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Quantum Coherence of a Narrow-Band Particle Interacting with Phonons and Static Disorder

Qian Niu[1,2]

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This work deals with the quantum dynamics of a narrow-band particle interacting with phonons and static disorder. The present theory is exact in the limit of small bandwidth compared with the Debye energy, and covers various regimes in the parameter space of temperature and disorder strength. Therefore, the theory provides a unified framework for studying when and how the particle motion changes from coherent bandlike behavior to incoherent hopping as the temperature and/or disorder strength are increased. The theory also includes the double-well problem as a special case, where rather complete description of the particle motion is obtained.

KEY WORDS: Quantum coherence; quantum diffusion; small polaron.

1. INTRODUCTION

In this paper, we study the quantum dynamics of a narrow-band particle moving in the bulk or on the surface of a crystalline solid. We are interested in the case where only the lowest level of each potential well can be occupied, and where the particle moves from one well to the next through quantum tunneling. We are concerned with the influence of phonons and static disorder on the particle motion. In particular, we want to know when and how the particle changes its behavior from coherent bandlike motion to incoherent hopping.

This is an old problem with lasting interest. It has been the subject of small-polaron theories[1–7] and is one of the central issues in the quantum diffusion of light atoms or muons.[8–14] In the general context of quantum

[1] Department of Physics, University of California, Santa Barbara, California 93106.
[2] Permanent address: Department of Physics, University of Texas, Austin, Texas 78712.

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dynamics with dissipation, the present system serves as a fine model for the so-called super-Ohmic coupling category.[15–22]

The main objective of the present work is to develop a general theory which is exact in the limit of small bandwidth compared with the Debye energy of the phonons. The theory will be valid for essentially the whole parameter space spanned by the temperature and disorder strength. It therefore not only unifies earlies theories for the various regimes of the parameter space, but also makes it possible to investigate the intermediate regions where transition from coherent to incoherent motion of the particle takes place.

The physics of transport phenomena usually has three levels of description: microscopic, macroscopic, and intermediate. On the macroscopic level, one observes a hydrodynamic law such as a diffusion equation characterized by a diffusion constant depending on temperature, isotope mass, etc. On the microscopic level, one tries to single out the part of the microscopic system which is eventually responsible for the macroscopic phenomenon and which is describable by the Schrödinger equation. These two worlds are connected by an intermediate level, where one describes the system in terms of Markovian equations involving a few degrees of freedom. Boltzmann equations and master equations are such examples. It is only on this level of description that the question of quantum coherence is relevant. On the microscopic level everything is coherent. On the macroscopic level everything is incoherent (excluding, of course, particular systems such as a superfluid). We emphasize that quantum coherence is not equivalent to the Markovian nature in the transport equations. It has something to do with the quantum uncertainty between position and momentum. In this paper, the particle motion is termed "incoherent" if it is Markovian in position basis. The usual Boltzmann equation is Markovian only in momentum basis, and therefore describes a coherent motion. Further refinement of this notion will be done in the text.

The derivation of transport equations usually starts from the microscopic level, following totally different routes for cases with qualitatively different behaviors. Unfortunately, such an approach can draw, at best, scattered pieces of a whole picture, and is unable to answer questions like how a transition from coherence to incoherence takes place. For example, the conventional small-polaron theory follows such a practice. For the low-temperature side, one starts with the renormalized Bloch states, and uses perturbation theory to determine their lifetimes. When the inverse lifetimes are smaller than the renormalized bandwidth, the particle motion is said to be coherent. When the inverse lifetimes are no longer small for high enough temperatures, it is said that the original picture of coherent motion breaks down. The theory for the high-

temperature side then takes a totally different route: one starts with the unperturbed site diagonal states, and then uses perturbation theory to calculate the rate of transitions.

The path integral approach of Leggett *et al.*[19] was designed to give a consistent picture of the particle motion in various regimes. Their noninteracting blip approximation works remarkably well for the sub-Ohmic and Ohmic cases, and has correctly predicted a bias-induced transition from coherent to incoherent tunneling for the super-Ohmic case. The approximation fails, however, for the intermediate region. It is valid in both the zero-bias limit and the large-bias limit, but for totally different reasons. Recently, Gorlich *et al.*[20] made an improvement of the approximation, giving a correct result also for moderate bias. However, it is still not clear how their results may be generalized to high-temperature cases and multisite problems.

In this paper, we take a different approach. We start with a path integral representation of the transition probability for the particle to move from one place to another in time t. This is a path integral defined in the phase space of the particle, i.e., the space spanned by the two position variables appearing in the particle density matrix.[3] The phase space path integral defines a phase space propagator (or Green function). A Dyson equation is then obtained by regrouping the terms of a diagrammatic expansion of the propagator in some small parameter to be specified below. The first-order approximation of the self-energy operator then reduces the original many-body problem involving the phonons, essentially to a single-particle eigenvalue problem in the phase space of the particle.[23-25] This provides a very convenient basis for further explorations of various regimes and their interconnections.

For a heavy particle such as the hydrogen atom, the tunneling energy splitting is extremely small compared with the Debye energy of the lattice vibrations.[12,13] The ratio of the two energy scales provides us with a small parameter. Our theory is based on a systematic expansion in this small parameter. Truncation after the first nontrivial order should give a very good approximation. This is somewhat in line with the philosophy of the small polaron theory of Holstein,[1] which also treats the tunneling energy splitting as a small parameter, but we do not make *a priori* assumptions on the character of the particle motion (band motion or hopping). The non-interacting-blip approximation of Leggett *et al.*[19] was also designed to take advantage of this small parameter, but our theory is more systematic.

[3] The double positional space here is equivalent to the Wigner phase space, whose position coordinate is the average of the two positions, and whose momentum coordinate is the Fourier conjugate of the relative position. The Wigner phase space is the quantum analog of the classical phase space.

Equipped with our general theory, we have studied the particle motion in various regimes: low temperature versus high temperature, weak static disorder versus strong disorder, and two wells versus an array of wells. We have rederived the transport equations in various extremes of the parameter space and revealed once again the fact that the particle motion is coherent at temperatures low compared with the Debye temperature and with site energy disorder weak compared with the renormalized tunneling energy splitting, whereas the motion is incoherent at high temperature or with strong disorder. The results on decay rates and diffusion constants have been reproduced exactly. We have given a very detailed analysis for the two-well case, and have obtained rather complete results for the time dependence of the interwell transition probability.

The organization of the paper is as follows. In Section 2, we set up our system Hamiltonian, define our problem, and derive an exact path integral expression for the transition probability. In Section 3, we make a systematic expansion of the expression, and derive a simple yet general result, useful for later explorations. Section 4 is devoted to the two-well case, where the effects of temperature and disorder are studied in great detail. In Section 5, we study the case of low temperature and large site energy disorder for an array of wells. In Section 6, we consider the translationally invariant case at low and high temperatures. Finally, we discuss and conclude in Section 7.

2. GENERAL FORMULATION

2.1. The System and the Problem

We begin with a discussion of the Hamiltonian governing the motion of our system. Consider first the case of an external particle moving in the balk or on the surface of a crystalline solid. A particular example in our mind is a hydrogen atom (or its isotopes) moving on the tungsten surface.[12,13,26,27] When the lattice atoms are fixed at their equilibrium positions, the particle sees a periodic array of potential wells. We assume that the temperature is sufficiently low such that only the lowest level of each potential well can be occupied. This is appropriately described by a tight-binding model. Let $|\mathbf{x}\rangle$ be the Wannier state corresponding to a well centered at $\mathbf{x}$, and the particle tunnels from one well to another according to

$$H_P |\mathbf{x}\rangle = \varepsilon |\mathbf{x}\rangle + \Delta \sum_{\boldsymbol{l}} |\mathbf{x}+\boldsymbol{l}\rangle \tag{2.1}$$

where ε is the site energy and Δ the tunneling energy splitting, and $\boldsymbol{l}$ is a vector connecting nearest neighboring sites.

The motion of the lattice atoms is described by a phonon field whose Hamiltonian in the absence of the external particle is given by

$$H_L = \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} \tag{2.2}$$

where $a_{\mathbf{k}}^{\dagger}$ creates a phonon of wave vector $\mathbf{k}$ (a mode branch index is omitted for simpler notations). When the lattice atoms are displaced from their equilibrium positions, the site energies of the particle also change. To first order in these displacement, the site energy ε changes by

$$H_I = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} g(\mathbf{k})\, e^{i\mathbf{k}\mathbf{x}} (a_{\mathbf{k}} + a_{-\mathbf{k}}^{\dagger}) \tag{2.3}$$

where N is the total number of lattice atoms. The actual form of $g(\mathbf{k})$ depends on the type of interaction between the particle and the lattice atoms.[28] In an ionic crystal, the particle interacts strongly with the optical longitudinal phonons through the dipole field that they generate. The coupling function takes the form $g(\mathbf{k}) = \kappa/k$, where κ is independent of the particle mass. In a piezoelectric material, the particle also interacts strongly with the acoustical longitudinal phonons. The coupling function is $g(\mathbf{k}) = \kappa(\hat{\mathbf{k}})/\sqrt{\omega_{\mathbf{k}}}$, and it is again independent of the particle mass. In Appendix A, we give a derivation of (2.3) for a short-ranged repulsive interaction, where we find that the particle interacts with the acoustical longitudinal phonons with a coupling function $g(\mathbf{k}) \sim k/\sqrt{\omega_k}$ for small k. The overall energy scale of the coupling is of the order of

$$\delta\varepsilon \left(\frac{\hbar}{M\omega_d l^2} \right)^{1/2} \tag{2.4}$$

In this expression, $\delta\varepsilon$ is the energy level spacing in a well, M is the mass of the lattice atoms, ω_d is the Debye frequency of the lattice, and l is the lattice constant. The coupling strongly depends on the particle mass through the level spacing $\delta\varepsilon$.

If (2.3) is the only form of particle–phonon interaction, our system Hamiltonian is then given by

$$H_{\text{tot}} = H_P + H_L + H_I \tag{2.5}$$

Before we proceed further, we would like to remark on the reality of this Hamiltonian. The reduction of the original continuous system to the tight-binding form has been worked out in various ways. Sethna[30] has given a quite detailed analysis, showing that the different reduction schemes are equally valid, but the interpretation of Δ may be different. Our interpreta-

tion of Δ as the bare tunneling amplitude relies on the assumption that the intrawall level spacing is large compared with $k_B T$ and with the Debye energy. Second, the hopping amplitude Δ may also have an explicit dependence on the positions of the lattice atoms and therefore give rise to an off-diagonal coupling to the phonons. This would give rise to the so-called "effect of fluctuation preparation of barrier."[30] It is estimated, however, that this effect is not important for a low-mass particle, such as a hydrogen atom, moving on a heavy substrate, such as the tungsten metal.[31]

The Hamiltonian (2.5) is translationally invariant. In our later discussions, we will, however, generalize our system to include situations without translational invariance: (1) the site energies may have a positional dependence, and (2) only a subset of the sites may be accessible to the particle. We thus modify (2.1) to

$$H_P |\mathbf{x}\rangle = \varepsilon_{\mathbf{x}} |\mathbf{x}\rangle + \Delta \sum_{l} |\mathbf{x}+\boldsymbol{l}\rangle \tag{2.6}$$

where $\{\mathbf{x}\}$ is the tight-binding lattice or a subset of it. Due to the smallness of the tunneling energy splitting, static disorder due to impurities or strain can play an important role. Also, the inclusion of a two-site case allows for a very detailed analysis of the fundamental step of the particle motion, and allows for direct comparison with results in the literature.

We wish to study the following problem. Suppose the particle was at $\mathbf{x}_0$ at time $t=0$, and the phonons were in equilibrium at temperature $\mathbf{T}$ with the particle fixed at $\mathbf{x}_0$; we ask for the probability of finding the particle at $\mathbf{x}_f$ at later times, regardless of the final states of the phonon field. It is, however, more convenient to pose the problem in an alternative but equivalent way.[19] We take a time t_0 in the distant past. We set up the initial distribution of the system as

$$\rho_{\text{tot}}(t_0) = |\mathbf{x}_0\rangle\langle\mathbf{x}_0| e^{-\beta H_L}/\text{tr}(e^{-\beta H_L}) \tag{2.7}$$

where $\beta = 1/(k_B T)$. We then allow the system to evolve according to

$$H_{\text{tot}}(t) = H_P(t) + H_L + H_I \tag{2.8}$$

where $H_P(t)$ is the same as given in (2.6), but with Δ replaced by $\Delta\theta(t)$, with $\theta(t)$ being the unit step function. We finally take $t_0 \to -\infty$, and ask for the probability $P(\mathbf{x}_f, \mathbf{x}_0, t)$ of finding the particle at $\mathbf{x}_f$ at time $t>0$. The evolution of the system in the infinite time interval $(t_0 < t < 0)$ should have prepared the system at $t=0$ in equilibrium with the particle fixed at $\mathbf{x}_0$.

2.2. Path Integral Expression for $P(\mathbf{x}_f, \mathbf{x}_0, t)$

In this subsection, we will derive a path integral expression for the probability $P(\mathbf{x}_f, \mathbf{x}_0, t)$. The mathematical details will be presented in Appendix B and C and references therein. Here we just illustrate the basic ideas and establish notations used throughout this paper. It is sufficient to know the reduced density matrix $\rho(t)$ for the particle, defined as the total density matrix of the system with the phonon degrees of freedom traced out. In the absence of the particle–phonon interactions, the reduced density matrix satisfies the Liouvillian equation

$$\frac{\partial}{\partial t}\rho(\mathbf{x}, \mathbf{y}, t) = \sum_{\mathbf{x}', \mathbf{y}'} \mathscr{L}_P(\mathbf{x}, \mathbf{y}; \mathbf{x}', \mathbf{y}'; t)\, \rho(\mathbf{x}', \mathbf{y}', t) \tag{2.9}$$

where $\mathscr{L}_P$ is the Liouvillian operator corresponding to the particle Hamiltonian $H_P(t)$, defined as

$$\mathscr{L}_P(\mathbf{x}, \mathbf{y}; \mathbf{x}', \mathbf{y}'; t) = \frac{1}{i\hbar}\{\langle \mathbf{x}|\, H_P(t)\, |\mathbf{x}'\rangle\langle \mathbf{y}'|\mathbf{y}\rangle - \langle \mathbf{x}|\mathbf{x}'\rangle\langle \mathbf{y}'|\, H_P(t)\, |\mathbf{y}\rangle\} \tag{2.10}$$

which is nothing but the commutator $[H_P(t), \cdot]/(i\hbar)$.

