation of the density-density correlation function for a diffusing particle. Our object is to calculate this correlation function, and the mean time of stay of a particle on an interstitial site derived from it, as a function of polaronic parameters such as the rigid-lattice bandwidth and the lattice relaxation energy. In the limit appropriate to light interstitial motion where the mean time of stay is long compared to a typical lattice-vibrational period and in a defect-free crystal, we develop a theory that reduces correctly to known results in both the low- and high-temperature limits and that passes smoothly from coherent propagation to stochastic jumping as the temperature is raised. Thus for this particular case a complete description of the band to stochastic hopping transition is possible.

In Sec. II we introduce a linear-phonon-coupling Hamiltonian and its displaced oscillator canonical transformation. The density-density correlation function and its relation to the mean time of stay are defined. The method of its calculation is outlined here and in the Appendix. For the particularly simple case of motion over a simple cubic lattice, real-space site correlation functions are derived for an arbitrary mixture of coherent and incoherent transport. In Sec. III we present the results of a numerical calculation of the mean time of stay assuming a Debye phonon spectrum. The transition temperature T^* between coherent and stochastic motion, manifested as a peak in the mean time of stay, is found to satisfy $0.3 \lesssim T^*/\Theta \lesssim 0.7$ for reasonable estimates of the lattice distortion energy and rigid-lattice tunneling matrix element appropriate for positive muons. In Sec. IV we generalize the Hamiltonian to include higher-order phonon couplings, and derive their effect upon the density-density correlation function of the linear-coupling model. A numerical calculation of the mean residence time is carried out to illustrate the severe depression of T^* by quadratic phonon interactions. Section V summarizes our conclusions and briefly discusses other effects that further reduce T^* in real physical systems.

II. CALCULATION OF THE DENSITY-DENSITY CORRELATION FUNCTION

A. The Hamiltonian

We consider a single particle in a periodic lattice that is coupled linearly to the lattice vibrations,

$$H=\frac{1}{2}\sum_{q\lambda}\omega_{q\lambda}(|p_{q\lambda}|^2+|u_{q\lambda}|^2)+J_0\sum_{i,\delta}c_i^\dagger c_{i+\delta}$$
$$-\frac{1}{\sqrt{N}}\sum_{q\lambda}\sum_i g_{q\lambda}u_{q\lambda}e^{-i\vec{q}\cdot\vec{R}_i}n_i \ . \qquad (2.1)$$

Here the first term is the harmonic Hamiltonian of the unperturbed lattice with $\omega_{q\lambda}$ taken to be the frequency of the vibrational mode of wave vector $\vec{q}$ and polarization λ. The canonical momentum and displacement operators are defined in second quantization as

$$u_{q\lambda}=(a_{q\lambda}+a^\dagger_{-q\lambda})/\sqrt{2} \ ,$$
$$p_{q\lambda}=(a_{-q\lambda}-a^\dagger_{q\lambda})/\sqrt{2}i \ . \qquad (2.2)$$

The parameter J_0 in the second term is the rigid-lattice tunneling matrix element between nearest-neighbor sites separated by a distance $\vec{\delta}$. The operator $c_i^\dagger$ creates a particle in the Wannier orbital centered around site i. We consider only crystals having a symmetry such that the length of a closed path connecting adjacent sites is an even multiple of δ. Because of the relatively large interstitial mass and consequent limited range of the Wannier orbitals, we take the rigid-lattice Hamiltonian to be of the tight-binding form and restrict consideration to jumps only between neighboring sites on a Bravais lattice. The third term in (2.1) represents the linear coupling of the interstitial to the lattice modes, with a coupling energy $g_{q\lambda}=g^*_{-q\lambda}$ to the mode $q\lambda$. We presume the lattice coupling to be strong so that this term cannot simply be treated in perturbation theory.

In adopting this Hamiltonian we are making a number of approximations that deserve further comment.

(i) An adiabatic approximation for electron screening of the interstitial derives from the smallness of the electron mass to the interstitial mass $m \ll m_I$. We assume that screening takes place essentially instantaneously on the time scale of the interstitial motion so that we can define the potential energy for a screened particle in the lattice.

(ii) A second adiabatic approximation results from the smallness of the interstitial mass to that of the lattice ions $m_I \ll M$. Thus we can define a potential energy for the interstitial as a function of instantaneous ion positions. This is analogous to the usual Born-Oppenheimer approximation used to decouple electronic and ionic degrees of freedom.

(iii) The linear particle-lattice interaction is an approximation that is potentially more serious. It clearly represents only the leading term in an expansion of the potential energy $V(\{\vec{R}_N\})$ about equilibrium. As pointed by Kagan and Klinger,[3] the higher-order terms may have important effects on the low-temperature motion of a particle in narrow energy bands. The effect of these terms is conceptually easier to understand with the context of the solution to the linear-coupling model, so we defer their treatment to Sec. IV.

(iv) We have restricted consideration to motion over a Bravais lattice (single-band model). If more than a single interstitial site per unit cell exists, there can in principle be important effects on the temperature dependence of the stochastic jump rate.[7,8] We comment upon this consideration later.

(v) We have adopted the Condon approximation, i.e., the bare tunneling matrix element J_0 is taken to be independent of lattice configuration. Teichler[9] has discussed the inclusion of effects beyond the Condon approximation, but their consideration here would take us beyond our immediate concerns. Thus we take the Hamiltonian to have the restricted property of dynamical but site-diagonal disorder resulting from the phonon coupling.

Following standard treatments[10,11] we perform a canonical displaced oscillator transformtion on H. Defining

$$\phi_i=\frac{1}{\sqrt{N}}\sum_{q\lambda} g^*_{q\lambda}p_{q\lambda}e^{i\vec{q}\cdot\vec{R}_i}\,,\qquad \phi=\sum_i \phi_i n_i\,, \tag{2.3}$$

we have

$$H'=e^{i\phi}He^{-i\phi}=\sum_{q\lambda}\omega_{q\lambda}(n_{q\lambda}+\tfrac{1}{2})-E_a\sum_i n_i+J_0\sum_{i,\delta}e^{i(\phi_i-\phi_{i+\delta})}c_i^\dagger c_{i+\delta}\,. \tag{2.4}$$

Here we have reexpressed the phonon Hamiltonian in more standard form and defined the polaron binding energy,

$$E_a=\frac{1}{2N}\sum_{q\lambda}\frac{|g_{q\lambda}|^2}{\omega_{q\lambda}}\,. \tag{2.5}$$

The energy of the interstitial is lowered by E_a as a result of distorting the lattice from equilibrium in its immediate vicinity. Note that the effect of this transformation is to transfer the site-diagonal disorder in H into off-diagonal disorder in H' while leaving the phonon frequencies unchanged. In contrast, if a quadratic term in the particle-lattice interaction were important, the site-diagonal disorder could not be eliminated by transformation.

It is convenient to separate the terms in H' responsible for coherent and incoherent motion. We set

$$H'=H_0+H_1 \tag{2.6}$$

with

$$H_0=\sum_{q\lambda}\omega_{q\lambda}(n_{q\lambda}+\tfrac{1}{2})+\sum_{i,\delta}\langle e^{i(\phi_i-\phi_{i+\delta})}\rangle_{\rm ph}c_i^\dagger c_{i+\delta}\,,$$

$$H_1=J_0\sum_{i,\delta}(e^{i(\phi_i-\phi_{i+\delta})}-\langle e^{i(\phi_i-\phi_{i+\delta})}\rangle_{\rm ph})c_i^\dagger c_{i+\delta}\,. \tag{2.7}$$

The expectation value $\langle\ \rangle_{\rm ph}$ above is taken with respect to the phonon portion of H_0. A straightforward calculation yields the usual temperature-dependent band-narrowing factor

$$\langle e^{i(\phi_i-\phi_{i+\delta})}\rangle_{\rm ph}=e^{-S}\,,$$

$$S=\frac{1}{N}\sum_{q\lambda}\frac{|g_{q\lambda}|^2}{\omega^2_{q\lambda}}\coth\left[\frac{\beta\omega_{q\lambda}}{2}\right]\sin^2\left[\frac{\vec{q}\cdot\vec{\delta}}{2}\right]\,, \tag{2.8}$$

$$\beta=\frac{1}{kT}\,.$$

Since S is independent of i and $\vec{\delta}$, H_0 may then be exactly diagonalized in terms of band eigenstates labeled by a wave vector $\vec{k}$ in the first Brillouin zone:

$$H_0=\sum_{q\lambda}\omega_{q\lambda}(n_{q\lambda}+\tfrac{1}{2})+\sum_k\epsilon_k n_k\,, \tag{2.9}$$

where

$$n_k=c_k^\dagger c_k\,,\qquad c_k^\dagger=\frac{1}{\sqrt{N}}\sum_i c_i^\dagger e^{i\vec{k}\cdot\vec{R}_i}\,,\qquad \epsilon_k=J_0e^{-S}\sum_\delta e^{i\vec{k}\cdot\vec{\delta}}\,. \tag{2.10}$$

The coherent Bloch motion governed by H_0 is clearly accompanied by a conservation of the phonon occupation numbers $n_{q\lambda}$ in each phonon mode.

The remaining term H_1 is normally treated in the second order of time-dependent perturbation theory,[2,3] and leads then to a stochastic or incoherent motion of the particle accompanied by the emission and absorption of phonons with the selection rule $n_{q\lambda} \rightarrow n_{q\lambda} \pm 1$. Such processes transfer a net momentum to the particle and hence destroy the significance of $\vec{k}$ as a good quantum number. At low temperatures we may view these processes as giving rise to intraband scattering, while at high temperature they are so frequent that the coherent motion is suppressed entirely and a stochastic hopping sets in.

B. The density-density correlation function

Our object is to develop a theory that passes smoothly between the low-temperature band limit and the high-temperature stochastic limit. To that end we introduce the density-density correlation function,

$$G_q(t) = \langle \rho_q(t) \rho_q^\dagger(0) \rangle \Theta(t) , \tag{2.11}$$

where

$$\rho_q(t) = e^{iH't} \sum_k c_k^\dagger c_{k+q} e^{-iH't} ,$$
$$\langle \ \rangle = \mathrm{Tr} e^{-\beta H'} \cdots / \mathrm{Tr} e^{-\beta H'} . \tag{2.12}$$

$\Theta(t)$ is the unit step function, and the trace is to be taken over single-particle states. $G_q(t)$ has a well-defined meaning in the coherent limit of propagation and also in the stochastic limit where the band states lose their significance. For example, from it we can calculate the real-space correlation functions $G_{ij}(t)$ encountered in the rate equation approach to the stochastic hopping regime:

$$G_{ij}(t) = \langle n_i(t) n_j(0) \rangle \Theta(t)$$
$$= \frac{1}{N} \sum_q e^{i\vec{q}\cdot(\vec{R}_i - \vec{R}_j)} G_q(t) . \tag{2.13}$$

For calculational purposes it is more convenient to introduce the Fourier transform

$$G_q(\omega) = \int_0^\infty dt\, e^{i\omega t} G_q(t) , \tag{2.14}$$

where $\omega = \omega + i\epsilon$ to guarantee convergence at $t \rightarrow \infty$.

Of particular interest to us will be the mean time of stay of the particle on a given site. This is defined in terms of the autocorrelation function $G_{ii}(t)$ as

$$\tau_c \equiv \int_0^\infty dt\, G_{ii}(t) = \int_0^\infty dt \frac{1}{N} \sum_q G_q(t)$$
$$= \lim_{\omega \rightarrow 0} \frac{1}{N} \sum_q G_q(\omega) . \tag{2.15}$$

τ_c is a simple measure of the rate of movement of the interstitial through the lattice. In the limit of pure stochastic motion it is inversely proportional to the jump rate, while for coherent motion it is inversely proportional to the bandwidth. We also note that in the interpretation of muon spin rotation (μSR) experiments involving motional narrowing of the spin depolarization rate of positive muons, it is τ_c that basically determines the amount of narrowing in *both* the coherent and stochastic limits.

In calculating $G_q(\omega)$ we restrict the trace in Eq. (2.12) to the zero-order Hamiltonian, i.e., $\beta H_1 \ll 1$, and assume further that the polaron bandwidth $W \ll kT$ so that

$$e^{-\beta\epsilon_k} \Big/ \sum_k e^{-\beta\epsilon_k} \approx \frac{1}{N} . \tag{2.16}$$

We introduce the interaction representation to write

$$G_q(t) = \frac{\mathrm{Tr} e^{-\beta H_0}}{Z_0} e^{iH_0 t} U(t,0) \rho_q U(0,t) e^{-iH_0 t} \rho_q^\dagger , \tag{2.17}$$

where $U(t,0)$ is the time-evolution operator

$$U(t,0) = T \exp\left[i \int_0^t dt' H_1(t') \right] ,$$
$$U(0,t) = U^\dagger(t,0) . \tag{2.18}$$

Here T is the usual time-ordering operator, and

$$H_1(t') = e^{-iH_0 t'} H_1 e^{iH_0 t'} . \tag{2.19}$$

The diagrammatic perturbation theory associated with H_1 has been discussed by Lang and Firsov[10] and Kudinov and Firsov[11] in connection with the polaron mobility derived from a current-current correlation function. We have found it most convenient to simply expand the time-ordered exponentials above order by order in perturbation theory. This has been done through fourth order and for selected terms in sixth order. From these the dominant terms in nth order may readily be inferred as the form of the perturbation series becomes clear, subject to certain limits that emerge naturally as the calculation progresses. For ease of presentation we will consider here only terms up to second order. Selected fourth-order terms are derived in the Appendix.

In zeroth order we have $U(t,0)=1$ and

$$G_q(\omega)=\frac{1}{N}\sum_k \frac{1}{-i(\omega+\epsilon_k-\epsilon_{k+q})}\ , \tag{2.20}$$

which corresponds to pure bandlike propagation. The first-order term is identically zero since $\langle H_1\rangle_{\text{ph}}=0$. In the second order there are three possible terms of the form 2:0, 1:1, and 0:2, where $m:m'$ denotes the number of H_1 factors coming from $U(t,0)$ and $U^{\dagger}(t,0)$, respectively. We consider the 1:1 term,

$$1{:}1=\frac{1}{N}\sum_{k'}\int_0^{\infty}dt\, e^{i(\omega+\epsilon_{k'}-\epsilon_{k'+q})t}\int_0^t dt_1\int_0^t dt_2\sum_k\langle k'\,|\,\langle H_1(t_1)c_k^{\dagger}c_{k+q}H_1(t_2)\rangle_{\text{ph}}\,|\,k'+q\rangle\ , \tag{2.21}$$

where the bracket $\langle\ \rangle_{\text{ph}}$ represents a trace over the phonon Hamiltonian. The matrix element in the integrand factors as

$$\sum_k\langle k'\,|\,\langle H_1(t_1)c_k^{\dagger}c_{k+q}H_1(t_2)\rangle_{\text{ph}}\,|\,k'+q\rangle$$
$$=J_0^2\sum_k\sum_{i,\delta}\sum_{j,s'}k_{j,\delta'}\langle k'\,|\,c_i^{\dagger}(t_1)c_{i+\delta}(t_1)c_k^{\dagger}c_{k+q}c_j^{\dagger}(t_2)c_{j+\delta'}(t_2)\,|\,k'+q\rangle\langle e^{i\chi_{i,i+\delta}(t_1)}e^{i\chi_{j,j+\delta'}(t_2)}-e^{-2s}\rangle_{\text{ph}}\ , \tag{2.22}$$

where we have defined

$$\chi_{i,i+\delta}\equiv\phi_i-\phi_{i+\delta}\ . \tag{2.23}$$

Expanding the Wannier operators in terms of their band counterparts and calculating the particle matrix elements above we find

$$\sum_k\langle k'\,|\,c_i^{\dagger}(t_1)c_{i+\delta}(t_1)c_k^{\dagger}c_{k+q}c_j^{\dagger}(t_2)c_{j+\delta'}(t_2)\,|\,k'+q\rangle$$
$$=\frac{1}{N^2}\sum_k e^{i(\vec{k}-\vec{k}')\cdot(\vec{R}_i-\vec{R}_j)}e^{i\vec{k}\cdot\vec{\delta}}e^{i(\vec{k}'+\vec{q})\cdot\vec{\delta}'}e^{-i(\epsilon_{k'}-\epsilon_k)t_1}e^{-i(\epsilon_{k+q}-\epsilon_{k'+q})t_2}\ . \tag{2.24}$$

The phonon expectation value is easily calculated by expressing the trace as a product of traces over each normal mode $q\lambda$ and using the harmonic time dependencies

$$e^{iH_0t}a_{q\lambda}^{\dagger}e^{-iH_0t}=a_{q\lambda}^{\dagger}e^{i\omega_{q\lambda}t},\quad e^{iH_0t}a_{q\lambda}e^{-iH_0t}=a_{q\lambda}e^{-i\omega_{q\lambda}t}\ . \tag{2.25}$$

We find the result

$$\langle e^{i\chi_{i,i+\delta}(t_1)}e^{i\chi_{j,j+\delta'}(t_2)}\rangle_{\text{ph}}=e^{-2S}\exp\left[-\frac{1}{N}\sum_{q\lambda}(1+n_{q\lambda})f_{q\lambda}(t_1-t_2)+n_{q\lambda}f_{q\lambda}^{*}(t_1-t_2)\right]\ , \tag{2.26}$$

where we have defined

$$n_{q\lambda}=(e^{\beta\omega_{q\lambda}}-1)^{-1},\quad f_{q\lambda}(t)=\gamma_{q\lambda}(\vec{R}_i-\vec{R}_j,\vec{\delta},\vec{\delta}')e^{i\omega_{q\lambda}t}\ ,$$
$$\gamma_{q\lambda}(\vec{R}_1,\vec{R}_2,\vec{R}_3)=\frac{|g_{q\lambda}|^2}{2\omega_{q\lambda}^2}e^{i\vec{q}\cdot\vec{R}_1}(1-e^{i\vec{q}\cdot\vec{R}_2})(1-e^{-i\vec{q}\cdot\vec{R}_3})\ . \tag{2.27}$$

At this point we adopt an approximation consistent with the existence of the small polaron. We take the narrowed bandwidth to be much smaller than an average phonon frequency appearing in the correlation function (2.26). Thus

$$\epsilon_k-\epsilon_{k'}\ll\hbar\omega_D,\ kT\ . \tag{2.28}$$

This condition is equivalent to the physical situation in which the particle is unable to tunnel away from a site before the polaronic state with its accompanying lattice deformation forms, and allows us to approximate the time-dependent exponentials in Eq. (2.24) by unity. The summation over $\vec{k}$ may then be performed and Eq.