The Liouvillian equation (2.9) has the same linear structure as the Schrödinger equation. The real space $\mathbf{x}$ is replaced with the phase space $(\mathbf{x}, \mathbf{y})$ (see footnote 3). The wave function is replaced with the density matrix. The Hamiltonian is replaced with the Liouvillian. Therefore, all the algebraic techniques developed for solving Schrödinger equations can be transplanted here. In order to simplify notations, from now on we denote the pair $(\mathbf{x}, \mathbf{y})$ by z, so that $\rho(z, t) = \rho(\mathbf{x}, \mathbf{y}, t)$ and $\mathscr{L}_P(z, z', t) = \mathscr{L}_P(\mathbf{x}, \mathbf{y}; \mathbf{x}', \mathbf{y}'; t)$. Also, it will be convenient to introduce a "bra-ket" notation [not to be confused with those for the states as in (2.10)] for the quantities in the linear equation (2.9):

$$\begin{aligned} |\rho(t)\rangle &\equiv \sum_z \rho(z)\, |z\rangle \\ \mathscr{L}_P(t) &\equiv \sum_{z, z'} |z\rangle\, \mathscr{L}_P(z, z', t)\, \langle z'| \\ \langle z|z'\rangle &= \delta_{zz'} = \delta_{xx'}\delta_{yy'} \end{aligned} \tag{2.11}$$

Equation (2.9) can then be written as

$$\frac{\partial}{\partial t}|\rho(t)\rangle = \mathscr{L}_P(t)\, |\rho(t)\rangle \tag{2.12}$$

This is integrated with the initial condition $|\rho(t_0)\rangle = |z_0\rangle$, $z_0 \equiv (\mathbf{x}_0, \mathbf{x}_0)$, yielding

$$|\rho(t)\rangle = \sum_{n=0}^{\infty} \int_{t_0}^{t} dt_n \int_{t_0}^{t_n} dt_{n-1} \cdots \int_{t_0}^{t_2} dt_1 \times e^{\mathscr{L}_s(t-t_0)} \hat{\mathscr{L}}_h(t_n)\, \hat{\mathscr{L}}_h(t_{n-1}) \cdots \hat{\mathscr{L}}_h(t_1)\, |z_0\rangle \tag{2.13}$$

where

$$\hat{\mathscr{L}}_h(t) = e^{-\mathscr{L}_s(t-t_0)}\, \mathscr{L}_h(t)\, e^{\mathscr{L}_s(t-t_0)} \tag{2.14}$$

with $\mathscr{L}_s$ (time independent) corresponding [as in (2.10)] to the site diagonal part of $H_P(t)$ and $\mathscr{L}_h(t)$ corresponding to the hopping part of $H_P(t)$. The probability of finding the particle at $\mathbf{x}_f$ is then given by

$$\langle z_f|\rho(t)\rangle = \sum_{n=0}^{\infty} \int_{t_0}^{t} dt_n \int_{t_0}^{t_n} dt_{n-1} \cdots \int_{t_0}^{t_2} dt_1 \sum_{\{z_j\}} \times \langle z_f|\mathscr{L}_h(t_n)|z_{n-1}\rangle\langle z_{n-1}|\mathscr{L}_h(t_{n-1})|z_{n-2}\rangle \cdots \langle z_1|\mathscr{L}_h(t_1)|z_0\rangle \times \exp\left\{\sum_{j=0}^{n} \lambda(z_j)(t_{j+1}-t_j)\right\} \tag{2.15}$$

where $z_j = (\mathbf{x}_j, \mathbf{y}_j)$ with $\mathbf{y}_f = \mathbf{x}_f$, and $\lambda(z_j) = (\varepsilon_{\mathbf{x}_j} - \varepsilon_{\mathbf{y}_j})/(i\hbar)$.

The expression (2.15) is in fact a sum over all possible paths z_τ in the phase space starting at z_0 and ending at z_f. A particular path is specified by the number of jumps n, the jumping instants $\{t_j\}$, and the "positions" $\{z_j\}$ between the jumps. More specifically, a path z_τ of n jumps is a sectionally constant function of time τ, given by

$$z_\tau = z_j, \qquad \text{for} \quad t_j < \tau < t_{j+1}, \quad j = 0, 1, \ldots, n \tag{2.16}$$

where $t_{n+1} = t$. The weighting factor is a product of jumping amplitudes and the phase factors accumulated between the jumps due to the site energies.

In the presence of interactions with the phonons, the expression (2.15) is modified by inserting an *influence functional* as (see Appendix B)

$$\langle z_f|\rho(t)\rangle = \sum_{n=0}^{\infty} \int_{t_0}^{t} dt_n \int_{t_0}^{t_n} dt_{n-1} \cdots \int_{t_0}^{t_2} dt_1 \sum_{\{z_j\}} \times \langle z_f|\mathscr{L}_h(t_n)|z_{n-1}\rangle\langle z_{n-1}|\mathscr{L}_h(t_{n-1})|z_{n-2}\rangle \cdots \langle z_1|\mathscr{L}_h(t_1)|z_0\rangle \times \exp\left\{\sum_{j=0}^{n} \lambda(z_j)(t_{j+1}-t_j)\right\} \exp(\Phi[z]) \tag{2.17}$$

where

$$\Phi[z] = -\int_{t_0}^{t} d\tau \int_{t_0}^{\tau} ds \sum_{\mathbf{k}} \frac{|g(\mathbf{k})|^2}{N\hbar^2} \times (e^{i\mathbf{k}\mathbf{x}_\tau} - e^{i\mathbf{k}\mathbf{y}_\tau})[\gamma_{\mathbf{k}}(\tau - s)e^{-i\mathbf{k}\mathbf{x}_s} - \gamma_{\mathbf{k}}^*(\tau - s)e^{-i\mathbf{k}\mathbf{y}_s}]$$

$$\gamma_{\mathbf{k}}(\tau) = \frac{2}{e^{\beta\hbar\omega_{\mathbf{k}}} - 1}\cos(\omega_{\mathbf{k}}\tau) + e^{-i\omega_{\mathbf{k}}\tau} \tag{2.18}$$

The influence functional fully takes care of the effects of the phonons on the particle motion.

With some tedious but straightforward manipulations (see Appendix C), the expression (2.17) can be rewritten as

$$\langle z_f | \rho(t) \rangle = \sum_{n=0}^{\infty} \int_0^t dt_n \int_0^{t_n} dt_{n-1} \cdots \int_0^{t_2} dt_1 \sum_{\{z_j\}} \times \langle z_f | \bar{\mathscr{L}}_h | z_{n-1} \rangle \langle z_{n-1} | \bar{\mathscr{L}}_h | z_{n-2} \rangle \cdots \langle z_1 | \bar{\mathscr{L}}_h | z_0 \rangle \times \exp\left\{ \lambda(z_0) t_1 + \sum_{j=1}^{n} \lambda(z_j)(t_{j+1} - t_j) \right\} \prod_{n \geq j > j' \geq 1} F_{jj'} \tag{2.19}$$

In this expression $\bar{\mathscr{L}}_h$ is the renormalized hopping Liouvillian operator, given by

$$\langle z | \bar{\mathscr{L}}_h | z' \rangle = \frac{\bar{\Delta}}{i\hbar} \sum_{\boldsymbol{l}} \{ \langle \mathbf{x} | \mathbf{x}' + \boldsymbol{l} \rangle \langle \mathbf{y}' | \mathbf{y} \rangle - \langle \mathbf{x} | \mathbf{x}' \rangle \langle \mathbf{y}' | \mathbf{y} + \boldsymbol{l} \rangle \}$$

$$\bar{\Delta} = \Delta \exp\left\{ -\frac{1}{2} \sum_{\mathbf{k}} J(\mathbf{k}) \coth\left(\frac{\beta\hbar\omega_{\mathbf{k}}}{2} \right) |1 - e^{i\mathbf{k}\boldsymbol{l}_1}|^2 \right\} \tag{2.20}$$

with $\boldsymbol{l}_1$ being any one lattice vector among those of the nearest neighboring ones $\{\boldsymbol{l}\}$, and $E_{jj'}$ is an *influence factor* given by

$$F_{jj'} \equiv F(t_j - t_{j'}, z_j, z_{j-1}, z_{j'}, z_{j'-1}) = \exp\left\{ -\sum_{\mathbf{k}} J(\mathbf{k}) [\coth(\beta\hbar\omega_{\mathbf{k}}/2) \cos\omega_{\mathbf{k}}(t_j - t_{j'})(U_j - U_{j-1})(U_{j'}^* - U_{j'-1}^*) - i \sin\omega_{\mathbf{k}}(t_j - t_{j'})(U_j - U_{j-1})(V_{j'}^* - V_{j'-1}^*)] \right\} \tag{2.21}$$

The other quantities in the above expressions are defined as

$$J(\mathbf{k}) = \frac{|g(\mathbf{k})|^2}{N(\hbar\omega_{\mathbf{k}})^2}$$
$$U_j = e^{i\mathbf{k}\mathbf{x}_j} - e^{i\mathbf{k}\mathbf{y}_j} \tag{2.22}$$
$$V_j = e^{i\mathbf{k}\mathbf{x}_j} + e^{i\mathbf{k}\mathbf{y}_j}$$

And it is understood that $U_{-1} = V_{-1} = U_{n+1} \equiv 0$.

It is seen that the hopping energy Δ gets renormalized by the phonons. The renormalization factor is just the usual Frank–Condon factor in small-polaron theory.[1] In the next section, we will make a closer examination of the physical contents in the expressions (2.19)–(2.21), and will present a useful approximation scheme to evaluate them.

3. THE "RARE HOPPING" APPROXIMATION

3.1. Diagram Expansion

In the last section, we derived a path integral expression (2.19) for the probability of finding the particle at $\mathbf{x}_f$ at time $t > 0$, assuming the particle was at $\mathbf{x}_0$ at $t = 0$, and that the phonons were in equilibrium with the particle fixed at $\mathbf{x}_0$. The effects of the phonons on the particle motion come in two ways: (1) to renormalize the hopping energy Δ by the Frank–Condon factor (2.20), and (2) to dress up the particle propagation by the influence factors $F_{jj'}$ of (2.21) for each pair of hopping events. An influence factor $F_{jj'}$ depends only on the time difference $(t_j - t_{j'})$ between the two hopping events, and on the "positions" immediately before and after each of the hops. From now on, we will use the expression (2.19) as the formal definition of a propagator, $G(z_f, z_0, t)$, even if z_0 and z_f are not in diagonal form. For diagonal (z_f, z_0), G coincides with the propagator of the reduced density matrix.

If the influence factors were unity, the expression (2.19) would be equal to

$$\langle z_f | e^{(\mathscr{L}_s + \mathscr{L}_h)t} | z_0 \rangle \equiv G_0(z_f, z_0, t) \tag{3.1}$$

that is, the particle would propagate under the action of the renormalized particle Liouvillian

$$\bar{\mathscr{L}}_P = \mathscr{L}_s + \bar{\mathscr{L}}_h \tag{3.2}$$

The typical time scale between two hopping events is $\hbar/\bar{\Delta}$.

On the other hand, an influence factor differs appreciably from unity only in a typical time scale of $1/\omega_d$, assuming that the coupling function

$J(\mathbf{k})$ varies smoothly. There is, in general, a long-time tail (decaying to zero as an inverse power of time) in $F_{jj'} - 1$ associated with the low-frequency end of the phonon spectrum, but this will be small due to the small spectral weight there.

We will from now on treat $\bar{\Delta}/(\hbar\omega_d)$ as a small parameter. It is then useful to write

$$F_{jj'} = 1 + (F_{jj'} - 1) \tag{3.3}$$

and to expand the product $\prod F_{jj'}$ in (2.19) in powers of $(F_{jj'} - 1)$. This is analogous to the technique used in the low-density expansion of thermodynamic quantities for a hard-core interacting gas. There, the expansion is in terms of $e^{-V/k_B T} - 1$ instead of the potential V. Here, we may say that we are dealing with a "low density" (in time) of scattering events.

Regarding the expression (2.19) as a propagator $G(z_f, z_0, t)$, then it is equal to $G_0(z_f, z_0, t)$ dressed with zero, one, two,..., factors of the retarded self-interactions $(F_{jj'} - 1)$ in all possible ways. Diagrammatically this is shown in Fig. 1, where a heavy directed line represents the dressed

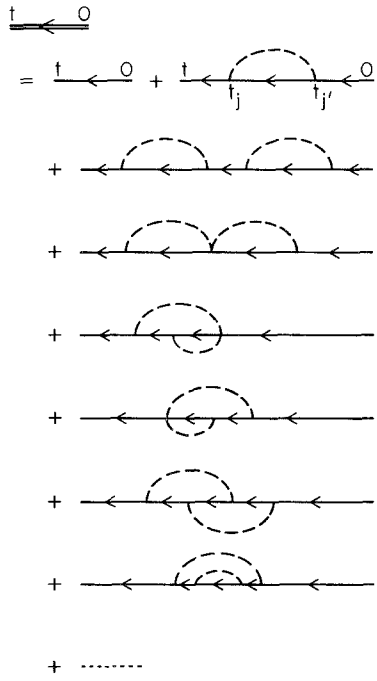

Fig. 1. Diagrams for the propagator in the time domain.

propagator G, a light directed line the "free" propagator G_0, and the dashed lines the self-interactions $(F_{jj'}-1)$. Two self-interactions can share at most one hopping time. The detailed structures of these diagrams will be made clear below.