(2.21) becomes with $\vec{R}_i-\vec{R}_j=-\vec{\delta}$,

$$1{:}1=\frac{(J_0e^{-S})^2}{N}\sum_{k'}\sum_{\delta,\delta'}e^{i\vec{k}'\cdot(\vec{\delta}+\vec{\delta}')}e^{i\vec{q}\cdot\vec{\delta}'}\int_0^{\infty}dt\,e^{i(\omega+\epsilon_{k'}-\epsilon_{k'+q})t}\times\int_0^t dt_1\int_0^t dt_2\exp\left[-\frac{1}{N}\sum_{q\lambda}(1+n_{q\lambda})f_{q\lambda}(t_1-t_2)+n_{q\lambda}f^*_{q\lambda}(t_1-t_2)\right]-1\;. \tag{2.29}$$

Finally, we note that by far the largest term contributing to the $\vec{\delta}'$ summation above is $\vec{\delta}'=-\vec{\delta}$. In the limit $\epsilon_{k'}-\epsilon_{k'+q}\to 0$ this is a rigorous identity, and further this is the only term for which the band narrowing is canceled at short times. All other terms are smaller by a factor $O(e^{-2S})$. Retaining just this term and integrating by parts, we recover

$$1{:}1\approx\frac{1}{N}\sum_{k',\delta}\frac{e^{-i\vec{q}\cdot\vec{\delta}}p(\omega)}{[-i(\omega+\epsilon_{k'}-\epsilon_{k'+q})]^2}\;, \tag{2.30}$$

where we define

$$p(\omega)=(J_0e^{-S})^2\times\int_0^{\infty}dt\,e^{i\omega t}\{\exp[2S(t)]+\exp[2S^*(t)]-2\}\;, \tag{2.31}$$

$$S(t)=\frac{1}{N}\sum_{q\lambda}\frac{|g_{q\lambda}|^2}{\omega_{q\lambda}^2}\sin^2\frac{\vec{q}\cdot\vec{\delta}}{2}\times[(1+n_{q\lambda})e^{i\omega_{q\lambda}t}+n_{q\lambda}e^{-i\omega_{q\lambda}t}]\;.$$

In keeping with our earlier approximations we have set $e^{i(\epsilon_{k'}-\epsilon_{k'+q})t}\approx 1$ in the final Fourier transform. A similar analysis applied to the two other second-order terms yields

$$T_2\equiv 2{:}0+0{:}2+1{:}1=-\frac{1}{N}\sum_{k,\delta}\frac{(1-e^{-i\vec{q}\cdot\vec{\delta}})p(\omega)}{[-i(\omega+\epsilon_k-\epsilon_{k+q})]^2}\;. \tag{2.32}$$

Under the same approximation used to derive Eq. (2.32), the odd-order terms in the perturbation series may be shown to be small. In fourth order there are five different terms of the form 4:0, 3:1, 2:2, 1:3, and 0:4. An illustrative calculation of the first of these is found in the Appendix, so we merely summarize our results here. Under the condition of narrow coherent bandwidth specified in Eq. (2.28), the neglect of small terms which do not cancel the band narrowing at short times, and for values of $\omega\ll\omega_D$, we find that in $2n$th order

$$T_{2n}=(-1)^n\frac{1}{N}\sum_k\frac{1}{-i(\omega+\epsilon_k-\epsilon_{k+q})}\times\left[\frac{\sum_{\delta}(1-e^{-i\vec{q}\cdot\vec{\delta}})p(\omega)}{-i(\omega+\epsilon_k-\epsilon_{k+q})}\right]^n\;. \tag{2.33}$$

Thus the entire perturbation series may be summed to yield

$$G_q(\omega)=\frac{1}{N}\sum_k\left[-i(\omega+\epsilon_k-\epsilon_{k+q})+p(\omega)\sum_{\delta}(1-e^{-i\vec{q}\cdot\vec{\delta}})\right]^{-1}\;. \tag{2.34}$$

This equation is the fundamental result of our calculation.

Let us consider the limits of this in various regimes of temperature. In the high-temperature limit the band energies $\epsilon_k\to 0$ exponentially with temperature. Then so long as the jump rate between sites remains small on the scale of ω_D, we may set $p(\omega)\approx p(0)=p$ for frequencies of interest in the diffusion process. Then

$$G_q(\omega)\to\frac{1}{-i\omega+p\sum_{\delta}(1-e^{-i\vec{q}\cdot\vec{\delta}})},\quad \omega_D\tau_c\gg 1\;. \tag{2.35}$$

where p is the usual temperature-dependent stochastic jump rate calculated in the second order of time-dependent perturbation theory. Then $G_q(\omega)$ is just what would be derived from a straightforward application of rate equations for the site-probability density. The pole on the imaginary axis in the ω plane indicates the purely stochastic nature of the propagation in this limit. The diffusion constant is

$$D = zp\delta^2/6 , \tag{2.36}$$

where z is the coordination number of the lattice.

In the opposite limit of low temperatures we are also justified in setting $p(\omega)\rightarrow p(0)$ so long as the polaron bandwidth is narrow compared to characteristic lattice energies. Since the stochastic jump rate vanishes[2] as T^7 as $T\rightarrow 0$, we recover the result for purely coherent motion,

$$G_q(\omega)\rightarrow \frac{1}{N}\sum_k \frac{1}{-i(\omega+\epsilon_k-\epsilon_{k+q})} . \tag{2.37}$$

Here the poles lie on the real axis, characteristic of coherent propagation. At intermediate temperatures the pole positions will be complex, corresponding to a mixture of coherent and stochastic processes.

The transition between coherent and stochastic motion occurs at a temperature T^* where the real and imaginary parts of the pole positions in $G_q(\omega)$ become roughly equivalent, i.e.,

$$J_0 e^{-S(T^*)} \approx p(T^*) \tag{2.38}$$

as also found by Holstein.[1] Equivalently, we note that $G_q(t)$ can be written as the product of a coherent and a stochastic factor,

$$G_q(t)=\frac{1}{N}\sum_k e^{i(\epsilon_k-\epsilon_{k+q})t} \times \exp\left[-pt\sum_\delta (1-e^{i\vec{q}\cdot\vec{\delta}})\right] . \tag{2.39}$$

Thus the decay will be governed by the factor with the most rapid time dependence.

To illustrate the manner in which the transition occurs it is instructive to derive the form of the real-space site correlation functions for the particularly simple case of motion over a simple cubic lattice. With

$$\epsilon_k = 2J_{\text{eff}}(\cos k_x\delta+\cos k_y\delta+\cos k_z\delta) ,$$
$$J_{\text{eff}} \equiv J_0 e^{-S} , \tag{2.40}$$

the sum over $\vec{k}$ may be converted to a product of three equivalent integrals, yielding

$$G_q(t)=\prod_{i=1}^{3} J_0\left[4J_{\text{eff}}t\sin\frac{q_i\delta}{2}\right] \times\exp[-2pt(1-\cos q_i\delta)] , \tag{2.41}$$

where J_0 is the zero-order Bessel function. We also write[12]

$$\exp(2pt\cos q_i\delta)=\sum_{n=-\infty}^{\infty} I_n(2pt)\cos(nq_i\delta) , \tag{2.42}$$

where I_n is a modified Bessel function of imaginary argument, and we define the vector distance between sites i and j as

$$\vec{R}_i-\vec{R}_j=\delta(n_1\hat{i}+n_2\hat{j}+n_3\hat{k}) . \tag{2.43}$$

Then using Eq. (2.13) the integrals over q_i are evaluated, yielding the final result

$$G_{ij}(t)=\prod_{i=1}^{3} g_{n_i}(t) ,$$
$$g_{n_i}(t)=\sum_{n=-\infty} J^2_{n+n_i}(2J_{\text{eff}}t)I_n(2pt)e^{-2pt} . \tag{2.44}$$

In particular, the autocorrelation function is

$$G_{ii}(t)=\left[\sum_{n=-\infty}^{\infty} J_n^2(2J_{\text{eff}}t)I_n(2pt)e^{-2pt}\right]^3 . \tag{2.45}$$

Both limits $J_{\text{eff}}\rightarrow 0$ or $p\rightarrow 0$ are contained in the paper of Kudinov and Firsov,[11] while the general case involving both stochastic and coherent motion is new. In the mixed regime where $p > J_{\text{eff}}$, the decay of the autocorrelation function is predominantly diffusive in that the arguments of the modified Bessel functions change more rapidly with time and $G_{ii}(t)$ is dominated by a diffusive $t^{-3/2}$ tail. In the opposite limit $J_{\text{eff}} > p$ the argument of the ordinary Bessel functions changes more rapidly and the autocorrelation exhibits a more rapid t^{-3} decay. Thus condition (2.38) effectively sets the boundary between the two types of transport.