Consider first the term with a single self-interaction,

$$\begin{aligned} G_1(z_f, z_0, t) = \sum_{n=0}^{\infty} \int_0^t dt_n \int_0^{t_n} dt_{n-1} \cdots \int_0^{t_2} dt_1 \sum_{\{z_j\}} \\ \times \langle z_f | \, \bar{\mathscr{L}}_h \, | z_{n-1} \rangle \langle z_{n-1} | \, \bar{\mathscr{L}}_h \, | z_{n-2} \rangle \cdots \langle z_1 | \, \bar{\mathscr{L}}_h \, | z_0 \rangle \\ \times \exp\left\{ \lambda(z_0) t_1 + \sum_{j=1}^{n} \lambda(z_j)(t_{j+1} - t_j) \right\} \sum_{n \geqslant j > j' \geqslant 1} (F_{jj'} - 1) \end{aligned} \tag{3.4}$$

The structure of this expression is more transparent if we make a Laplace transform of it. The result is

$$\begin{aligned} & G_1(z_f, z_0, \lambda) \\ & = \int_{-\infty}^{\infty} d\omega \sum_{n=2}^{\infty} \sum_{j=2}^{n} \sum_{j'=1}^{j-1} \sum_{\{z_j\}} \\ & \quad \times \left\{ \frac{1}{\lambda - \lambda(z_f)} \langle z_f | \, \bar{\mathscr{L}}_h \, | z_{n-1} \rangle \frac{1}{\lambda - \lambda(z_{n-1})} \cdots \langle z_{j+1} | \, \bar{\mathscr{L}}_h \, | z_j \rangle \frac{1}{\lambda - \lambda(z_j)} \right\} \\ & \quad \times \left\{ \frac{1}{\lambda - \lambda(z_{j-1}) + i\omega} \langle z_{j-1} | \, \bar{\mathscr{L}}_h \, | z_{j-2} \rangle \frac{1}{\lambda - \lambda(z_{j-2}) + i\omega} \right. \\ & \qquad \left. \cdots \langle z_{j'+1} | \, \bar{\mathscr{L}}_h \, | z_{j'} \rangle \frac{1}{\lambda - \lambda(z_{j'}) + i\omega} \right\} \\ & \quad \times \left\{ \frac{1}{\lambda - \lambda(z_{j'-1})} \langle z_{j'-1} | \, \bar{\mathscr{L}}_h \, | z_{j'-2} \rangle \frac{1}{\lambda - \lambda(z_{j'-2})} \right. \\ & \qquad \left. \cdots \langle z_1 | \, \bar{\mathscr{L}}_h \, | z_0 \rangle \frac{1}{\lambda - \lambda(z_0)} \right\} \\ & \quad \times \{ \langle z_j | \, \bar{\mathscr{L}}_h \, | z_{j-1} \rangle \tilde{F}(\omega, z_j, z_{j-1}, z_{j'}, z_{j'-1}) \langle z_{j'} | \, \bar{\mathscr{L}}_h \, | z_{j'-1} \rangle \} \end{aligned} \tag{3.5}$$

where $\tilde{F}$ is defined by

$$\begin{aligned} & \int_{-\infty}^{\infty} d\omega \, e^{-i\omega\tau} \tilde{F}(\omega, z_j, z_{j-1}, z_{j'}, z_{j'-1}) \\ & \qquad = F(\tau, z_j, z_{j-1}, z_{j'}, z_{j'-1}) - 1 \end{aligned} \tag{3.6}$$

with $F(\cdots)$ given in (2.21). We now change the labels such that $z^4 = z_j$, $z^3 = z_{j-1}$, $z^2 = z_{j'}$, and $z^1 = z_{j'-1}$. After summing up the intermediate positions other than these z's, the expression (3.5) becomes

$$\begin{aligned} G_1(z_f, z_0, \lambda) = \int_{-\infty}^{\infty} d\omega \sum_{n=2}^{\infty} \sum_{j=2}^{n} \sum_{j'=1}^{j-1} \sum_{\{z^l\}} \\ \times \left\{ \langle z_f | \frac{1}{\lambda - \mathscr{L}_s} \left(\bar{\mathscr{P}}_h \frac{1}{\lambda - \mathscr{L}_s} \right)^{n-j} | z^4 \rangle \right\} \\ \times \left\{ \langle z^3 | \frac{1}{\lambda - \mathscr{L}_s + i\omega} \left(\bar{\mathscr{P}}_h \frac{1}{\lambda - \mathscr{L}_s + i\omega} \right)^{j-j'-1} | z^2 \rangle \right\} \\ \times \left\{ \langle z^1 | \frac{1}{\lambda - \mathscr{L}_s} \left(\bar{\mathscr{P}}_h \frac{1}{\lambda - \mathscr{L}_s} \right)^{j'-1} | z_0 \rangle \right\} \\ \times \{ \langle z^4 | \bar{\mathscr{P}}_h | z^3 \rangle \tilde{F}(\omega, z^4, z^3, z^2, z^1) \langle z^2 | \bar{\mathscr{P}}_h | z^1 \rangle \} \end{aligned} \tag{3.7}$$

Now, the powers $n-j$, $j-j'-1$, and $j'-1$ are ranged from 0 to ∞ independent of one another, and the summation over them gives

$$\begin{aligned} G_1(z_f, z_0, \lambda) = \int_{-\infty}^{\infty} d\omega \sum_{\{z^l\}} \langle z_f | \frac{1}{\lambda - \mathscr{L}_s - \bar{\mathscr{P}}_h} | z^4 \rangle \\ \times \langle z^3 | \frac{1}{\lambda - \mathscr{L}_s - \bar{\mathscr{P}}_h + i\omega} | z^2 \rangle \langle z^1 | \frac{1}{\lambda - \mathscr{L}_s - \bar{\mathscr{P}}_h} | z_0 \rangle \\ \times \langle z^4 | \bar{\mathscr{P}}_h | z^3 \rangle \tilde{F}(\omega, z^4, z^3, z^2, z^1) \langle z^2 | \bar{\mathscr{P}}_h | z^1 \rangle \end{aligned} \tag{3.8}$$

Notice that the quantity

$$\langle z | \frac{1}{\lambda - \mathscr{L}_s - \bar{\mathscr{P}}_h} | z' \rangle \equiv G_0(z, z', \lambda) \tag{3.9}$$

appearing in (3.8) is just the Laplace transform of $G_0(z, z', t)$ defined in (3.1).

As a result of the above analysis, the first-order diagram in Fig. 1, after Laplace transformation, has the detailed structure shown in Fig. 2. A

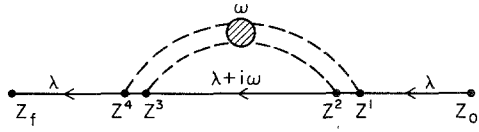

Fig. 2. The first-order diagram for the propagator.

directed line still represents a free propagator G_0, with its position variables labeled at the ends of the line, and its Laplace variable labeled beside the line. The hatched circle with four legs represents the self-interaction $\tilde{F}$, with its position variables labeled at the ends of the legs, and its frequency labeled beside the circle. Finally, the undirected short lines between pairs of dots are the hops, $\langle z^4| \bar{\mathscr{L}}_h |z^3\rangle$ and $\langle z^2| \bar{\mathscr{L}}_h |z^1\rangle$. The "value" $G_1(z_f, z_0, \lambda)$ of the diagram is equal to the product of the quantities associated with the parts of the diagram, with the internal positions summed up and the frequency integrated out.

Similarly, the second-order diagrams in Fig. 1 can be shown to have the detailed structures displayed in Fig. 3. The meanings of the various parts of these diagrams are the same as for the first-order one. Once the first- and second-order diagrams are understood, it is not difficult to imagine how the higher-order ones should look. In an mth-order diagram, the otherwise free propagation of the particle is interrupted by m self-interactions between m pairs of hopping steps. Two self-interactions can share at most one hopping step, but one hopping step can be shared by any

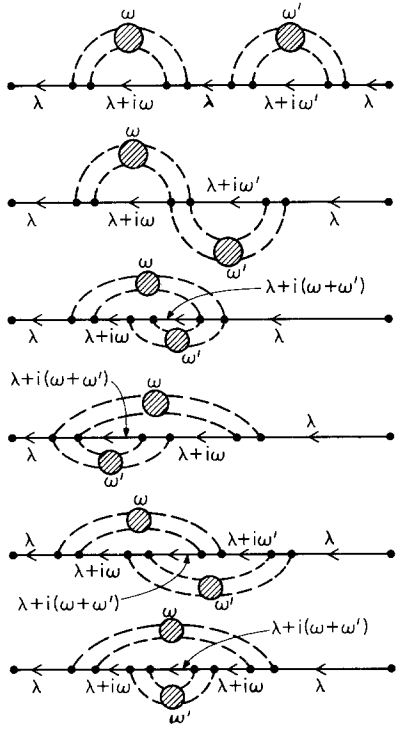

Fig. 3. The second-order diagrams for the propagator.

number of self-interactions. Each allowed topologically distinct diagram contributes a term for G.

The propagator G satisfies the Dyson equation (in operator notation),

$$G(\lambda) = G_0(\lambda) + G_0(\lambda)\, \Sigma(\lambda)\, G(\lambda) \tag{3.10}$$

where the self-energy

$$\langle z|\, \Sigma(\lambda)\, |z'\rangle \equiv \Sigma(z, z', \lambda) \tag{3.11}$$

is given by the diagrams shown in Fig. 4. These diagrams start and end with hops and each of them cannot be disconnected by removing one G_0 line. The first-order diagram has the value

$$\langle z|\, \Sigma_1(\lambda)\, |z'\rangle = \int_{-\infty}^{\infty} d\omega \sum_{z_1 z_1'} \tilde{F}(\omega, z, z_1, z_1', z') \times \langle z|\, \bar{\mathscr{P}}_h\, |z_1\rangle\, G_0(z_1, z_1', \lambda + i\omega) \langle z_1'|\, \bar{\mathscr{P}}_h\, |z'\rangle \tag{3.12}$$

as can also be read off from (3.8).

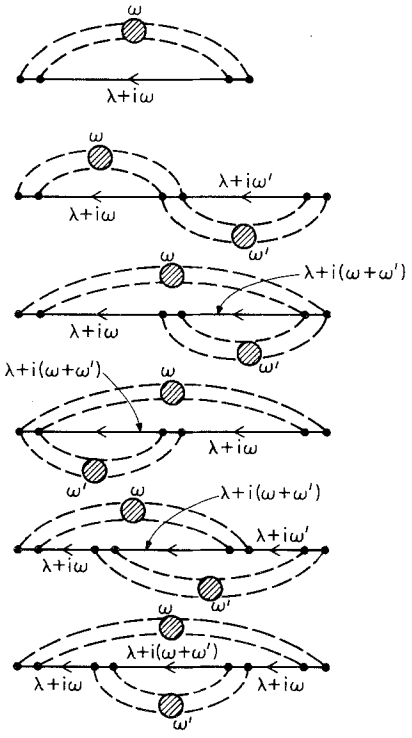

Fig. 4. The self-energy diagrams.

3.2. The Approximation

The interaction kernel $\tilde{F}(\omega, z, z_1, z_1', z')$ in (3.12) has a typical frequency scale of ω_d. The integration over ω should make the propagator $G_0(z_1, z_1', \lambda + i\omega)$ to be of order $1/\omega_d$. (The interaction kernel itself has the dimension of $1/\omega$.) The two hopping factors in (3.12) then make Σ_1 to be of order of $(\bar{\Delta}/\hbar)^2/\omega_d$.

From Fig. 4 we see that the second-order terms for the self-energy involve at least three "hops" and two self-interactions. Quite similar arguments as given above then lead to the conclusion that they are $\bar{\Delta}/(\hbar\omega_d)$ times smaller than the first-order term. The higher-order terms are even smaller.

We then make the approximation

$$\Sigma(z, z', \lambda) \approx \Sigma_1(z, z', \lambda) \tag{3.13}$$

With this approximation, we can write

$$G(\lambda) = \frac{1}{\lambda - \bar{\mathscr{L}}_P - \Sigma_1(\lambda)} \tag{3.14}$$

The Laplace transform of the probability $P(\mathbf{x}_f, \mathbf{x}_0, t)$ is then given by

$$\begin{aligned} P(\mathbf{x}_f, \mathbf{x}_0, \lambda) &= \langle z_f | G(\lambda) | z_0 \rangle \\ &= \langle z_f | \frac{1}{\lambda - \bar{\mathscr{L}}_P - \Sigma_1(\lambda)} | z_0 \rangle \end{aligned} \tag{3.15}$$

where z_f and z_0 are in diagonal form. Thus, the problem becomes solving for $\Sigma_1(\lambda)$, finding the inverse of $\lambda - \bar{\mathscr{L}}_P - \Sigma_1(\lambda)$, and inverting the Laplace transform.

The expresions (3.12) and (3.15) are the central result of this section. The operator inversion is facilitated by studying the eigenvalue problem,

$$\lambda | \psi \rangle = [\bar{\mathscr{L}}_P + \Sigma_1(\lambda)] | \psi \rangle$$

This is analogous to the generalized Boltzmann equations in the literature.[23–25] The problem is further simplified by restricting to small value of λ, if we are interested only in the long-time behavior of the particle.

The rest of this subsection gives details of the expression (3.12). The reader may wish to skip this part, and come back later when the formulas are referred to.

It will be useful to write (3.12) in a more detailed form. It is easy to see that (3.12) is the Laplace transform of the following expression:

$$\langle z|\,\Sigma_1(\tau)\,|z'\rangle = \sum_{z_1, z_1'} [F(\tau, z, z_1, z_1', z') - 1] \times \langle z|\,\bar{\mathscr{L}}_h\,|z_1\rangle\langle z_1|\,e^{\bar{\mathscr{L}}_P\tau}\,|z_1'\rangle\langle z_1'|\,\bar{\mathscr{L}}_h\,|z'\rangle \tag{3.16}$$

From (2.20) we have

$$\langle z|\,\bar{\mathscr{L}}_h\,|z_1\rangle\langle z_1| = \frac{\bar{\Delta}}{i\hbar}\sum_{\boldsymbol{l}} \{\delta_{\mathbf{x},\mathbf{x}_1+\boldsymbol{l}}\delta_{\mathbf{y},\mathbf{y}_1}\langle \mathbf{x}-\boldsymbol{l}, \mathbf{y}| - \delta_{\mathbf{x},\mathbf{x}_1}\delta_{\mathbf{y},\mathbf{y}_1-\boldsymbol{l}}\langle \mathbf{x}, \mathbf{y}+\boldsymbol{l}|\}$$

$$|z_1'\rangle\langle z_1'|\,\bar{\mathscr{L}}_h\,|z'\rangle = \frac{\bar{\Delta}}{i\hbar}\sum_{\boldsymbol{l}'} \{\delta_{\mathbf{x}_1',\mathbf{x}'+\boldsymbol{l}'}\delta_{\mathbf{y}_1',\mathbf{y}'}\,|\mathbf{x}'+\boldsymbol{l}', \mathbf{y}'\rangle - \delta_{\mathbf{x}_1',\mathbf{x}'}\delta_{\mathbf{y}_1',\mathbf{y}'-\boldsymbol{l}'}\,|\mathbf{x}', \mathbf{y}'-\boldsymbol{l}'\rangle\} \tag{3.17}$$