III. NUMERICAL CALCULATION OF THE MEAN TIME OF STAY

We have defined the mean time of stay in Eq. (2.15). A numerical calculation of τ_c has been made in two steps. We have first calculated $\tau_c(p,J_{\text{eff}})$ as a function of the variables p and J_{eff} on a suitably chosen mesh. Second, we have calculated the parameters $J_{\text{eff}}(T)$ and $p(T)$ as a function of temperature for a given set of model parameters J_0 and E_a, and then interpolated to find τ_c. For ease of numerical approximation all work was performed assuming a simple cubic lattice. However, when expressed in terms of slightly renormalized parameters, e.g., bandwidth, the results should also be appropriate for other Bravais lattices.

In the first step τ_c was calculated by integrating Eq. (2.41) over q_i and t using the Simpson rule. A numerical approximation for the zero-order Bessel function[13] was employed, and the time integration was extended to a sufficiently large value of $t=T$ such that the integral between T and ∞ was negligible. For $p>J_{\text{eff}}$ the reduced time variable $4pt$ was chosen and $4p\tau_c$ was calculated as a function of $J_{\text{eff}}/p\le 1$. For $J_{\text{eff}}>p$ the reduced time variable was $4J_{\text{eff}}t$ and $4J_{\text{eff}}\tau_c$ was calculated for a ratio $p/J_{\text{eff}}\le 1$. In the first case $4p\tau_c$ decreased smoothly from approximately unity at $J_{\text{eff}}=0$ to about 0.65 for $J_{\text{eff}}=p$, while in the latter case $4J_{\text{eff}}\tau_c$ decreased smoothly from about 1.4 at $p=0$ to 0.65 for $p=J_{\text{eff}}$.

To calculate $J_{\text{eff}}(T)$ and $p(T)$ we have adopted a Debye approximation for the phonon spectrum. The band-narrowing factor was approximated as

$$\begin{aligned} S(T) &= 6(E_a/\Theta)(T/\Theta)^4\int_0^{\Theta/T} dz\, z^3\coth(z/2) \\ &= 1.5(E_a/\Theta)+12(E_a/\Theta)(T/\Theta)^4 \\ &\quad\times\int_0^{\Theta/T} dz\frac{z^3}{e^z-1}\,, \end{aligned} \tag{3.1}$$

where for all longitudinal modes we have set

$$\begin{aligned} E_a &= \frac{|g_{q\lambda}|^2}{2\omega_{q\lambda}}\,, \\ \sin^2\frac{\vec{q}\cdot\vec{\delta}}{2} &= \frac{\omega_{q\lambda}^2}{\omega_D^2}\,, \end{aligned} \tag{3.2}$$

The first term in Eq. (3.1) is due to the zero-point motion. The second temperature-dependent term was evaluated analytically by extending the upper limit to ∞ and then subtracting a correction by expanding $(e^z-1)^{-1}$ in a power series of up to 15 terms in e^{-z}.

In the calculation of $p(T)$, the reduced time variable $x=\omega_D t$ was used, together with a reduced jump rate p/ω_D and reduced tunneling matrix element J_0/Θ. The $\vec{q}$ integration in Eq. (2.31) for $S(t)$ was performed analytically using similar techniques to those employed in the evaluation of the band-narrowing factor. The calculation of the remaining time integral was done using 10 000-point Simpson-rule quadrature out to $X_{\max}=100$. Care was exercised to minimize the error due to the cutoff by first analytically calculating the one-phonon term (equal to 0) and the two-phonon term (which varies as T^7 at low temperature) without the truncation. The truncation was then applied only to the multiphonon (three or more) contributions to $p(T)$. Such a treatment is necessary because of the extremely slow $[(\sin x)/x]$ falloff of $S(t)$ at large times. With this subtraction, the integrand falls as $[(\sin x)/x]^3$ for large times so that the truncation error is negligible.

In the case of $p(T)$ we found the jump rate to be dominated by two-phonon processes for $T/\Theta\lesssim 0.1$ with multiphonon events contributing typically less than 10% of the total. As expected for smaller values of E_a/Θ the range of temperature dominated by two-phonon processes was considerably larger. These results seem to be slightly at variance with an earlier calculation of Stoneham.[14] In the high-temperature limit $T/\Theta\gtrsim 0.5$, $p(T)$ exhibited the expected activated behavior with an activation energy close to the predicted value[2] $E_a/2$, but with a substantially temperature-independent prefactor. This activated form obtains only for sufficiently large values of E_a.

Calculations for the reduced mean time of stay $\omega_D\tau_c$ were performed for parameters ranging over $0\le T/\Theta\le 1.5$, $10^{-3}\le J_0/\Theta\le 1$, and $0.5\le E_a/\Theta\le 10$. We show only typical results in Figs. 1 and 2. As mentioned earlier the peak in the residence time is indicative of the transition between stochastic and coherent behavior. This occurs typically for $0.3\le T^*/\Theta\le 0.7$ for reasonable values of phonon coupling and bandwidth. For a Debye temperature $\Theta\sim 300$ K our choices of J_0 correspond to $J_0\sim 0.1$ and 1 meV, thought to be roughly characteristic of positive muons in metals.

Our value of T^* is in line with the original estimate of Holstein,[1] and is undoubtedly a feature of the polaronic model we have treated. There are, however, several other effects neglected in this model that act to depress T^*. One of these is discussed in the following section.

IV. EFFECT OF QUADRATIC PHONON COUPLING

Comparing Figs. 1 and 2 one immediately notices a result that follows quite generally from a linear coupling model—a *smaller* value of J_0 leads to a *higher* transition temperature T^*. Thus one is led to the seemingly parodoxial conclusion that in a

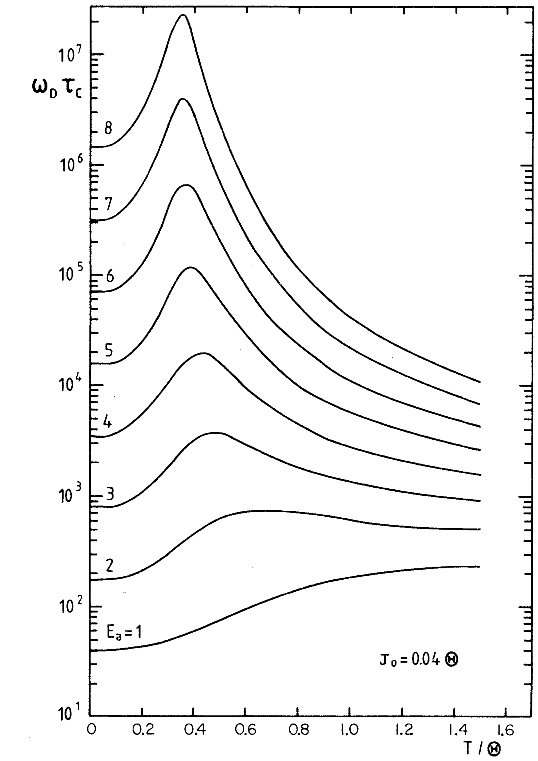

FIG. 1. Mean residence time as a function of temperature. The curves correspond to various values of the polaron binding energy for a fixed rigid-lattice tunneling matrix element $J_0/\Theta=0.04$.