Substituting this into (3.16) and using the definition (2.21) for $F(\tau, z, z_1, z_1', z')$, we have

$$\begin{aligned}
&\langle z|\,\Sigma_1(\tau)\,|z'\rangle \\
&= (\bar{\Delta}/\hbar)^2\sum_{\boldsymbol{l},\boldsymbol{l}'}\{-\langle \mathbf{x}-\boldsymbol{l}, \mathbf{y}|\,e^{\bar{\mathscr{L}}_P\tau}\,|\mathbf{x}'+\boldsymbol{l}', \mathbf{y}'\rangle\, F_{\boldsymbol{l}\boldsymbol{l}'}(\tau + i\hbar\beta/2, \mathbf{x}-\mathbf{x}'-\boldsymbol{l}/2-\boldsymbol{l}'/2) \\
&\quad - \langle \mathbf{x}, \mathbf{y}+\boldsymbol{l}|\,e^{\bar{\mathscr{L}}_P\tau}\,|\mathbf{x}', \mathbf{y}'-\boldsymbol{l}'\rangle\, F_{\boldsymbol{l}\boldsymbol{l}'}(\tau - i\hbar\beta/2, \mathbf{y}-\mathbf{y}'+\boldsymbol{l}/2+\boldsymbol{l}'/2) \\
&\quad + \langle \mathbf{x}-\boldsymbol{l}, \mathbf{y}|\,e^{\bar{\mathscr{L}}_P\tau}\,|\mathbf{x}', \mathbf{y}'-\boldsymbol{l}'\rangle\, F_{\boldsymbol{l}\boldsymbol{l}'}(\tau - i\hbar\beta/2, \mathbf{x}-\mathbf{y}'-\boldsymbol{l}/2+\boldsymbol{l}'/2) \\
&\quad + \langle \mathbf{x}, \mathbf{y}+\boldsymbol{l}|\,e^{\bar{\mathscr{L}}_P\tau}\,|\mathbf{x}'+\boldsymbol{l}', \mathbf{y}'\rangle\, F_{\boldsymbol{l}\boldsymbol{l}'}(\tau + i\hbar\beta/2, \mathbf{y}-\mathbf{x}'+\boldsymbol{l}/2-\boldsymbol{l}'/2)\}
\end{aligned} \tag{3.18}$$

where

$$F_{\boldsymbol{l}\boldsymbol{l}'}(\tau, \mathbf{x}) = \exp\left(-4\sum_{\mathbf{k}} \frac{J(\mathbf{k})\sin(\mathbf{k}\boldsymbol{l}/2)\sin(\mathbf{k}\boldsymbol{l}'/2)}{\sinh(\beta\hbar\omega_{\mathbf{k}}/2)}\cos(\omega_{\mathbf{k}}\tau)e^{i\mathbf{k}\mathbf{x}}\right) - 1 \tag{3.19}$$

The Laplace transform of (3.18) then gives

$$\begin{aligned}
&\langle z|\,\Sigma_1(\lambda)\,|z'\rangle \\
&= \left(\frac{\bar{\Delta}}{\hbar}\right)^2 \sum_{\boldsymbol{l},\boldsymbol{l}'}\sum_{\omega,\mathbf{k}} \tilde{F}_{\boldsymbol{l}\boldsymbol{l}'}(\omega, k)\left\{-\langle x-\boldsymbol{l}, \mathbf{y}|\,\frac{e^{\beta\hbar\omega/2}e^{i\mathbf{k}(\mathbf{x}-\mathbf{x}'-\boldsymbol{l}/2-\boldsymbol{l}'/2)}}{\lambda + i\omega - \bar{\mathscr{L}}_P}\,|\mathbf{x}'+\boldsymbol{l}', \mathbf{y}'\rangle\right. \\
&\quad - \langle \mathbf{x}, \mathbf{y}+\boldsymbol{l}|\,\frac{e^{-\beta\hbar\omega/2}e^{i\mathbf{k}(\mathbf{y}-\mathbf{y}'+\boldsymbol{l}/2+\boldsymbol{l}'/2)}}{\lambda + i\omega - \bar{\mathscr{L}}_P}\,|\mathbf{x}', \mathbf{y}'-\boldsymbol{l}'\rangle \\
&\quad + \langle \mathbf{x}-\boldsymbol{l}, \mathbf{y}|\,\frac{e^{-\beta\hbar\omega/2}e^{i\mathbf{k}(\mathbf{x}-\mathbf{y}'-\boldsymbol{l}/2+\boldsymbol{l}'/2)}}{\lambda + i\omega - \bar{\mathscr{L}}_P}\,|\mathbf{x}', \mathbf{y}'-\boldsymbol{l}'\rangle \\
&\quad \left. + \langle \mathbf{x}, \mathbf{y}+\boldsymbol{l}|\,\frac{e^{\beta\hbar\omega/2}e^{i\mathbf{k}(\mathbf{y}-\mathbf{x}'+\boldsymbol{l}/2-\boldsymbol{l}'/2)}}{\lambda + i\omega - \bar{\mathscr{L}}_P}\,|\mathbf{x}'+\boldsymbol{l}', \mathbf{y}'\rangle\right\}
\end{aligned} \tag{3.20}$$

where $\tilde{F}_{ll'}(\omega, \mathbf{k})$ is the Fourier transform of $F_{ll'}(\tau, \mathbf{x})$ given by

$$\sum_{\omega,\mathbf{k}} \tilde{F}_{ll'}(\omega, \mathbf{k}) \exp(-i\omega\tau) \exp(i\mathbf{kx})$$
$$= \exp\left[-4 \sum_{\mathbf{k}} \frac{J(\mathbf{k}) \sin(\mathbf{k}\boldsymbol{l}/2) \sin(\mathbf{k}\boldsymbol{l}'/2)}{\sinh(\beta\hbar\omega_k/2)} \cos(\omega_k\tau) \exp(i\mathbf{kx}) \right] - 1 \quad (3.21)$$

At temperatures low compared with the Debye temperature, the exponent in the above exponential is small. To first order in the exponent, we have

$$\tilde{F}_{ll'}(\omega, \mathbf{k}) = -2(\delta_{\omega,\omega_\mathbf{k}} + \delta_{-\omega,\omega_\mathbf{k}}) \frac{J(\mathbf{k}) \sin(\mathbf{k}\boldsymbol{l}/2) \sin(\mathbf{k}\boldsymbol{l}'/2)}{\sinh(\beta\hbar\omega_\mathbf{k}/2)} \quad (3.22)$$

It is not difficult to see that we can obtain the same result from (3.16) if we replace $F(\tau, z, z_1, z_1', z') - 1$ by

$$-\sum_{\mathbf{k}} J(\mathbf{k}) \{ \coth(\beta\hbar\omega_\mathbf{k}/2) \cos(\omega_\mathbf{k}\tau)(U - U_1)(U_1'^* - U'^*)$$
$$- i \sin(\omega_\mathbf{k}\tau)(U - U_1)(V_1'^* - V'^*) \} \quad (3.23)$$

which is the argument of the exponential in the definition (2.21).

4. TWO-LEVEL SYSTEM

In this section, we consider the case that the particle is restricted to only two sites, which are located, for instance, at $\mathbf{x} = \boldsymbol{l}_1/2$ and $\mathbf{x} = -\boldsymbol{l}_1/2$. Our system then becomes a two-level system coupled to a heat bath of phonons. The analysis will be done in three subsections: (1) general considerations, (2) the case of low temperature, but arbitrary bias, and (3) the case of zero bias, but arbitrary temperature.

4.1. General Considerations

We can parametrize the position of the particle as $\mathbf{x} = x\boldsymbol{l}_1/2$ and $\mathbf{y} = y\boldsymbol{l}_1/2$ with $x, y = \pm 1$. Then we can write

$$U \equiv e^{i\mathbf{kx}} - e^{i\mathbf{ky}}$$
$$= i(x - y) \sin(\mathbf{k}\boldsymbol{l}_1/2) \quad (4.1)$$

and

$$V \equiv e^{i\mathbf{kx}} + e^{i\mathbf{ky}}$$
$$= 2 \cos(\mathbf{k}\boldsymbol{l}_1/2) + i(x + y) \sin(\mathbf{k}\boldsymbol{l}_1/2) \quad (4.2)$$

The influence factor in (2.21) is then simplified as

$$F_{jj'} \equiv F(t_j - t_{j'}, z_j, z_{j-1}, z_{j'}, z_{j'-1})$$
$$= \exp\left\{ - \int_0^\infty \frac{d\omega}{\omega^2} J(\omega) \left[\coth\left(\frac{\beta\hbar\omega}{2}\right) \cos\omega(t_j - t_{j'})(\xi_j - \xi_{j-1})(\xi_{j'} - \xi_{j'-1}) \right.\right.$$
$$\left.\left. - i \sin\omega(t_j - t_{j'})(\xi_j - \xi_{j-1})(\eta_{j'} - \eta_{j'-1}) \right] \right\} \tag{4.3}$$

where $\xi = x - y$, $\eta = x + y$, and

$$J(\omega) = \omega^2 \sum_{\mathbf{k}} J(\mathbf{k}) \sin^2(\mathbf{k}\boldsymbol{l}_1/2)\, \delta(\omega - \omega_{\mathbf{k}})$$
$$= (1/N\hbar^2) \sum_{\mathbf{k}} |g(\mathbf{k})|^2 \sin^2(\mathbf{k}\boldsymbol{l}_1/2)\, \delta(\omega - \omega_{\mathbf{k}}) \tag{4.4}$$

The renormalization relation (2.20) becomes

$$\bar{\Delta} = \Delta \exp\left[-2 \int_0^\infty \frac{d\omega}{\omega^2} J(\omega) \coth\left(\frac{\beta\hbar\omega}{2}\right) \right] \tag{4.5}$$

The spectral density $J(\omega)$, with a dimension of frequency, contains all the information of the phonons relevant to the dynamics of the two-level system.[19] It vanishes beyond a frequency around ω_d. At the low-frequency side, it vanishes as a power of ω. For short-ranged repulsive interaction between the particle and the lattice atoms, $|g(\mathbf{k})|^2$ goes to zero linearly with $\omega_{\mathbf{k}}$, so $J(\omega)$ vanishes like ω^5 at low frequency. For a piezoelectric coupling $J(\omega)$ vanishes like ω^3. In ref. 19, the general case of $J(\omega) \sim \omega^s$ has been studied for the low-temperature dynamics of a two-level system. Our case lies well in the regime of super-Ohmic coupling ($s > 1$), where the low spectral density at small ω makes the coupling effectively weak at low temperatures. However, the low-frequency behavior of $J(\omega)$ will not be so important for higher temperatures.

It will be convenient to introduce the Pauli matrices $\{\sigma_\mu, \mu = 1, 2, 3\}$, defined as

$$\sigma_1 |x, y\rangle = |\bar{x}, y\rangle$$
$$\sigma_2 |x, y\rangle = ix |\bar{x}, y\rangle \tag{4.6}$$
$$\sigma_3 |x, y\rangle = x |x, y\rangle$$

Similarly, we define σ'_μ, which acts on the y variable, but is otherwise the same as σ_μ. The probability (3.15) can then be written as (see Appendix D)

$$P(x_f, x_0, \lambda)$$
$$= \langle x_f, x_f | \, e^{-i\theta(\sigma_2+\sigma_2')} \frac{1}{\lambda + i(\sigma_3 - \sigma_3')\Omega/\hbar - \tilde{\Sigma}_1(\lambda)} e^{i\theta(\sigma_2+\sigma_2')} \, | x_0, x_0 \rangle \quad (4.7)$$

where $\Omega = (\bar{\Delta}^2 + \varepsilon^2)^{1/2}$ and $\theta = (1/2)\tan^{-1}(\bar{\Delta}/\varepsilon)$. The self-energy operator in the above expression is given by

$$\tilde{\Sigma}_1(\lambda) = -\left(\frac{\bar{\Delta}}{\hbar}\right)^2 \int_{-\infty}^{\infty} d\omega \, [C(\omega)A_1 + S(\omega)A_2] \quad (4.8)$$

where

$$C(\omega) = \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i\omega t} \{\cosh[g(t)] - 1\}$$
$$S(\omega) = \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i\omega t} \sinh[g(t)] \quad (4.9)$$
$$g(t) = 4 \int_0^{\infty} \frac{d\omega}{\omega^2} \frac{J(\omega)}{\sinh(\beta\hbar\omega/2)} \cos(\omega t)$$

and the A's are given by

$$\begin{aligned} A_1 = \Bigg\{ & \left(\frac{\varepsilon}{\Omega}\sigma_1 + \frac{\bar{\Delta}}{\Omega}\sigma_3\right) \frac{e^{\beta\hbar\omega/2}}{\lambda + i\omega + i(\sigma_3 - \sigma_3')\Omega/\hbar} \left(\frac{\varepsilon}{\Omega}\sigma_1 + \frac{\bar{\Delta}}{\Omega}\sigma_3\right) \\ & + \left(\frac{\varepsilon}{\Omega}\sigma_1' + \frac{\bar{\Delta}}{\Omega}\sigma_3'\right) \frac{e^{-\beta\hbar\omega/2}}{\lambda + i\omega + i(\sigma_3 - \sigma_3')\Omega/\hbar} \left(\frac{\varepsilon}{\Omega}\sigma_1' + \frac{\bar{\Delta}}{\Omega}\sigma_3'\right) \\ & - \left(\frac{\varepsilon}{\Omega}\sigma_1 + \frac{\bar{\Delta}}{\Omega}\sigma_3\right) \frac{e^{-\beta\hbar\omega/2}}{\lambda + i\omega + i(\sigma_3 - \sigma_3')\Omega/\hbar} \left(\frac{\varepsilon}{\Omega}\sigma_1' + \frac{\bar{\Delta}}{\Omega}\sigma_3'\right) \\ & - \left(\frac{\varepsilon}{\Omega}\sigma_1' + \frac{\bar{\Delta}}{\Omega}\sigma_3'\right) \frac{e^{\beta\hbar\omega/2}}{\lambda + i\omega + i(\sigma_3 - \sigma_3')\Omega/\hbar} \left(\frac{\varepsilon}{\Omega}\sigma_1 + \frac{\bar{\Delta}}{\Omega}\sigma_3\right) \Bigg\} \\ A_2 = \Bigg\{ & \sigma_3\sigma_1 \frac{e^{\beta\hbar\omega/2}}{\lambda + i\omega + i(\sigma_3 - \sigma_3')\Omega/\hbar} \sigma_1\sigma_3 \\ & + \sigma_3'\sigma_1' \frac{e^{-\beta\hbar\omega/2}}{\lambda + i\omega + i(\sigma_3 - \sigma_3')\Omega/\hbar} \sigma_1'\sigma_3' \\ & + \sigma_3\sigma_1 \frac{e^{-\beta\hbar\omega/2}}{\lambda + i\omega + i(\sigma_3 - \sigma_3')\Omega/\hbar} \sigma_1'\sigma_3' \\ & + \sigma_3'\sigma_1' \frac{e^{\beta\hbar\omega/2}}{\lambda + i\omega + i(\sigma_3 - \sigma_3')\Omega/\hbar} \sigma_1\sigma_3 \Bigg\} \end{aligned} \quad (4.10)$$

For the special case of $x_f = -1$, $x_0 = +1$, we have

$$P(-, +, \lambda) = \langle \psi_{--} | \frac{1}{\lambda + i(\sigma_3 - \sigma_3')\Omega/\hbar - \tilde{\Sigma}_1(\lambda)} | \psi_{++} \rangle \tag{4.11}$$

where

$$\begin{aligned} |\psi_{++}\rangle &= \frac{1}{2}\left[\left(1+\frac{\varepsilon}{\Omega}\right)|_{++}\rangle + \left(1-\frac{\varepsilon}{\Omega}\right)|_{--}\rangle - \frac{\bar{\Delta}}{\Omega}|_{+-}\rangle - \frac{\bar{\Delta}}{\Omega}|_{-+}\rangle\right] \\ |\psi_{--}\rangle &= \frac{1}{2}\left[\left(1-\frac{\varepsilon}{\Omega}\right)|_{++}\rangle + \left(1+\frac{\varepsilon}{\Omega}\right)|_{--}\rangle + \frac{\bar{\Delta}}{\Omega}|_{+-}\rangle + \frac{\bar{\Delta}}{\Omega}|_{-+}\rangle\right] \end{aligned} \tag{4.12}$$

4.2. Low-Temperature and Arbitrary Bias

When the temperature is low compared with the Debye temperature, the function $g(t)$ in (4.9) will be small due to the high-frequency cutoff by $\sinh(\beta\hbar\omega/2)$ and the low spectral weight of $J(\omega)$ at low frequencies. We can therefore set $C(t) = 0$ and $S(t) = g(t)$ to leading order in $k_B T/(\hbar\omega_d)$. The expression (4.8) then becomes

$$\tilde{\Sigma}_1(\lambda) = -\left(\frac{\bar{\Delta}}{\hbar}\right)^2 \int_{-\infty}^{\infty} \frac{d\omega}{\omega^2} \frac{2J(\omega)}{\sinh(\beta\hbar\omega/2)} A_2 \tag{4.13}$$

where $J(\omega) \equiv -J(-\omega)$ for $\omega < 0$.