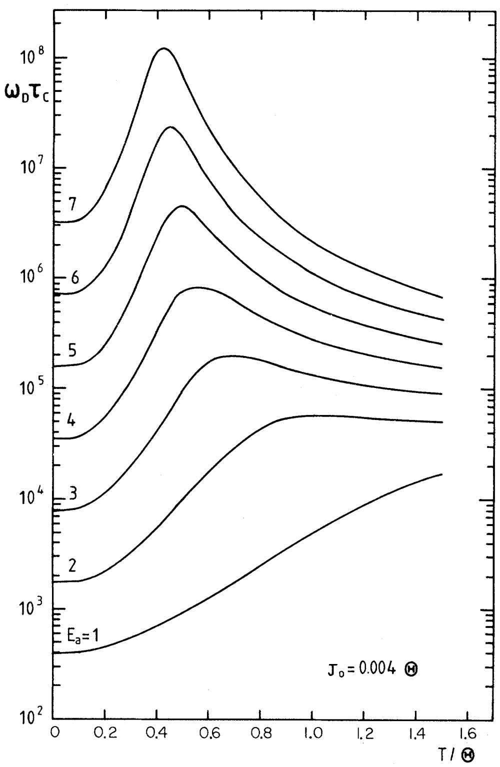

FIG. 2. Mean residence time as a function of temperature for $J_0/\Theta=0.004$.

defect-free material coherent motion is more favorable in extremely narrow bandwidth situations. This follows directly from Eq. (2.38) since for fixed-lattice relaxation energy, the left-hand side decreases linearly with J_0 while $p(T)$ decreases proportional to J_0^2. Thus T^* must increase to maintain the equality. Stated another way, we note that the stochastic jump rate is essentially the decay rate of a coherent state.[1] Thus this decay rate decreases faster with decreasing J_0 than the corresponding linear decrease in single-particle bandwidth.

This fact led Kagan and Klinger[3] to investigate other mechanisms that can limit coherent propagation, but that are independent of the small parameter J_0. They introduced the idea of the "dynamical destruction of the band" through phonon interactions that are ignored in the usual linear-coupling model. As one example of such interactions, consider the full Taylor-series expansion for the potential energy of the interstitial as a function of the ionic positions $\vec{R}_N=\vec{R}_N^0+\vec{u}_N$. Thus,

$$V(\{\vec{R}_N\})=V_0+\sum_N \vec{u}_N\cdot\vec{\nabla}_N V_0 +\frac{1}{2}\sum_{N,N'}\vec{u}_N\cdot\vec{\nabla}_N\vec{\nabla}_{N'}V_0\cdot\vec{u}_{N'}+\cdots \ . \tag{4.1}$$

The first term gives rise to the periodic potential in the static lattice. The second is the linear phonon interaction that we have previously treated. The third and higher-order terms, while usually not considered important in other contexts, can be essential for the mechanism of light interstitial transport since they may lead to scattering rates for coherent states that are large compared to typically narrow bandwidths. The most important term at low temperatures is the quadratic interaction that leads to a two-phonon scattering process. Kagan and Klinger[3] also considered a further two-phonon interaction that results from a virtual excitation of the interstitial particle to a higher state. In either case one finds the same temperature dependence for the scattering rate, so we do not discuss this second mechanism further.

After reexpressing the interaction in terms of canonical phonon-displacement operators and taking matrix elements with the interstitial wave function on a given site (Condon approximation), one finds an interaction of the form

$$U=\frac{1}{N}\sum_i \sum_{q\lambda} \sum_{q'\lambda'} C_{\lambda\lambda'}(\vec{q},\vec{q}\,')e^{-i(\vec{q}-\vec{q}\,')\cdot\vec{R}_i}u_{q\lambda}u_{q'\lambda'}n_i, \tag{4.2}$$

where $C_{\lambda\lambda'}(\vec{q},\vec{q}\,')$ is a coupling energy whose magnitude depends upon microscopic details, but whose wave-vector dependence for small wave vectors is known. If we add such a term to the Hamiltonian (2.1), we can perform a canonical transformation similar to Eq. (2.3), but with $g_{q\lambda}$ altered so that the total linear phonon interaction vanishes in the transformed Hamiltonian. The net result of the transformation is then to generate an H' similar to Eq. (2.4) but with an additional term (4.2), where the $u_{q\lambda}$ refer now to the displaced oscillator coordinates. The definition of E_a and the ϕ_i are of course altered, but the functional form of the latter (dependence on $p_{q\lambda}$) is unchanged.

The physical effect of the new term is apparent from Eq. (4.2). The phonon interactions lead to a site-diagonal dynamical disorder of the interstitial energies that cannot be eliminated by canonically transforming, in contrast to the site-diagonal linear-coupling term. This dynamical modulation, if sufficiently strong in comparison to the bandwidth, serves to destroy coherent tunneling processes. Because the time dependence $U(t)$ induced by H_0 is rapid on the time scale of interstitial motion we may to a good approximation calculate the lifetime of a coherent state from second-order time-dependent perturbation theory. This calculation has been done before[3,7] for a Debye phonon spectrum so that we merely summarize the result here. The scattering rate is found to be

$$\nu(T)=\text{const}\times\int_0^\Theta d\omega\,\omega^8\text{csch}^2(\beta\omega/2)\ . \tag{4.3}$$

This may be parametrized as

$$\nu(T)=\nu_0\omega_D f(T/\Theta)\ , \tag{4.4}$$

where ν_0 is a dimensionless measure of the scattering rate at $T=\Theta$ and $f(T/\Theta)$ is a universal function of temperature with $f(1)=1$. The numerically calculated value of $f(T/\Theta)$ is shown in Fig. 3. In the high-temperature limit we have $f(T/\Theta)\propto T^2$, while in the low-temperature limit $f(T/\Theta)\propto T^9$. This limiting behavior at low temperature is only reached for temperatures $T\lesssim 0.1\Theta$. We also remark that $\nu(T)$ can have a different temperature dependence in crystals with several equivalent sites per unit cell.[7]

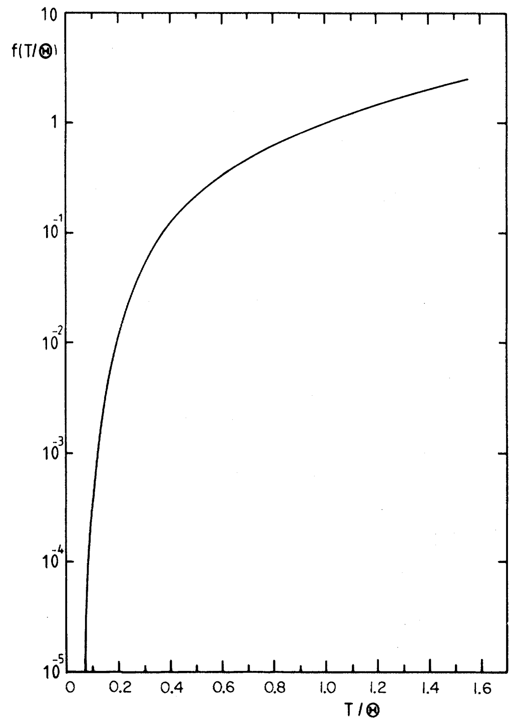

FIG. 3. Normalized two-phonon scattering rate $f(T/\Theta)$ as a function of temperature.

Let us now investigate the effects of $\nu(T)$ on the coherent portion of the density-density correlation function. We consider this in a spirit similar to that adopted in treatments of motional or exchange narrowing in NMR theory.[15] This yields results essentially equivalent to the earlier calculation of Kagan and Klinger[3] but is more transparent in the earlier context of the linear-coupling model. We expand the coherent portion of the correlation function out to second order in time,

$$\frac{1}{N}\sum_k e^{i(\epsilon_k-\epsilon_{k+q})t}=\frac{1}{N}\sum_k\left[1+i(\epsilon_k-\epsilon_{k+q})t-\frac{(\epsilon_k-\epsilon_{k+q})^2}{2}t^2+\cdots\right] \tag{4.5}$$

The term linear in t vanishes, while in the presence of rapid scattering,

$$\tfrac{1}{2}t^2\rightarrow\int_0^t(t-\tau)\psi(\tau)d\tau\ , \tag{4.6}$$

where the correlation function $\psi(\tau)$ is the probability that the interstitial particle remains in its initial state at time τ. Thus,

$$\psi(\tau)\approx e^{-\nu\tau} . \tag{4.7}$$

If the scattering rate ν is large on the scale of the bandwidth we have

$$\int_0^t (t-\tau)\psi(\tau)d\tau \rightarrow t\int_0^\infty \psi(\tau)d\tau = t/\nu . \tag{4.8}$$

The decay of the "coherent" correlation function then proceeds stochastically through repetitive scattering, its phase coherence essentially destroyed after a single scattering event. Thus

$$\frac{1}{N}\sum_k e^{i(\epsilon_k-\epsilon_{k+q})t} \rightarrow \exp\left[-\frac{1}{N}\sum_k (\epsilon_k-\epsilon_{k+q})^2 \int_0^t (t-\tau)\psi(\tau)d\tau\right] \underset{\nu \gg J_{\rm eff}}{\longrightarrow} \exp\left[-\frac{1}{N}\sum_k (\epsilon_k-\epsilon_{k+q})^2 t/\nu\right] . \tag{4.9}$$

Finally the sum over $\vec{k}$ can be done using the definition of the single-particle energy-level equation (2.10),

$$\frac{1}{N}\sum_k (\epsilon_k-\epsilon_{k+q})^2 = 2J_{\rm eff}^2 \sum_\delta (1-e^{i\vec{q}\cdot\vec{\delta}}) . \tag{4.10}$$

We define a "coherent" jump rate between neighboring sites,

$$p_c \equiv 2J_{\rm eff}^2/\nu . \tag{4.11}$$

Then under conditions of rapid intraband scattering $\nu \gg J_{\rm eff}$, we find the total density-density correlation function to be

$$G_q(t) = \exp\left[-(p_c+p_s)t\sum_\gamma (1-e^{i\vec{q}\cdot\vec{\delta}})\right], \tag{4.12}$$

where p_s is the stochastic jump rate p calculated in Sec. II. Thus the particle motion is purely diffusive but with a jump rate that is the sum of those deriving from the "coherent" and stochastic portions of the linear-coupling-model correlation function. In the opposite limit $\nu \ll J_{\rm eff}$, the coherent diffusion returns smoothly to the true coherent bandlike form evident on the left-hand side of Eq. (4.5).

The interesting behavior of $G_q(t)$ derives from the totally opposite temperature dependences of p_c and p_s. In the high-temperature regime dominated by p_s the particle moves *slower* as the temperature decreases, while in the lower-temperature regime dominated by p_c the particle moves *faster* as the temperature decreases. The transition between these two types of behavior is thus again marked by a peak in the mean residence time τ_c. This peak occurs at a temperature T^*, where

$$p_s(T^*) = 2J_{\rm eff}^2/\nu(T^*) . \tag{4.13}$$

Since both sides of this equation are proportional to J_0^2, T^* is independent of the rigid-lattice bandwidth and dependent only upon linear and quadratic lattice-coupling energies. Thus the depression of T^* due to quadratic coupling is more severe for the smaller bandwidths. The actual transition to a true coherent bandlike behavior of the particle will of course occur at a still lower temperature T_c where

$$\nu(T_c) \sim J_{\rm eff} . \tag{4.14}$$

T_c is thus a decreasing function of decreasing rigid-lattice bandwidth.

To illustrate this behavior we have performed a numerical calculation of the mean residence time τ_c appropriate again for a simple cubic lattice. In the limit of diffusive motion we have from Sec. III,

$$\tau_c^{-1} = 4(p_s+p_c) . \tag{4.15}$$

To treat properly the transition around the temperature T_c, we have used an interpolation formula based upon previous results,

$$\tau_c^{-1} = 4p_s + 8J_{\rm eff}^2/(\nu+2\sqrt{2}J_{\rm eff}) . \tag{4.16}$$

In the limit $\nu \rightarrow 0$ we recover essentially the mean residence time calculated in Sec. III, while in the limit of large ν Eq. (4.15) results. We have used as adjustable parameters J_0, E_a, and ν_0. In Figs. 4 and 5 we display illustrative results for a fixed value of the lattice-relaxation energy $E_a/\Theta = 4$ and two values of the tunneling matrix element differing by a factor of 50. The lattice relaxation energy and the tunneling matrix element $J_0 = 8\times 10^{-4}\Theta$ correspond roughly to a fit of high-temperature μSR data in Cu.[16,17]

One sees immediately the features mentioned in our previous discussion. The first effect of the two-phonon scattering rate is to depress the temperature T^* to a common temperature independent of J_0, so long as the value of ν_0 is large enough that this temperature is lower than that derived from the linear coupling alone. The residence time τ_c for the

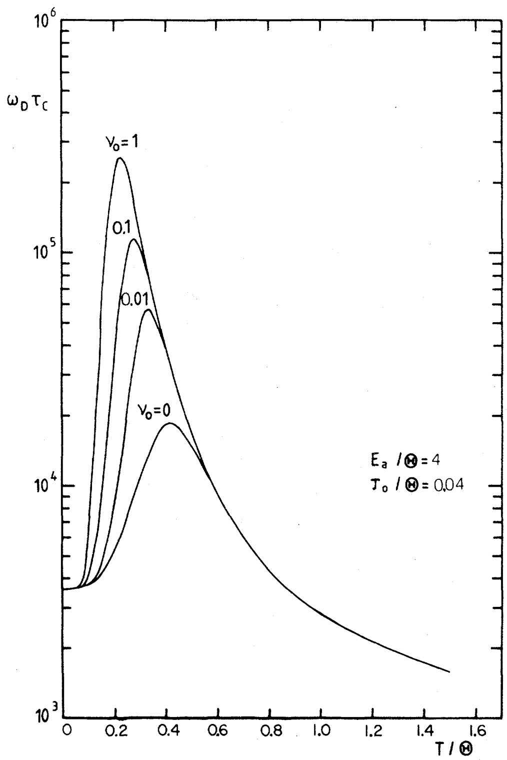

FIG. 4. Mean residence time as a function of temperature for $J_0/\Theta=0.04$ and $E_a/\Theta=4$. The various curves correspond to different values of the two-phonon scattering rate at the Debye temperature.

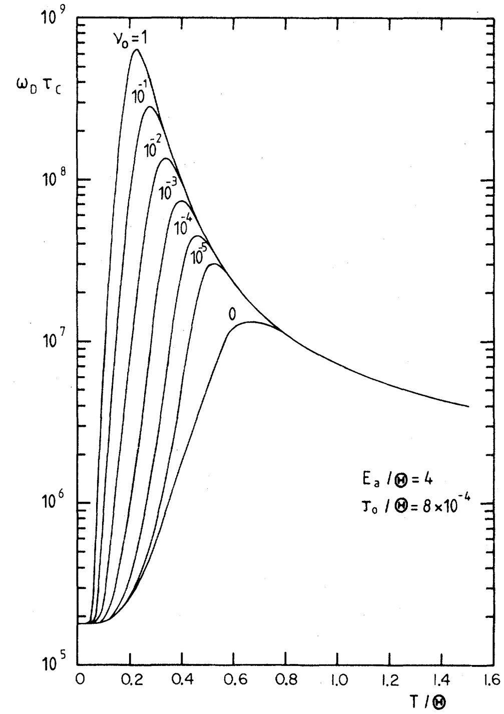

FIG. 5. Mean residence time as a function of temperature for $J_0/\Theta=8\times10^{-4}$ and $E_a/\Theta=4$, corresponding roughly to μ^+ in Cu.

smaller value of J_0 is thus affected over a much wider range of temperature than is the case for the larger value of J_0. Above T^* the main effect of the quadratic coupling is simply to extend the temperature region in which the stochastic jump rate derived from the linear-coupling model determines τ_c.

It is also apparent that the temperature T^* continues to be an appreciable (though lower) fraction of Θ. The parameter ν_0 is essentially an unknown, yet from Fig. 5 it is apparent that T^* is not a terribly sensitive function of it. Thus a change of 3 orders of magnitude in ν_0 changes T^* by less than a factor of 2. It is difficult to imagine that the transition could drop much below $T^*\sim0.2\Theta$ since unphysically large scattering rates would be required.

Finally we note that the mean residence time returns for sufficiently low temperatures to the value appropriate to pure coherent motion, and that this transition is preceded by a precipitous drop in τ_c—an effect caused primarily by the rapid variation of $\nu(T)$. In this region the diffusion constant $D=zp_c\delta^2/6$ continues to diverge as T^{-9}, but this divergence has no effect on the mean residence time since the interstitial moves primarily by quantum tunneling interrupted only infrequently by scattering events.

V. SUMMARY AND CONCLUSION

Even after inclusion of the quadratic phonon interactions our estimates of the transition temperatures T^* are still quite high. However, there exist at least two further effects that serve to suppress T^*—the presence of more than one interstitial site per unit cell and the presence of static lattice disorder introduced through defects in the host.

The first of these is of particular importance for the bcc metals that have three octahedral and six tetrahedral sites per unit cell. None of these sites possesses a cubic symmetry. Thus when a stochastic jump is made between two neighboring sites the accompanying lattice deformation must also be reoriented as well as translated. This can have a profound effect upon the temperature dependence of the stochastic jump rate. Instead of disappearing as T^7 at low temperatures, the two-phonon contribution[7] can vary as T^3, and even single-phonon processes may occur with a linear temperature dependence.[8] These results depend crucially upon the detailed form of the phonon coupling. However, if present, they clearly enhance the low-temperature stochastic processes while leaving the coherent processes relatively unaffected. This acts to lower T^*.

With regard to the second effect, it is well known that crystalline defects can produce relatively long-range strain fields. In finite concentration the superposition of defect strain fields acts to render neighboring interstitial sites slightly inequivalent in energy. Except in the immediate environment of a defect, the effect on stochastic propagation is minimal so long as the energy inequivalence Δ_s between neighboring sites is small on the scale of kT and $h\omega_D$. However, the effect on coherent tunneling may be such as to almost completely destroy it. For example, if two nominally equivalent sites with tunneling matrix element J_{eff} acquire a strain splitting Δ_s, the effective transition rate for $\Delta_s \gg J_{\mathrm{eff}}$ becomes

$$w \sim J_{\mathrm{eff}}^2/\Delta_s \; . \tag{5.1}$$

This clearly has the effect of depressing the coherent processes and hence reducing T^*.