Now, both $\tilde{\Sigma}_1(\lambda)$ and $i(\sigma_3 - \sigma_3')\Omega/\hbar$ are block diagonal in the sectors with $\sigma_3\sigma_3' = \pm 1$. Written in matrix form, $\lambda + i(\sigma_3 - \sigma_3')\Omega/\hbar - \tilde{\Sigma}_1(\lambda)$ is equal to

$$\begin{pmatrix} \lambda + a(\lambda) & -b(\lambda) \\ -a(\lambda) & \lambda + b(\lambda) \end{pmatrix} \tag{4.14}$$

in the subspace of $\{|_{++}\rangle, |_{--}\rangle\}$, and it is equal to

$$\begin{pmatrix} \lambda + i2\Omega/\hbar + c(\lambda) & c(\lambda) \\ c(\lambda) & \lambda - i2\Omega/\hbar + c(\lambda) \end{pmatrix} \tag{4.15}$$

in the subspace of $\{|_{+-}\rangle, |_{-+}\rangle\}$, where

$$\begin{aligned} a(\lambda) &= \left(\frac{\bar{\Delta}}{\hbar}\right)^2 \int_{-\infty}^{\infty} \frac{d\omega}{\omega^2} \frac{2J(\omega)}{\sinh(\beta\hbar\omega/2)} \frac{2\lambda e^{-\beta\hbar\omega/2}}{\lambda^2 + (\omega + 2\Omega/\hbar)^2} \\ b(\lambda) &= \left(\frac{\bar{\Delta}}{\hbar}\right)^2 \int_{-\infty}^{\infty} \frac{d\omega}{\omega^2} \frac{2J(\omega)}{\sinh(\beta\hbar\omega/2)} \frac{2\lambda e^{\beta\hbar\omega/2}}{\lambda^2 + (\omega + 2\Omega/\hbar)^2} \\ c(\lambda) &= \left(\frac{\bar{\Delta}}{\hbar}\right)^2 \int_{-\infty}^{\infty} \frac{d\omega}{\omega^2} \frac{2J(\omega)}{\sinh(\beta\hbar\omega/2)} \frac{2\lambda e^{-\beta\hbar\omega/2}}{\lambda^2 + \omega^2} \end{aligned} \tag{4.16}$$

The matrices (4.14) and (4.15) can be easily inverted to give an explicit expression for $P(-, +, \lambda)$ in (4.11) as

$$P(-, +, \lambda)=\frac{1}{2\lambda}-\frac{(\varepsilon/\Omega)[b(\lambda)-a(\lambda)]+(\varepsilon/\Omega)^2\lambda}{2\lambda[\lambda+a(\lambda)+b(\lambda)]}-\frac{1}{2}\frac{\lambda(\bar{\Delta}/\Omega)^2}{\lambda^2+2\lambda c(\lambda)+4\Omega^2/\hbar^2} \tag{4.17}$$

This expression has four poles located at

$$\begin{aligned}
&\lambda=0\\
&\lambda=-[a(\lambda)-b(\lambda)]\approx-[a(0_+)+b(0_+)]\\
&\lambda\approx i2\Omega/\hbar-c(0_++i2\Omega/\hbar)\\
&\lambda\approx -i2\Omega/\hbar-c(0_+-i2\Omega/\hbar)
\end{aligned} \tag{4.18}$$

respectively. With their residues approximated to first order in $(\bar{\Delta}/\hbar)^2$, we have

$$\begin{aligned}
P(-, +, \lambda)=&\frac{1}{2\lambda}\left[1+\frac{\varepsilon}{\Omega}\tanh(\beta\Omega)\right]\\
&-\frac{(\varepsilon/\Omega)\tanh(\beta\Omega)+(\varepsilon/\Omega)^2}{2(\lambda+2\Gamma)}\\
&-\frac{1}{2}\left(\frac{\bar{\Delta}}{\Omega}\right)^2\frac{\lambda+\Gamma}{(\lambda+\Gamma)^2+(2\Omega'/\hbar)^2}
\end{aligned} \tag{4.19}$$

where

$$\begin{aligned}
\Gamma&=\pi\left(\frac{\bar{\Delta}}{\Omega}\right)^2 J\left(\frac{2\Omega}{\hbar}\right)\coth(\beta\Omega)\\
\Omega'&=\Omega\left[1+\left(\frac{\bar{\Delta}}{\hbar}\right)^2\int_0^\infty\frac{d\omega}{\omega^2}\frac{8J(\omega)\coth(\beta\hbar\omega/2)}{(2\Omega/\hbar)^2-\omega^2}\right]
\end{aligned} \tag{4.20}$$

Recall that Ω is the eigenvalue of the renormalized particle Hamiltonian $\bar{H}_P$; now Ω is further renormalized to Ω' by the residual interaction with the phonons. After transforming back to the time domain, we finally have

$$\begin{aligned}
P(-, +, t)=&\frac{1}{2}\left[1+\frac{\varepsilon}{\Omega}\tanh(\beta\Omega)\right]\\
&-\frac{1}{2}\left[\frac{\varepsilon}{\Omega}\tanh(\beta\Omega)+\left(\frac{\varepsilon}{\Omega}\right)^2\right]e^{-2\Gamma t}\\
&-\frac{1}{2}\left(\frac{\bar{\Delta}}{\Omega}\right)^2\cos\left(\frac{2\Omega' t}{\hbar}\right)e^{-\Gamma t}
\end{aligned} \tag{4.21}$$

This agrees with the results of Leggett *et al.*[19] in the limits of zero bias ($\varepsilon = 0$) and large bias ($\varepsilon \gg \bar{\Delta}$), and it fills out the intermediate region where the noninteracting-blips approximation used by these authors is invalid. The above result has also been obtained by Gorlich *et al.*[20] using a path integral method beyond the noninteracting-blips approximation.

The solusion for the full density matrix has a particularly simple form in the new representation where $\bar{H}_P = \varepsilon\sigma_3 + \bar{\Delta}\sigma_1$ is diagonalized. Specifically, the diagonal elements are given by

$$\rho(+,+;t) + \rho(-,-;t) = 1$$

$$\rho(+,+;t) - \rho(-,-;t) = -\tanh(\beta\Omega) + e^{-2\Gamma t}[\rho(+,+;0) - \rho(-,-;0) + \tanh(\beta\Omega)]$$

The off-diagonal parts are given by

$$\rho(+,-;t) = e^{-\Gamma t} e^{-i2\Omega t/\hbar} \rho(+,-;0)$$

$$\rho(-,+;t) = e^{-\Gamma t} e^{i2\Omega t/\hbar} \rho(-,+;0)$$

The results in (4.21) may be obtained by transforming the density matrix back to the original representation where σ_3 is diagonalized.

The above simple result may be interpreted as follows. At low enough temperatures, our system is effectively described by the renormalized particle Hamiltonian $\bar{H}_P$, which is weakly perturbed by the residual interaction with the phonons.[7] In the representation where $\bar{H}_P$ is diagonalized, the diagonal parts of the particle density matrix relax exponentially at a rate of 2Γ to the equilibrium distribution $\exp(-\beta\bar{H}_P)/\mathrm{tr}\exp(-\beta\bar{H}_P)$, while the off-diagonal parts oscillate with a frequency $2\Omega'/\hbar \approx 2\Omega/\hbar$ and damp to zero at a rate of Γ, the inverse lifetime of the eigenstates of $\bar{H}_P$. The result suggests that the Bloch equation formulation is suitable as is advocated in ref. 19. In the new representation, the z component of the spin relaxes to its equilibrium value exponentially with a rate of 2Γ, while the x–y component rotates about the z axis with a frequency of $2\Omega/\hbar$ and damps with a rate of Γ. The Bloch equation may look slilghtly complicated after transforming back to the original representation. (The Bloch equations as given in ref. 20 are incorrect for the biased case. We expect that all three components should have oscillatory terms.)

4.3. Zero Bias and Arbitrary Temperature

When the potential bias ε is zero, $\lambda + i(\sigma_3 - \sigma_3')\Omega/\hbar - \tilde{\Sigma}_1(\lambda)$ is again block diagonal in the sectors with $\sigma_3\sigma_3' = \pm 1$. In matrix form, it is equal to

$$\begin{pmatrix} \lambda + a(\lambda) & -b(\lambda) \\ -a(\lambda) & \lambda + b(\lambda) \end{pmatrix} \tag{4.22}$$

in the subspace of $\{|_{++}\rangle, |_{--}\rangle\}$, and it is equal to

$$\begin{pmatrix} \lambda_+ + d(\lambda_+) + c(\lambda) & c(\lambda) \\ c(\lambda) & \lambda_- + d(\lambda_-) + c(\lambda) \end{pmatrix} \tag{4.23}$$

in the subspace of $\{|_{+-}\rangle, |_{-+}\rangle\}$, where $\lambda_\pm = \lambda \pm i2\bar{\Delta}/\hbar$, and

$$\begin{aligned} a(\lambda) &= \left(\frac{\bar{\Delta}}{\hbar}\right)^2 \int_{-\infty}^{\infty} d\omega\, S(\omega) \frac{2\lambda e^{-\beta\hbar\omega/2}}{\lambda^2 + (\omega + 2\Omega/\hbar)^2} \\ b(\lambda) &= \left(\frac{\bar{\Delta}}{\hbar}\right)^2 \int_{-\infty}^{\infty} d\omega\, S(\omega) \frac{2\lambda e^{\beta\hbar\omega/2}}{\lambda^2 + (\omega + 2\Omega/\hbar)^2} \\ c(\lambda) &= \left(\frac{\bar{\Delta}}{\hbar}\right)^2 \int_{-\infty}^{\infty} d\omega\, S(\omega) \frac{2\lambda e^{-\beta\hbar\omega/2}}{\lambda^2 + \omega^2} \\ d(\lambda) &= \left(\frac{\bar{\Delta}}{\hbar}\right)^2 \int_{-\infty}^{\infty} d\omega\, C(\omega) \frac{4\cosh(\beta\hbar\omega/2)}{\lambda + i\omega} \end{aligned} \tag{4.24}$$

With the above matrices inverted and substituted into (4.11), we have

$$\begin{aligned} &P(-, +, \lambda) \\ &\quad = \frac{1}{2\lambda} - \frac{1}{2} \frac{\lambda + \frac{1}{2}[d(\lambda_+) + d(\lambda_-)]}{[\lambda_+ + d(\lambda_+)][\lambda_- + d(\lambda_-)] + 2c(\lambda)[\lambda + \frac{1}{2}(d(\lambda_+) + d(\lambda_-))]} \end{aligned} \tag{4.25}$$

Using the definitions of $S(\omega)$ and $C(\omega)$, we can rewrite $c(\lambda)$ and $d(\lambda)$ explicitly as

$$\begin{aligned} c(\lambda) &= 2\left(\frac{\bar{\Delta}}{\hbar}\right)^2 \int_0^{\infty} dt\, e^{-\lambda t} \sinh(R(t)) \cos(I(t)) \\ d(\lambda) &= 4\left(\frac{\bar{\Delta}}{\hbar}\right)^2 \int_0^{\infty} dt\, e^{-\lambda t} [\cosh(R(t)) \cos(I(t)) - 1] \end{aligned} \tag{4.26}$$

where

$$\begin{aligned} R(t) &= 4 \int_0^{\infty} \frac{d\omega}{\omega^2} J(\omega) \coth\left(\frac{\beta\hbar\omega}{2}\right) \cos(\omega t) \\ I(t) &= 4 \int_0^{\infty} \frac{d\omega}{\omega^2} J(\omega) \sin(\omega t) \end{aligned} \tag{4.27}$$

The expression (4.25) is valid for any temperature. In the last subsection, we considered the case of low temperature, where we found an underdamped oscillation for $P(-, +, t)$, indicating a coherent motion of the particle. Here we explore the possibility of a transition to incoherent motion as the temperature is raised.

We first give an estimate of the poles in the second term of the expression (4.25). So long as λ and $\lambda_{\pm}$ are small compared with ω_d, the frequency scale of $R(t)$ and $I(t)$, we may replace them by zero in $c(\lambda)$ and $d(\lambda_{\pm})$. We then find that

$$\lambda = -[d(0)+c(0)] \pm \left\{ [c(0)]^2 - 4\left(\frac{\bar{\Delta}}{\hbar}\right)^2 \right\}^{1/2} \tag{4.28}$$

It is seen that the poles become real when $c(0)^2 \geqslant 4(\bar{\Delta}/\hbar)^2$, or when

$$\frac{\bar{\Delta}}{\hbar}\int_0^\infty dt \sinh(R(t))\cos(I(t)) \geqslant 1 \tag{4.29}$$

which can be satisfied only when the temperature is high enough. The transition temperature may be estimated by a steepest descent evaluation of the time integral,

$$\int_0^\infty dt \sinh(R(t))\cos(I(t))$$

$$\approx \frac{1}{8}\left(\frac{1}{\pi}\int_0^\infty d\omega \frac{J(\omega)}{\sinh(\beta\hbar\omega/2)}\right)^{-1/2} \exp\left(\int_0^\infty \frac{d\omega}{\omega^2}\frac{4J(\omega)}{\sinh(\beta\hbar\omega/2)}\right) \tag{4.30}$$

The left-hand side of the inequality (4.29) then becomes

$$\frac{1}{8}\frac{\Delta}{\hbar}\left(\frac{1}{\pi}\int_0^\infty d\omega \frac{J(\omega)}{\sinh(\beta\hbar\omega/2)}\right)^{-1/2}$$

$$\times \exp\left\{2\int_0^\infty \frac{d\omega}{\omega^2}J(\omega)\left[\frac{2}{\sinh(\beta\hbar\omega/2)} - \coth\left(\frac{\beta\hbar\omega}{2}\right)\right]\right\}$$

$$\approx \frac{1}{8}\frac{\Delta}{\hbar}\left(\frac{2k_B T}{\pi\hbar}\int_0^\infty \frac{d\omega}{\omega}J(\omega)\right)^{-1/2} \exp\left(\frac{4k_B T}{\hbar}\int_0^\infty \frac{d\omega}{\omega^3}J(\omega)\right) \tag{4.31}$$

where in the last step we have made a high-temperature expansion. This result can also be obtained from the condition that the lifetime of bonding or antibondinig state be shorter than $\hbar/2\bar{\Delta}$, a time scale associated with the level spacing $2\bar{\Delta}$.

Right at the transition temperature, the two poles merge together at

$$\lambda = -[d(0)+c(0)]$$
$$\approx -\frac{3}{4}\left(\frac{\pi}{2}\right)^{1/2}\frac{\Delta}{\hbar}\frac{\Delta}{k_B T}\left(\frac{T}{T_0}\right)^{1/2} e^{-T_0/T} \tag{4.32}$$

where

$$T_0 = \frac{\hbar}{k_B}\int_0^\infty \frac{d\omega}{\omega} J(\omega) \tag{4.33}$$

and we have used again the steepest descent method and high-temperature expansion. It is seen that the pole is of order $\Delta/\hbar$ or smaller, which is much smaller than ω_d, justifying the replacements of λ and $\lambda_\pm$ by zero in $c(\lambda)$ and $d(\lambda_\pm)$, respectively.

When the inequality (4.29) is well satisfied, we can write (4.25) as

$$P(-,+,\lambda) = \frac{1}{2\lambda} - \frac{1}{2}\frac{\lambda + d(0)}{[\lambda + d(0)][\lambda + d(0) + 2c(0)]}$$
$$= \frac{1}{2\lambda} - \frac{1}{2(\lambda + \Gamma)} \tag{4.34}$$

and therefore

$$P(-,+,t) = \tfrac{1}{2} - \tfrac{1}{2}e^{-\Gamma t} \tag{4.35}$$

where

$$\Gamma = d(0) + 2c(0)$$
$$= 4\left(\frac{\bar{\Delta}}{\hbar}\right)^2 \int_0^\infty dt\,[\exp(R(t))\cos(I(t)) - 1]$$
$$\approx \left(\frac{\pi}{2}\right)^{1/2}\frac{\Delta}{\hbar}\frac{\Delta}{k_B T}\left(\frac{T}{T_0}\right)^{1/2} e^{-T_0/T} \tag{4.36}$$

The initial transition rate is $\Gamma/2$ according to (4.35), and its value agrees with the result obtained from the Fermi golden rule by Holstein.[1]

4. STRONG SITE ENERGY DISORDER AND MARKOVIAN MOTION

In this section we consider a general multisite case with site energy fluctuations $\delta\varepsilon$ large compared with the renormalized hopping energy $\bar{\Delta}$. For the two-site case studied in the last section, we found an exponential

time dependence in $P(-, +, t)$, suggesting a Markovian description of the particle motion. This motivates us to derive a master equation for the particle motion for the general multisite case here.

We consider first the self-energy operator given in (3.12). We will restrict our attention to low temperatures ($k_B T \ll \hbar\omega_d$) to simplify calculations. According to the arguments given at the end of Section 3, we may make the approximation

$$
\begin{aligned}
&F(\tau, z, z_1, z_1', z') - 1 \\
&\quad \approx -\sum_{\mathbf{k}} \frac{J(\mathbf{k})}{\sinh(\beta\hbar\omega_{\mathbf{k}}/2)} \left\{ \cos\omega_{\mathbf{k}} \left(\tau + \frac{i\hbar\beta}{2}\right) (e^{i\mathbf{k}\mathbf{x}} - e^{i\mathbf{k}\mathbf{x}_1})(e^{-i\mathbf{k}\mathbf{x}_1'} - e^{-i\mathbf{k}\mathbf{x}'}) \right. \\
&\qquad + \cos\omega_{\mathbf{k}} \left(\tau - \frac{i\hbar\beta}{2}\right) (e^{i\mathbf{k}\mathbf{y}} - e^{i\mathbf{k}\mathbf{y}_1})(e^{-i\mathbf{k}\mathbf{y}_1'} - e^{-i\mathbf{k}\mathbf{y}'}) \\
&\qquad - \cos\omega_{\mathbf{k}} \left(\tau - \frac{i\hbar\beta}{2}\right) (e^{i\mathbf{k}\mathbf{x}} - e^{i\mathbf{k}\mathbf{x}_1})(e^{-i\mathbf{k}\mathbf{y}_1'} - e^{-i\mathbf{k}\mathbf{y}'}) \\
&\qquad \left. - \cos\omega_{\mathbf{k}} \left(\tau + \frac{i\hbar\beta}{2}\right) (e^{i\mathbf{k}\mathbf{y}} - e^{i\mathbf{k}\mathbf{y}_1})(e^{-i\mathbf{k}\mathbf{x}_1'} - e^{-i\mathbf{k}\mathbf{x}'}) \right\} \qquad (5.1)
\end{aligned}
$$

Substituting this into (3.16), we have (in operator notation)

$$
\begin{aligned}
\Sigma_1(\tau) = \sum_{\mathbf{k}} \frac{J(\mathbf{k})}{\sinh(\beta\hbar\omega_{\mathbf{k}}/2)} &\left\{ \cos\omega_{\mathbf{k}} \left(\tau + \frac{i\hbar\beta}{2}\right) [X, \bar{\mathscr{L}}_P]\, e^{\bar{\mathscr{L}}_P \tau} [\bar{\mathscr{L}}_P, X^*] \right. \\
&+ \cos\omega_{\mathbf{k}} \left(\tau - \frac{i\hbar\beta}{2}\right) [Y, \bar{\mathscr{L}}_P]\, e^{\bar{\mathscr{L}}_P \tau} [\bar{\mathscr{L}}_P, Y^*] \\
&- \cos\omega_{\mathbf{k}} \left(\tau - \frac{i\hbar\beta}{2}\right) [X, \bar{\mathscr{L}}_P]\, e^{\bar{\mathscr{L}}_P \tau} [\bar{\mathscr{L}}_P, Y^*] \\
&\left. - \cos\omega_{\mathbf{k}} \left(\tau + \frac{i\hbar\beta}{2}\right) [Y, \bar{\mathscr{L}}_P]\, e^{\bar{\mathscr{L}}_P \tau} [\bar{\mathscr{L}}_P, X^*] \right\} \qquad (5.2)
\end{aligned}
$$

where $[\cdot, \cdot]$ denotes a commutator. and X and Y are operators corresponding to $e^{i\mathbf{k}\mathbf{x}}$ and $e^{i\mathbf{k}\mathbf{y}}$, respectively.

Suppose $|m\rangle$ is an eigenstate of $\bar{H}_P$ with energy ε_m, then an eigenstate of $\bar{\mathscr{L}}_P$ may be written as $|m, n\rangle$ with eigenvalue $(\varepsilon_m - \varepsilon_n)/(i\hbar)$. The "diagonal" states $\{|n, n\rangle\}$ are special: they share the same eigenvalue 0 of $\bar{\mathscr{L}}_P$, and are separated from others by a frequency scale of $\delta\varepsilon/\hbar$. Under the condition $\delta\varepsilon \gg \bar{\Delta}$, they are effectively not mixed with the others by $\Sigma_1(\lambda)$. The inverse in (3.15) may therefore be carried out within the subspace of the diagonal states.

The matrix element of $\Sigma_1(\tau)$ between two diagonal states is given by

$$\begin{aligned}
&\langle n, n|\ \Sigma_1(\tau)\ |n', n'\rangle \\
&\quad = \sum_{\mathbf{k}} \frac{-J(\mathbf{k})}{\hbar^2 \sinh(\beta\hbar\omega_{\mathbf{k}}/2)} \\
&\qquad \times \left\{ \cos\omega_{\mathbf{k}}\left(\tau + \frac{i\hbar\beta}{2}\right) \delta_{nn'} \sum_{n_1} |\langle n|\ X\ |n_1\rangle|^2\, (\varepsilon_{n_1} - \varepsilon_n)^2\, e^{(\tau/i\hbar)(\varepsilon_{n_1} - \varepsilon_n)} \right. \\
&\qquad + \cos\omega_{\mathbf{k}}\left(\tau - \frac{i\hbar\beta}{2}\right) \delta_{nn'} \sum_{n_2} |\langle n_2|\ Y\ |n\rangle|^2\, (\varepsilon_n - \varepsilon_{n_2})^2\, e^{(\tau/i\hbar)(\varepsilon_n - \varepsilon_{n_2})} \\
&\qquad - \cos\omega_{\mathbf{k}}\left(\tau - \frac{i\hbar\beta}{2}\right) \langle n|\ X\ |n'\rangle\langle n'|\ Y^*\ |n\rangle (\varepsilon_{n'} - \varepsilon_n)^2\, e^{(\tau/i\hbar)(\varepsilon_{n'} - \varepsilon_n)} \\
&\qquad \left. - \cos\omega_{\mathbf{k}}\left(\tau + \frac{i\hbar\beta}{2}\right) \langle n'|\ Y\ |n\rangle\langle n|\ X^*\ |n'\rangle (\varepsilon_n - \varepsilon_{n'})^2\, e^{(\tau/i\hbar)(\varepsilon_n - \varepsilon_{n'})} \right\}
\end{aligned} \tag{5.3}$$

where, with the definition $\langle \mathbf{x}\,|\,n\rangle \equiv \psi_n(\mathbf{x})$, we have

$$\begin{aligned}
\langle n|\ X\ |n'\rangle &= \sum_{\mathbf{x}} \psi_n^*(\mathbf{x})\, e^{i\mathbf{k}\mathbf{x}} \psi_{n'}(\mathbf{x}) \\
\langle n|\ Y\ |n'\rangle &= \sum_{\mathbf{y}} \psi_n^*(\mathbf{y})\, e^{i\mathbf{k}\mathbf{y}} \psi_{n'}(\mathbf{y})
\end{aligned} \tag{5.4}$$

We then Laplace transform (5.3) and set $\lambda = 0_+$, yielding

$$\begin{aligned}
&\langle n, n|\ \Sigma_1(\lambda = 0_+)\ |n', n'\rangle \\
&\quad = \sum_{\mathbf{k}} \frac{\pi J(\mathbf{k})\omega_{\mathbf{k}}^2}{\sinh(\beta\hbar\omega_{\mathbf{k}}/2)} \left\{ |\langle n|\ X\ |n'\rangle|^2 e^{\beta(\varepsilon_{n'} - \varepsilon_n)/2} \right. \\
&\qquad \times \left[\delta\left(\omega_{\mathbf{k}} + \frac{\varepsilon_n - \varepsilon_{n'}}{\hbar}\right) + \delta\left(\omega_{\mathbf{k}} - \frac{\varepsilon_n - \varepsilon_{n'}}{\hbar}\right) \right] \\
&\qquad - \delta_{nn'} \sum_{n_1} |\langle n|\ X\ |n_1\rangle|^2\, e^{\beta(\varepsilon_n - \varepsilon_{n_1})/2} \\
&\qquad \left. \times \left[\delta\left(\omega_{\mathbf{k}} + \frac{\varepsilon_{n_1} - \varepsilon_n}{\hbar}\right) + \delta\left(\omega_{\mathbf{k}} - \frac{\varepsilon_{n_1} - \varepsilon_n}{\hbar}\right) \right] \right\}
\end{aligned} \tag{5.5}$$

The density matrix then satisfies the master equation

$$\frac{\partial}{\partial t}\rho(n, n, t) = \sum_{n'} W_{nn'} [e^{\beta(\varepsilon_{n'} - \varepsilon_n)/2} \rho(n', n', t) - e^{\beta(\varepsilon_n - \varepsilon_{n'})/2} \rho(n, n, t)] \tag{5.6}$$

where $\rho(n, n, t) = \langle n, n | \rho(t) \rangle$, and

$$W_{nn'} = \sum_{\mathbf{k}} \frac{\pi J(\mathbf{k}) \omega_{\mathbf{k}}^2}{\sinh(\beta \hbar \omega_{\mathbf{k}}/2)} |\langle n| e^{i\mathbf{k}\mathbf{x}} |n'\rangle|^2 \delta\left(\omega_{\mathbf{k}} - \frac{|\varepsilon_n - \varepsilon_{n'}|}{\hbar}\right) \tag{5.7}$$

The master equation involves only the probabilities on the eigenstates of $\bar{H}_P$, indicating the incoherence of the particle motion.

We have the following physical picture. The major effect of the phonon field is to renormalize the hopping energy. As a first approximation, the scattering of the particle by the phonons may be ignored at temperatures low compared with the Debye temperature. The eigenstates of the particle are extremely localized at various sites, because we are in the limit of $\bar{\Delta} \ll \delta\varepsilon$. In fact, the wave function falls off exponentially as $(\bar{\Delta}/\delta\varepsilon)^l$, where l is the distance (in units of lattice constant) from the localization center. When we take the scattering effect into account, the particle gets knocked from one localized state to another in an incoherent way as described by the master equation (5.6).

At temperatures even lower than $\delta\varepsilon$, the Boltzmann factors will limit the hopping rates considerably. The Mott variable range hopping[32] scenario then emergies as a result of the competition between the following two factors: (1) the overlapping integral, which falls off exponentially with the distance between the centers of the initial and final states, and (2) the Boltzmann factor, which favors longer-range hopping because small energy differences is more likely to be found between states of large seperation.