In this connection it is interesting to note that if the decline in the spin depolarization rate measured for positive muons in Cu (Ref. 18) at low temperatures is indicative of coherent motion, the use of Eqs. (5.1) and (4.15) to estimate τ_c, together with the estimated value of disorder $\Delta_s \sim 5\ \mu\mathrm{V}$, leads to rough agreement with the experimental depolarization rate below 1 K. Further evidence for the importance of lattice disorder stems from the observation that a different, less pure Cu sample exhibited a significantly higher depolarization rate at low temperatures.[19] However, in the purer sample the temperature dependence of the depolarization rate above 1 K is still not understood. This is perhaps indicative of the fact that a satisfactory treatment of diffusion processes in the presence of static lattice disorder has not yet been developed.

In conclusion, under the stated limitations of the theory, we have developed a comprehensive picture of the transition between coherent and stochastic behavior of a light interstitial particle based upon a polaronic transport model including both linear and quadratic phonon couplings. The theory agrees in detail with previously known limits at both high and low temperatures, and also passes smoothly between these extremes. We have focused attention on the temperature dependence of the mean residence time τ_c since this single parameter is perhaps the best single indicator of interstitial motion in both the coherent and stochastic limits. For a Debye phonon spectrum the analytic theory has been supplemented with numerical calculations of τ_c using a wide range of model parameters. For positive muons the transition temperature between coherent and stochastic processes is typically found to be a significant fraction of the Debye temperature. However, this estimate is contingent upon the neglect of the two effects discussed above, and will probably be significantly lower in real physical systems.

ACKNOWLEDGMENT

The author wishes to thank the μSR group at the Swiss Institute for Nuclear Research for many stimulating discussions and for its hospitality during the course of this work. This research was supported in part by the National Science Foundation under Grant No. DMR-8007059.

APPENDIX: CALCULATION OF FOURTH-ORDER PERTURBATION TERMS

To illustrate the manner in which perturbation series (2.33) is constructed and the conditions under which it is valid, we calculate below the 4:0 term. We adopt from the outset the approximation in which the slow-time dependence of the internal particle operators is ignored in comparison to the fast-time dependence of the phonon operators. For bandwidths that are small compared to kT we have

$$\begin{aligned} 4{:}0 = J_0^4 \frac{1}{N} \sum_{k,k'} \int_0^\infty dt\, e^{i(\omega+\epsilon_{k'}-\epsilon_{k'+q})t} \\ \times \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \sum_{i,j,l,n} \sum_{\delta,\delta',\delta'',\delta'''} \langle k' \,|\, c_i^\dagger c_{i+\delta} c_j^\dagger c_{j+\delta'} c_l^\dagger c_{l+\delta''} c_n^\dagger c_{n+\delta'''} c_k^\dagger c_{k+q} \,|\, k'+q \rangle \\ \times \langle (e^{i\chi_{i,i+\delta}(t_1)} - e^{-S})(e^{i\chi_{jj+\delta'}(t_2)} - e^{-S})\,(e^{i\chi_{l,l+\delta''}(t_3)} - e^{-S})(e^{i\chi_{n,n+\delta'''}(t_4)} - e^{-S}) \rangle_{\mathrm{ph}} \; . \end{aligned} \tag{A1}$$

The particle matrix elements above are trivially calculated as

$$\langle k' \mid c_i^\dagger \cdots c_{k+q} \mid k'+q \rangle = \frac{1}{N} e^{i\vec{k}\cdot(\vec{\delta}+\vec{\delta}'+\vec{\delta}''+\vec{\delta}''')} \delta_{k,k'} \delta_{j,i+\delta} \delta_{j+\delta',l} \delta_{l+\delta'',n} \; . \tag{A2}$$

The sums over site indices n, l, and j in Eq. (A1) may then be performed. The remaining summation over i yields a factor N since the phonon expectation value is independent of the site index i. After reversing the signs of $\vec{\delta}$ and $\vec{\delta}'$ we recover

$$\begin{aligned} 4{:}0 = J_0^4 \frac{1}{N} \sum_k \int_0^\infty dt \, e^{i(\omega+\epsilon_k-\epsilon_{k+q})t} & \\ \times \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \sum_{\delta,\delta',\delta'',\delta'''} & e^{-i\vec{k}\cdot(\vec{\delta}+\vec{\delta}'-\vec{\delta}''-\vec{\delta}''')} \\ & \times \langle (e^{i\chi_{\delta+\delta',\delta'}(t_1)} - e^{-S})(e^{i\chi_{\delta',0}(t_2)} - e^{-S}) \\ & \times (e^{i\chi_{0,\delta''}(t_3)} - e^{-S})(e^{i\chi_{\delta'',\delta''+\delta'''}(t_4)} - e^{-S}) \rangle_{\text{ph}} \; . \end{aligned} \tag{A3}$$

The dominant term in the summations over nearest-neighbor distances corresponds to the condition $\vec{\delta}+\vec{\delta}'=\vec{\delta}''+\vec{\delta}'''$ above. This choice is the only one that cancels the band-narrowing factor at short times and is also a rigorous selection rule in the limit of small coherent bandwidth.

The phonon expectation value may be calculated by forming the trace as a product of traces over each mode $q\lambda$, expanding exponentials for each mode out to $O(N^{-1})$ and then reforming the final product into an exponential again. We calculate here just the product of the four time-dependent terms in Eq. (A3). The correction due to the remaining terms multiplied by powers of e^{-S} may be derived by straightforward techniques, and we shall indicate their effect at the conclusion. We find

$$\begin{aligned} & \langle e^{i\chi_{\delta+\delta',\delta'}(t_1)} e^{i\chi_{\delta',0}(t_2)} e^{i\chi_{0,\delta''}(t_3)} e^{i\chi_{\delta'',\delta''+\delta'''}(t_4)} \rangle_{\text{ph}} \\ & = e^{-4S} \exp\left[\frac{1}{N} \sum_{q\lambda} \{ (1+n_{q\lambda}) [f_{q\lambda}^{(1)}(t_1-t_2) - f_{q\lambda}^{(2)}(t_1-t_3) + f_{q\lambda}^{(3)}(t_1-t_4) \right. \\ & \qquad \left. + f_{q\lambda}^{(4)}(t_2-t_3) - f_{q\lambda}^{(5)}(t_2-t_4) + f_{q\lambda}^{(6)}(t_3-t_4)] + n_{q\lambda}[\text{c.c.}] \} \right] \end{aligned} \tag{A4}$$

where c.c. indicates the complex conjugate, and we define

$$\begin{aligned} & f_{q\lambda}^{(1)}(\tau) = \gamma_{q\lambda}(0,\vec{\delta},-\vec{\delta}') e^{i\omega_{q\lambda}\tau}, \quad f_{q\lambda}^{(2)}(\tau) = \gamma_{q\lambda}(\vec{\delta}+\vec{\delta}',-\vec{\delta},\vec{\delta}'') e^{i\omega_{q\lambda}\tau}, \\ & f_{q\lambda}^{(3)}(\tau) = \gamma_{q\lambda}(0,\vec{\delta}''',\vec{\delta}) e^{i\omega_{q\lambda}\tau}, \; f_{q\lambda}^{(4)}(\tau) = \gamma_{q\lambda}(0,\vec{\delta}',\vec{\delta}'') e^{i\omega_{q\lambda}\tau}, \\ & f_{q\lambda}^{(5)}(\tau) = \gamma_{q\lambda}(-\vec{\delta}''-\vec{\delta}''',\vec{\delta}',-\vec{\delta}''') e^{i\omega_{q\lambda}\tau}, \quad f_{q\lambda}^{(6)}(\tau) = \gamma_{q\lambda}(0,-\vec{\delta}'',\vec{\delta}''') e^{i\omega_{q\lambda}\tau} \; . \end{aligned} \tag{A5}$$

We insert this result into Eq. (A3) and perform two integrations by parts on the t variable, finding

$$\begin{aligned} 4{:}0 = (J_0 e^{-S})^4 \frac{1}{N} \sum_k \sum_{\delta,\delta',\delta'',\delta'''} \delta_{\delta+\delta',\delta''+\delta'''} \int_0^\infty dt \frac{e^{i(\omega+\epsilon_k-\epsilon_{k+q})t}}{[-i(\omega+\epsilon_k-\epsilon_{k+q})]^2} \int_0^t d\tau_2 \int_0^{t-\tau_2} d\tau_3 & \\ \times \exp\left[\frac{1}{N} \sum_{q\lambda} \{ (1+n_{q\lambda}) [f_{q\lambda}^{(1)}(\tau_2) - f_{q\lambda}^{(2)}(t-\tau_3) + f_{q\lambda}^{(3)}(t) + f_{q\lambda}^{(4)}(t-\tau_2-\tau_3) \right. & \\ \left. - f_{q\lambda}^{(5)}(t-\tau_2) + f_{q\lambda}^{(6)}(\tau_3)] + n_{q\lambda}[\text{c.c.}] \} \right] \; . & \end{aligned} \tag{A6}$$