In the following we will limit our attention to the intermediate case, $\delta\varepsilon \ll k_B T \ll \hbar\omega_d$. The Boltzmann factors are unity, and the dominant hopping steps are the nearest ones. The overlapping factor $|\langle n| e^{i\mathbf{k}\mathbf{x}} |n'\rangle|^2$ can be calculated perturbatively as

$$\left| \frac{\bar{\Delta}}{\varepsilon_n - \varepsilon_{n'}} (e^{i\mathbf{k}\boldsymbol{l}} - 1) \right|^2$$

where $\boldsymbol{l}$ is the vector between the sites at which the two states are localized. The master equation (5.6) describes a random walk in a random environment.[33] Various techniques have been developed for the evaluation of the diffusion constant. If the hopping probabilities do not vary too much, we can ignore the percolation effect.[34] The diffusion constant may be estimated by

$$D = Wl^2 \tag{5.8}$$

where l is the lattice constant, and W the typical value of the quantity in

(5.7) for a pair of states localized at nearest neighboring sites. We then have

$$
\begin{aligned}
&W_{nn'} \\
&= \frac{\pi}{\hbar^2}\left(\frac{\bar{\Delta}}{\varepsilon_n - \varepsilon_{n'}}\right)^2 \frac{1}{N}\sum_{\mathbf{k}} \frac{|g(\mathbf{k})|^2\,|e^{i\mathbf{k}\boldsymbol{l}}-1|^2}{\sinh(\beta\hbar\omega_{\mathbf{k}}/2)}\,\delta\left(\omega_{\mathbf{k}} - \frac{|\varepsilon_n - \varepsilon_{n'}|}{\hbar}\right) \\
&= \frac{\pi}{\hbar^2}\left(\frac{\bar{\Delta}}{\varepsilon_n - \varepsilon_{n'}}\right)^2 \frac{1}{\sinh(\beta\,|\varepsilon_n - \varepsilon_{n'}|/2)}\,\frac{1}{N}\sum_{\mathbf{k}} |g(\mathbf{k})|^2 |e^{i\mathbf{k}\boldsymbol{l}}-1|^2\,\delta\left(\omega_{\mathbf{k}} - \frac{|\varepsilon_n - \varepsilon_{n'}|}{\hbar}\right) \\
&\approx \frac{2\pi}{\hbar^2}\left(\frac{\bar{\Delta}}{\varepsilon_n - \varepsilon_{n'}}\right)^2 \frac{k_{\mathrm{B}}T}{|\varepsilon_n - \varepsilon_{n'}|}\,\frac{1}{N}\sum_{\mathbf{k}} |g(\mathbf{k})|^2\,|e^{i\mathbf{k}\boldsymbol{l}}-1|^2\,\delta\left(\omega_{\mathbf{k}} - \frac{|\varepsilon_n - \varepsilon_{n'}|}{\hbar}\right) \qquad (5.9)
\end{aligned}
$$

The diffusion constant thus depends quadratically on the renormalized tunneling energy splitting $\bar{\Delta}$, linearly on temperature, and quadratically on the particle–phonon coupling energy $g(\mathbf{k})$. The dependence on the strength of disorder $\delta\varepsilon$ differs for different types of couplings. For short-ranged interaction we have $|g(\mathbf{k})|^2 \sim k^2/\omega_{\mathbf{k}}$ [see the remarks on (2.3)]; therefore $D \sim (\delta\varepsilon)^2$ for 3D phonons, and $D \sim (\delta\varepsilon)$ for 2D phonons. The diffusion constant increases with disorder! A more surprising thing occurs for a piezoelectric coupling, for which $|g(\mathbf{k})|^2 \sim 1/\omega_{\mathbf{k}}$; therefore $W_{nn'}$ is independent of $\varepsilon_n - \varepsilon_{n'}$ for 3D phonons. The diffusion constant is independent of disorder! These results may be understood by noticing that the phonon spectral density increases with frequency, and that the frequency sampled is equal to $\delta\varepsilon$.

6. LATTICE WITH CONSTANT SITE ENERGIES

6.1. General Consideration

In the case of translational invariance, it will be convenient to work in the momentum space. Introducing the momentum eigenstates,

$$
|\mathbf{p}, \mathbf{q}\rangle = \frac{1}{N_s}\sum_{x,y} e^{-i\mathbf{p}\mathbf{x}} e^{-i\mathbf{q}\mathbf{y}}\,|\mathbf{x}, \mathbf{y}\rangle \qquad (6.1)
$$

where N_s is the total number of sites, then the probability (3.15) may be written as

$$
\begin{aligned}
&P(\mathbf{x}_f, \mathbf{x}_0, \lambda) \\
&\quad = \frac{1}{N_s^2}\sum_{\mathbf{p},\mathbf{q},\mathbf{p}',\mathbf{q}'} e^{i[(\mathbf{p}'+\mathbf{q}')\mathbf{x}_0 - (\mathbf{p}+\mathbf{q})\mathbf{x}_f]}\langle \mathbf{p}, \mathbf{q}|\,\frac{1}{\lambda - \mathscr{D}_P - \Sigma_1(\lambda)}\,|\mathbf{p}', \mathbf{q}'\rangle \qquad (6.2)
\end{aligned}
$$

We now make a variable change $(\mathbf{p}, \mathbf{q}) \to (\mathbf{u}, \mathbf{v})$, where $\mathbf{u} = \mathbf{p} + \mathbf{q}$ and $\mathbf{v} = (\mathbf{p} - \mathbf{q})/2$; then both $\bar{\mathscr{L}}_P$ and $\Sigma_1(\lambda)$ are diagonal in $\mathbf{u}$ (see below), and we may write

$$P(\mathbf{x}_f, \mathbf{x}_0, \lambda) = \frac{1}{N_s} \sum_{\mathbf{u}} P(\mathbf{u}, \lambda) e^{i\mathbf{u}(\mathbf{x}_0 - \mathbf{x}_f)}$$
$$P(\mathbf{u}, \lambda) = \frac{1}{N_s} \sum_{\mathbf{v}, \mathbf{v}'} \langle \mathbf{v} | \frac{1}{\lambda - \bar{\mathscr{L}}_P(\mathbf{u}) - \Sigma_1(\mathbf{u}, \lambda)} | \mathbf{v}' \rangle \tag{6.3}$$

We will be interested in the hydrodynamic modes corresponding to poles of $P(\mathbf{u}, \lambda)$ at small λ and small $\mathbf{u}$. As we will show later, there is a pole $\lambda(\mathbf{u})$ that approaches zero as

$$\lambda(\mathbf{u}) = -D\mathbf{u}^2 \tag{6.4}$$

for small $\mathbf{u}$. The coefficient D is the diffusion constant.

We first derive the operator $\Sigma_1(\mathbf{u}, \lambda)$. From (3.20) and the definition (6.1), we have

$$\begin{aligned}\langle \mathbf{p}, \mathbf{q} | \Sigma_1(\lambda) = \left(\frac{\bar{\Delta}}{\hbar}\right)^2 \sum_{l,l'} \sum_{\omega, \mathbf{k}} \tilde{F}_{ll'}(\omega, \mathbf{k}) \Bigg\{ & \frac{-e^{\beta\hbar\omega/2} e^{-i(\mathbf{p} - \mathbf{k}/2)(l + l')}}{\lambda + i\omega + i(\varepsilon_{\mathbf{p}-\mathbf{k}} - \varepsilon_{\mathbf{q}})/\hbar} \langle \mathbf{p}, \mathbf{q} | \\ & - \frac{e^{-\beta\hbar\omega/2} e^{i(\mathbf{q} - \mathbf{k}/2)(l + l')}}{\lambda + i\omega + i(\varepsilon_{\mathbf{p}} - \varepsilon_{\mathbf{q}-\mathbf{k}})/\hbar} \langle \mathbf{p}, \mathbf{q} | \\ & + \frac{e^{-\beta\hbar\omega/2} e^{-i(\mathbf{p} - \mathbf{k}/2)l + i(\mathbf{q} + \mathbf{k}/2)l'}}{\lambda + i\omega + i(\varepsilon_{\mathbf{p}-\mathbf{k}} - \varepsilon_{\mathbf{q}})/\hbar} \langle \mathbf{p} - \mathbf{k}, \mathbf{q} + \mathbf{k} | \\ & + \frac{e^{\beta\hbar\omega/2} e^{-i(\mathbf{p} + \mathbf{k}/2)l' + i(\mathbf{q} - \mathbf{k}/2)l}}{\lambda + i\omega + i(\varepsilon_{\mathbf{p}} - \varepsilon_{\mathbf{q}-\mathbf{k}})/\hbar} \langle \mathbf{p} + \mathbf{k}, \mathbf{q} - \mathbf{k} | \Bigg\}\end{aligned} \tag{6.5}$$

where $\varepsilon_{\mathbf{p}}$ is the band energy function of $\bar{\mathscr{L}}_h$. It is seen that $\mathbf{u} = \mathbf{p} + \mathbf{q}$ is conserved under $\Sigma_1(\lambda)$. Within the sector of a given $\mathbf{u}$, we write $\langle \mathbf{p}, \mathbf{q} | = \langle \mathbf{v} |$, and define $\bar{\mathscr{L}}_P(\mathbf{u})$ by $\langle \mathbf{v} | \bar{\mathscr{L}}_P(\mathbf{u}) = \langle \mathbf{p}, \mathbf{q} | \bar{\mathscr{L}}_P$; therefore

$$\langle \mathbf{v} | \bar{\mathscr{L}}_P(\mathbf{u}) = \langle \mathbf{v} | \frac{1}{i\hbar} (\varepsilon_{\mathbf{v} + \mathbf{u}/2} - \varepsilon_{\mathbf{v} - \mathbf{u}/2}) \tag{6.6}$$

where we have used the fact that $\varepsilon_{\mathbf{p}} = \varepsilon_{-\mathbf{p}}$. Similarly, we define $\Sigma_1(\mathbf{u}, \lambda)$ by $\langle \mathbf{v} | \Sigma_1(\mathbf{u}, \lambda) = \langle \mathbf{p}, \mathbf{q} | \Sigma_1(\lambda)$. We therefore have

$$\begin{aligned}\langle \mathbf{v} | \Sigma_1(\mathbf{u}, \lambda) = \left(\frac{\bar{\Delta}}{\hbar}\right)^2 & \sum_{l,l'} \sum_{\omega, \mathbf{k}} \tilde{F}_{ll'}(\omega, \mathbf{k}) e^{-i(\mathbf{v} + \mathbf{k}/2)(l + l')} \\ & \times [-f_1 e^{-\beta\hbar\omega/2} \langle \mathbf{v} | + f_2 e^{\beta\hbar\omega/2} \langle \mathbf{v} + \mathbf{k} |]\end{aligned} \tag{6.7}$$

where the f's are defined as

$$\begin{aligned} f_1 = & \frac{e^{-i\mathbf{u}(l+l')/2}}{\lambda - i\omega + i(\varepsilon_{\mathbf{v}+\mathbf{k}+\mathbf{u}/2} - \varepsilon_{\mathbf{v}-\mathbf{u}/2})/\hbar} \\ & + \frac{e^{i\mathbf{u}(l+l')/2}}{\lambda + i\omega - i(\varepsilon_{\mathbf{v}+\mathbf{k}-\mathbf{u}/2} - \varepsilon_{\mathbf{v}+\mathbf{u}/2})/\hbar} \\ f_2 = & \frac{e^{-i\mathbf{u}(l-l')/2}}{\lambda - i\omega + i(\varepsilon_{\mathbf{v}+\mathbf{k}+\mathbf{u}/2} - \varepsilon_{\mathbf{v}-\mathbf{u}/2})/\hbar} \\ & + \frac{e^{i\mathbf{u}(l-l')/2}}{\lambda + i\omega - i(\varepsilon_{\mathbf{v}+\mathbf{k}-\mathbf{u}/2} - \varepsilon_{\mathbf{v}+\mathbf{u}/2})/\hbar} \end{aligned} \tag{6.8}$$

and we have used the fact that $\tilde{F}_{ll'}(\omega, \mathbf{k})$ is invariant under the change of sign in $\mathbf{k}$ and ω. In the limit of $\mathbf{u} = 0$ and $\lambda = 0$, we have

$$\begin{aligned} \langle \mathbf{v}| \Sigma_1(\mathbf{0}, 0) = 2\pi \left(\frac{\Delta}{\hbar}\right)^2 \sum_{l,l'} \sum_{\omega,\mathbf{k}} \tilde{F}_{ll'}(\omega, \mathbf{k}) e^{-i(\mathbf{v}+\mathbf{k}/2)(l+l')} \delta(\omega - (\varepsilon_{\mathbf{v}+\mathbf{k}} - \varepsilon_{\mathbf{v}})/\hbar) \\ \times [-e^{-\beta\hbar\omega/2} \langle \mathbf{v}| + e^{\beta\hbar\omega/2} \langle \mathbf{v}+\mathbf{k}|] \end{aligned} \tag{6.9}$$

6.2. Low Temperature

According to (6.3), the poles of $P(\mathbf{u}, \lambda)$ are given by the eigenmodes of the equation

$$\lambda |\psi\rangle = \bar{\mathscr{L}}_P(\mathbf{u}) |\psi\rangle + \Sigma_1(\mathbf{u}, \lambda) |\psi\rangle \tag{6.10}$$

We are interested in solutions with small λ and $\mathbf{u}$. We can set $\Sigma_1(\mathbf{u}, \lambda) = \Sigma_1(\mathbf{0}, 0)$, if its λ derivative is small compared with unity, and if its $\mathbf{u}$ derivative is small compared with the typical band velocity [the $\mathbf{u}$ derivative of $\bar{\mathscr{L}}_P(\mathbf{u})$, to be precise]. When the temperature is not high compared with the Debye temperature, these conditions are satisfied. Equation (6.10) can then be written in the form of a Boltzmann equation

$$\lambda\psi(\mathbf{v}) = \mathbf{u} \frac{\partial\varepsilon_{\mathbf{v}}}{i\hbar} \psi(\mathbf{v}) + \sum_{\mathbf{v}'} W_{\mathbf{v}\mathbf{v}'} [e^{\beta(\varepsilon_{\mathbf{v}'} - \varepsilon_{\mathbf{v}})/2} \psi(\mathbf{v}') - e^{\beta(\varepsilon_{\mathbf{v}} - \varepsilon_{\mathbf{v}'})/2} \psi(\mathbf{v})] \tag{6.11}$$

where $\partial\varepsilon_{\mathbf{v}}$ stands for derivative of $\varepsilon_{\mathbf{v}}$ with respect to $\mathbf{v}$, and $W_{\mathbf{v}'\mathbf{v}} = W_{\mathbf{v}'\mathbf{v}}$ is given by

$$W_{\mathbf{v}\mathbf{v}'} = 2\pi \left(\frac{\Delta}{\hbar}\right)^2 \sum_{l,l'} \sum_{\omega} \tilde{F}_{ll'}(\omega, \mathbf{v}' - \mathbf{v}) e^{-i(\mathbf{v}'+\mathbf{v})(l+l')/2} \delta(\omega - (\varepsilon_{\mathbf{v}'} - \varepsilon_{\mathbf{v}})/\hbar) \tag{6.12}$$

The left-hand side of (6.11) corresponds to the time derivative term. The first term on the right-hand side of the equation corresponds to a drifting term, while the second term corresponds to the collision term. The rate of "scattering in" is $W_{\mathbf{v}\mathbf{v}'}\exp[\beta(\varepsilon_{\mathbf{v}'}-\varepsilon_{\mathbf{v}})/2]$ and the rate of "scattering out" is $W_{\mathbf{v}\mathbf{v}'}\exp[\beta(\varepsilon_{\mathbf{v}}-\varepsilon_{\mathbf{v}'})/2$. The two rates have the ratio of $\exp[\beta(\varepsilon_{\mathbf{v}'}-\varepsilon_{\mathbf{v}})]$, the Boltzmann factor. This immediately gives to the equilibrium distribution

$$\psi_0(\mathbf{v}) = e^{-\beta\varepsilon_{\mathbf{v}}} \tag{6.13}$$

in the absence of the drifting term ($\mathbf{u}=0$). When $\mathbf{u}\neq 0$, the Boltzmann distribution is no longer a zero mode of (6.11). As $\mathbf{u}$ deviates from zero, the pole of the original zero mode gets shifted to $\lambda(\mathbf{u})<0$. In Appendix E, we show that $\lambda(\mathbf{u})$ depends quadratically on $\mathbf{u}$ as in (6.4). We find that the diffusion constant is given by

$$D = \frac{2}{\hbar^2 d}\frac{\{\sum_{\mathbf{v}}(\partial\varepsilon_{\mathbf{v}})^2 e^{-\beta\varepsilon_{\mathbf{v}}}\}^2}{\sum_{\mathbf{v}} e^{-\beta\varepsilon_{\mathbf{v}}}\sum_{\mathbf{v}\mathbf{v}'} W_{\mathbf{v}\mathbf{v}'} e^{-\beta(\varepsilon_{\mathbf{v}}+\varepsilon_{\mathbf{v}'})/2}(\partial\varepsilon_{\mathbf{v}}-\partial\varepsilon_{\mathbf{v}'})^2} \tag{6.14}$$

where d is the dimension of the tight-binding lattice. When the temperature is much higher than the bandwidth $\bar{\Delta}$, we may replace the Boltzmann factors by unity. Thus,

$$D = \frac{2}{\hbar^2 d}\frac{\langle(\partial\varepsilon_{\mathbf{v}})^2\rangle^2}{(1/N_s)\sum_{\mathbf{v}\mathbf{v}'} W_{\mathbf{v}\mathbf{v}'}(\partial\varepsilon_{\mathbf{v}}-\partial\varepsilon_{\mathbf{v}'})^2} \tag{6.15}$$

where the angular brackets denote average over the energy band.