We now show that the middle four terms in the second set of square brackets above may be approximately set to zero in calculating the remaining time integrals provided that $|\omega+\epsilon_k-\epsilon_{k+q}| \ll \bar{\omega}$, where $\bar{\omega}$ is an average phonon frequency. To prove this we first integrate once more by parts on the t variable. There are two types of terms that result—the first (I) from differentiating the upper limit of the τ_3 integral, and the second correction term (II) from differentiating the exponential inside the integrand. Dropping the leading multiplicative factors in Eq. (A6) we get

$$\mathrm{I}=\int_0^\infty dt\frac{e^{i(\omega+\epsilon_k-\epsilon_{k+q})t}}{[-i(\omega+\epsilon_k-\epsilon_{k+q})]^3}\times\int_0^t d\tau_2 \exp\left[\frac{1}{N}\sum_{q\lambda}\{(1+n_{q\lambda})[f_{q\lambda}^{(1)}(\tau_2)-f_{q\lambda}^{(2)}(\tau_2)+f_{q\lambda}^{(3)}(t)+f_{q\lambda}^{(4)}(0)-f_{q\lambda}^{(5)}(t-\tau_2)+f_{q\lambda}^{(6)}(t-\tau_2)]+n_{q\lambda}[\mathrm{c.c.}]\}\right] \tag{A7}$$

and

$$\begin{aligned}\mathrm{II}=\int_0^\infty dt\frac{e^{i(\omega+\epsilon_k-\epsilon_{k+q})t}}{[-i(\omega+\epsilon_k-\epsilon_{k+q})]^3}&\times\int_0^t d\tau_2\int_0^{t-\tau_2}d\tau_3 \exp\Bigg[\frac{1}{N}\sum_{q\lambda}\{(1+n_{q\lambda})[f_{q\lambda}^{(1)}(\tau_2)-f_{q\lambda}^{(2)}(t-\tau_3)+f_{q\lambda}^{(3)}(t)\\&+f_{q\lambda}^{(4)}(t-\tau_2-\tau_3)-f_{q\lambda}^{(5)}(t-\tau_2)+f_{q\lambda}^{(6)}(\tau_3)]+n_{q\lambda}[\mathrm{c.c.}]\}\Bigg]\\&\times\frac{1}{N}\sum_{p\lambda}\{(1+n_{p\lambda})i\omega_{p\lambda}[-f_{p\lambda}^{(2)}(t-\tau_3)+f_{p\lambda}^{(3)}(t)\\&+f_{p\lambda}^{(4)}(t-\tau_2-\tau_3)-f_{p\lambda}^{(5)}(t-\tau_2)]-n_{p\lambda}i\omega_{p\lambda}[\mathrm{c.c.}]\}\ .\end{aligned} \tag{A8}$$

We now perform another parts integration on the correction term II. There are again two terms—one from differentiating the τ_3 upper limit, and the second correction term from differentiating the exponential

$$\begin{aligned}\mathrm{II}=\int_0^\infty dt\frac{e^{i(\omega+\epsilon_k-\epsilon_{k+q})t}}{[-i(\omega+\epsilon_k-\epsilon_{k+q})]^3}&\times\int_0^t d\tau_2 \exp\Bigg[\frac{1}{N}\sum_{q\lambda}\{(1+n_{q\lambda})[f_{q\lambda}^{(1)}(\tau_2)-f_{q\lambda}^{(2)}(\tau_2)+f_{q\lambda}^{(3)}(t)+f_{q\lambda}^{(4)}(0)\\&-f_{q\lambda}^{(5)}(t-\tau_2)+f_{q\lambda}^{(6)}(t-\tau_2)]+n_{q\lambda}[\mathrm{c.c.}]\}\Bigg]\\&\times\frac{1}{N}\sum_{p\lambda}\Bigg[-(1+n_{p\lambda})\frac{\omega_{p\lambda}}{\omega+\epsilon_k-\epsilon_{k+q}+\omega_{p\lambda}}\\&\times[-f_{p\lambda}^{(2)}(\tau_2)+f_{p\lambda}^{(3)}(t)+f_{p\lambda}^{(4)}(0)-f_{p\lambda}^{(5)}(t-\tau_2)]+n_{p\lambda}\frac{\omega_{p\lambda}}{\omega+\epsilon_k-\epsilon_{k+q}-\omega_{p\lambda}}[\mathrm{c.c.}]\Bigg]+\cdots\ ,\end{aligned} \tag{A9}$$

where the ellipsis stands for a second-order correction. Under conditions where $|\omega+\epsilon_k-\epsilon_{k+q}| \ll \omega_{p\lambda}$ above we may set

$$\frac{\omega_{p\lambda}}{\omega+\epsilon_k-\epsilon_{k+q}\pm\omega_{p\lambda}}\approx\pm1\ . \tag{A10}$$

Since the typical phonon frequencies above, when weighted by their occupation probabilities, are of order kT or ω_D, this replacement is valid provided $\omega_D \tau_c \gg 1$ and $kT\tau_c \gg 1$. Notice then, that, apart from the second-order correction term, the sum over $p\lambda$ in Eq. (A9) is nothing more than the negative of the four terms in square brackets of the argument of the exponential.

The second correction term in Eq. (A9) may be similarly integrated by parts subject to condition (A10), and this process may be continued up to infinite order in the parts integrations of successive correction terms. It is then easily shown that the infinite number of terms resulting may be exactly summed to an exponential series that completely cancels the four middle terms in the first set of square brackets in Eq. (A7). Thus

$$4{:}0 \approx (J_0 e^{-S})^4 \frac{1}{N} \times \sum_k \sum_{\delta,\delta',\delta'',\delta'''} \delta_{\delta+\delta',\delta''+\delta'''} \int_0^\infty dt \frac{e^{i(\omega+\epsilon_k-\epsilon_{k+q})t}}{[-i(\omega+\epsilon_k-\epsilon_{k+q})]^3} \times \int_0^t d\tau_2 \exp\left[\frac{1}{N}\sum_{q\lambda}(1+n_{q\lambda})[f_{q\lambda}^{(1)}(\tau_2)+f_{q\lambda}^{(6)}(t-\tau_2)]+n_{q\lambda}[\text{c.c.}]\right] . \tag{A11}$$

Finally we note that the dominant terms in the remaining sums over nearest-neighbor distances will be those that cancel the band-narrowing factor at short times if the lattice coupling is sufficiently strong, i.e., $S \gg 1$. This requires $\vec{\delta}+\vec{\delta}'=0$. Keeping only this contribution and noting that the remaining double integral is in the form of a convolution, we find

$$\begin{aligned} 4{:}0 &= (J_0 e^{-S})^4 \frac{1}{N} \sum_k \sum_{\delta,\delta''} \int_0^\infty dt \frac{e^{i(\omega+\epsilon_k-\epsilon_{k+q})t}}{[-i(\omega+\epsilon_k-\epsilon_{k+q})]^3} \int_0^t d\tau_2 e^{2[S(\tau_2)+S(t-\tau_2)]} \\ &= \frac{1}{N} \sum_k \sum_{\delta,\delta''} \frac{\pi^2(\omega+\epsilon_k-\epsilon_{k+s})}{[-i(\omega+\epsilon_k-\epsilon_{k+q})]^3} , \end{aligned} \tag{A12}$$

where we define

$$\pi(\omega) = (J_0 e^{-S})^2 \int_0^\infty dt\, e^{i\omega t}(e^{2S(t)}-1) . \tag{A13}$$

It is easily verified, and we state without proof, that the effect of a similar mathematical treatment of the terms involving only 2 or 3 internal times in Eq. (A3) simply leads to the replacement $e^{2S(\tau)} \to e^{2S(\tau)}-1$ as we have indicated in Eq. (A13). As such Eq. (A12) clearly represents a portion of the $n=2$ term in Eq. (2.33). The calculation of the other terms in fourth order is slightly more complicated due to the different ranges of time integrations when two time-ordered products are expanded, e.g., for the 3:1 or 2:2 terms. However, an exactly analogous treatment of these shows the final result to be that given by Eq. (2.33).

Calculation of higher-order terms is considerably more complicated and time consuming, since there are $N(N-1)/2$ distinct internal time differences contained in the Nth-order phonon correlation function. Nevertheless, the general term of Eq. (2.33) has been verified out to sixth order so that there is little doubt that Eq. (2.34) is a correct summation of the dominant terms in the entire perturbation series at frequencies and coherent bandwidths subject to the restrictions of Eq. (A10).

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