The quantity $W_{\mathbf{v}\mathbf{v}'}$ can be written more explicitly as

$$W_{\mathbf{v}\mathbf{v}'} = \left(\frac{\bar{\Delta}}{\hbar}\right)^2 \frac{1}{N_s}\sum_{\mathbf{x}}\int_{-\infty}^{\infty} d\tau\, e^{i(\mathbf{v}-\mathbf{v}')\mathbf{x}} e^{i(\varepsilon_{\mathbf{v}'}-\varepsilon_{\mathbf{v}})\tau/\hbar} \times \sum_{l,l'} F_{ll'}(\tau,\mathbf{x}) e^{-i(\mathbf{v}'+\mathbf{v})(l+l')/2} \tag{6.16}$$

where $F_{ll'}(\tau,\mathbf{x})$ was given in (3.9). For temperatures lower than the Debye temperature, we may expand the exponential in the expression (3.19) for $F_{ll'}(\tau,\mathbf{x})$. The first-order term is zero, due to energy and momentum conservation. A somewhat tedious but straightforward evaluation of the second-order term gives $D\sim 1/T^{2s-1}$, where s is the power of ω with which the quantity $J(\omega)$ in (4.4) goes to zero. For short-ranged interaction, $s=5$, so $D\sim 1/T^9$, in agreement with Gogolin.[35] For a piezoelectric interaction, $s=3$, so $D\sim 1/T^5$.

6.3. High Temperature

What will happen when the temperature gets high? Let us look back to Eq. (6.10). The temperature dependences of $\bar{\mathscr{P}}_P(\mathbf{u})$ and $\Sigma_1(\mathbf{u}, \lambda)$ are quite different. The Frank–Condon factor decreases exponentially with temperature, so do $\bar{\Delta}$ and $\bar{\mathscr{P}}_P(\mathbf{u})$. However, the Frank–Condon factor in $\Sigma_1(\mathbf{u}, \lambda)$ in (6.7) will be largely canceled by $\tilde{F}_{ll'}(\omega, \mathbf{k})$, which grows exponentially with temperature for $l' = -l$. Therefore, we can no longer ignore the $\mathbf{u}$ dependence in $\Sigma_1(\mathbf{u}, \lambda)$. As the temperature is raised to a certain point, the linear $\mathbf{u}$ correction to $\Sigma_1(\mathbf{0}, 0)$ will dominate the $\bar{\mathscr{P}}_P(\mathbf{u})$ term, marking the transition out of the coherent regime.

At very high temperatures we can ignore all the exponentially small terms; then (6.10) becomes

$$\lambda\psi(\mathbf{v}) = \left(\frac{\bar{\Delta}}{\hbar}\right)^2 \sum_{l} \sum_{\omega,\mathbf{k}} \tilde{F}(\omega, \mathbf{k}) \frac{2\lambda}{\lambda^2 + \omega^2} \times [-e^{-\beta\hbar\omega/2}\psi(\mathbf{v}) + \cos(\mathbf{u}\boldsymbol{l}) e^{\beta\hbar\omega/2}\psi(\mathbf{v} + \mathbf{k})] \tag{6.17}$$

where $\tilde{F} = \tilde{F}_{ll'}$ with $l' = -l$, and is actually independent of l dues to the cubic symmetry of the system. This equation has the solution of $\psi(\mathbf{v}) =$ const, with

$$\lambda = z\left(\frac{\bar{\Delta}}{\hbar}\right)^2 \sum_{\omega,\mathbf{k}} \tilde{F}(\omega, \mathbf{k}) \frac{2\lambda}{\lambda^2 + \omega^2} [-e^{-\beta\hbar\omega/2} + \langle \cos(\mathbf{u}\boldsymbol{l}) \rangle e^{\beta\hbar\omega/2}] \tag{6.18}$$

where z is the coordination number of the lattice, and the angular brackets denote an average over l. Finally, we let $\lambda \to 0_+$ on the right-hand side of the above expression, and substitute (3.19) into it; we obtain

$$\lambda = z\left(\frac{\bar{\Delta}}{\hbar}\right)^2 \int_0^\infty d\tau\, F(\tau, \mathbf{0})[-1 + \langle \cos(\mathbf{u}\boldsymbol{l}) \rangle] \tag{6.19}$$

where z is the coordination number of the tight-binding lattice, and $F(\tau, \mathbf{x})$ is just $F_{ll'}(\tau, \mathbf{x})$ in (3.19) with $l' = -l$. The diffusion constant is then given by

$$D = l^2\left(\frac{\bar{\Delta}}{\hbar}\right)^2 \int_0^\infty d\tau \left\{\exp\left[4\sum_{\mathbf{k}} \frac{J(\mathbf{k}) \sin^2(\mathbf{k}\boldsymbol{l}_1/2)}{\sinh(\beta\hbar\omega_{\mathbf{k}}/2)} \cos(\omega_{\mathbf{k}}\tau)\right] - 1\right\} \tag{6.20}$$

The physics behind these arguments can be more clearly seen by examining the self-energy operator (3.20) in the position representation. At high temperatures, the terms with $l' = -l$ dominate, so that

$$\langle z|\,\Sigma_1(\lambda)\,|z'\rangle$$
$$=\left(\frac{\bar{\Delta}}{\hbar}\right)^2\sum_l\sum_{\omega,\mathbf{k}}\tilde{F}(\omega,\mathbf{k})\left\{-\frac{e^{\beta\hbar\omega/2}}{\lambda+i\omega}\delta_{\mathbf{x},\mathbf{x}'}\delta_{\mathbf{y},\mathbf{y}'}-\frac{e^{-\beta\hbar\omega/2}}{\lambda+i\omega}\delta_{\mathbf{x},\mathbf{x}'}\delta_{\mathbf{y},\mathbf{y}'}\right.$$
$$\left.+\frac{e^{-\beta\hbar\omega/2}e^{i\mathbf{k}(\mathbf{x}-\mathbf{y})}}{\lambda+i\omega}\delta_{\mathbf{x},\mathbf{x}'+l}\delta_{\mathbf{y},\mathbf{y}'+l}+\frac{e^{\beta\hbar\omega/2}e^{i\mathbf{k}(\mathbf{y}-\mathbf{x})}}{\lambda+i\omega}\delta_{\mathbf{x},\mathbf{x}'-l}\delta_{\mathbf{y},\mathbf{y}'-l}\right\} \quad (6.21)$$

It is noted that only the diagonal transitions take place, i.e., the changes in $\mathbf{x}$ and $\mathbf{y}$ are the same. This is in fact a general feature of high-temperature transport theory known as the quasiclassical limit.[36]

7. CONCLUSION AND DISCUSSION

In summary, we have studied the question of quantum coherence for a narrow-band particle interacting with phonons and static disorders. We have focused our attention on the transition probability $P(\mathbf{x}_f, \mathbf{x}_0, t)$ for the particle to move from position $\mathbf{x}_0$ to $\mathbf{x}_f$ in time t. The calculation of $P(\mathbf{x}_f, \mathbf{x}_0, t)$ and its properties has been reduced to an eigenvalue problem in the phase space of the particle, i.e., the space coordinated by the two position variables appearing in the particle density matrix. The reduction is essentially a renormalization of the tunneling amplitude by the Frank–Cordon factor, followed by an expansion in the small parameter $\bar{\Delta}/(\hbar\omega_d)$, i.e., the ratio of the renormalized bandwidth to the Debye energy of the substrate lattice. The eigenvalue problem is simple yet general enough to serve as a convenient basis for further explorations of the various regimes and their interconnections: low temperature versus high temperature, weak versus strong static disorder, two wells versus an array of wells.

We have studied the two-well problem in great detail. We have obtained complete solutions for $P(\mathbf{x}_f, \mathbf{x}_0, t)$ in the case of low temperature but arbitrary bias, and the case of zero bias but arbitrary temperatures. We have demonstrated how the particle motion becomes incoherent as the temperature or bias is increased. In the extreme cases, our results agree with earlier ones in the literature.[1,19] These results provide useful guidance in our study of the many-well cases discussed below.

For the case where the site energy disorder becomes much stronger than the tunneling amplitude, we have derived a master equation for the particle motion. We have found a rather surprising result in the regime defined by $\bar{\Delta} \ll \delta\varepsilon \ll k_B T \ll \hbar\omega_d$. The diffusion constant is independent of the disorder if the particle couples with the phonons through the piezoelectric effect, and it increases with disorder if the coupling is mediated by a short-ranged interaction. We also find that the diffusion constant depends

linearly on temperature, and depends quadratically on the renormalized tunneling amplitude.

In the translationally invariant case, we have rederived the Boltzmann equation at low temperatures, yielding $D \sim T^{1-2s}$, where $s=3$ for piezoelectric coupling and $s=5$ for short-ranged interaction. At higher temperatures, the Boltzmann desciption breaks down, and a transition to incoherent hopping occurs. We have confirmed the Holstein formula for the hopping rate on more rigorous grounds.

In this paper, the term "incoherence" is used to indicate the Markovian nature of the particle motion in positional basis. There is, however, a difference between the incoherence occurring at high temperatures and that induced by disorder at low temperatures. The physical principle operating in the former case is the quasiclassical tendency, the tendency to move in parallel witgh the diagonal ($\mathbf{x}=\mathbf{y}$) of the phase space. In the strongly disordered case, the phase space diagonal itself acquires a special meaning. It decouples from the off-diagonal sites, and becomes the main channel for the particle motion.

It should be noticed that even at zero temperature, the relaxation rate Γ is nonzero for the two-well case, biased or unbiased. One might think that this is the reason for the temperature independence of the diffusion constant reported in refs. 26 and 27. In view of our results for the case of an infinite lattice, one has to conclude, however, that this is not the case. We expect that the zero-bias and zero-temperature relaxation rate should go as $\Gamma \sim J(2\delta\bar{\Delta}/\hbar)$ [see Eq. (4.20)] for a multiwell case, where $\delta\bar{\Delta}$ is the level spacing of the renormalized particle Hamiltonian. This rate decreases to zero as the number of wells increases to infinity. The coherence of the particle motion makes it impossible to obtain a finite diffusion constant at zero temperature.

It is also noticed that the coherence (in zero bias) persists up to a temperature of the order of the Debye temperature rather than the tunneling amplitude. This is in line with the results of Leggett *et al.*,[19] who have studied the general case of a two-well particle interacting with a heat bath through the coupling spectral function $J(\omega) \sim \omega^s$ [see (4.4)]. They concluded that the transition to incoherence occurs at $k_B T = 0$ for $0 < s < 1$, and at $k_B T \sim \hbar\omega_c (\Delta/\hbar\omega_c)^{2-s}$ for $1 < s < 2$, where ω_c is a typical frequency of the heat bath modes. It is easy to see from (4.40) that the transition takes place at $k_B T \sim \hbar\omega_c$ for $s > 2$. For the piezoelectric coupling we have $s=3$, and for the short-ranged interaction we have $s=5$. Thus, a narrow band does not necessarily imply an incoherent motion. In fact, the low-temperature relaxation rate goes like $\Gamma \sim \bar{\Delta}^s$, whose ratio with the tunneling amplitude decreases with Δ for $s > 1$, indicating that the motion is more coherent when the bandwidth gets narrower. The important

scattering phonons have frequencies of the order of the renormalized bandwidth of the particle, and their spectral weight decreases with decreasing frequency.

Finally, it should be pointed out that the incoherent hopping rate at high temperature is proportional to the square of the bare tunneling amplitude Δ rather than the renormalized one, $\bar{\Delta}$. The Frank–Condon factor cancels out. In ref. 13, the high-temperature rate of Flynn and Stoneham[37] was used, but the tunneling amplitude was still interpreted as the renormalized one. We think this is inappropriate.

APPENDIX A. SITE ENERGY CHANGE DUE TO DISPLACEMENTS OF LATTICE ATOMS

Suppose the particle interacts with the lattice atoms through short-ranged repulsive forces. The potential wells seen by the particle are centered at the interstitials of the atomic lattice. Suppose the lowest level energy $\varepsilon(L)$ of a potential well depends on the linear dimension L of the well. If $\{\mathbf{X}_j\}$ are the positions of the lattice atoms bordering a well, the length scale L may be taken as

$$L=\left[\sum_j (\mathbf{X}_j-\mathbf{x})^2\right]^{1/2} \tag{A.1}$$

where $\mathbf{x}$ is the center of mass of $\{\mathbf{X}_j\}$. This choice of L is invariant under uniform translation of the bordering atoms, as it should be.

Expanding to first order in the displacements $\mathbf{X}_j-\mathbf{X}_j^0$, and re-expressing them in terms of the phonon field operators, we then obtain the correction to the site energy as given in (2.3). The coupling function $g(\mathbf{k})$ has the expression

$$\varepsilon'(L_0)\left(\frac{\hbar}{2M\omega_{\mathbf{k}}L_0^2}\right)^{1/2}\sum_j (\mathbf{X}_j^0-\mathbf{x})\cdot\boldsymbol{\varepsilon}_{\mathbf{k}}e^{i\mathbf{k}(\mathbf{X}_j^0-\mathbf{x})} \tag{A.2}$$

where $\mathbf{x}$ now stands for the center of mass of $\{\mathbf{X}_j^0\}$, and $\boldsymbol{\varepsilon}_{\mathbf{k}}$ is a polarization vector of the phonon mode.

At small $\mathbf{k}$ we may expand the exponential in (A.2). The zeroth-order term is zero because $\sum_j (\mathbf{X}_j^0-\mathbf{x})=0$ by definition. The first-order term gives $g(\mathbf{k})\sim k/\sqrt{\omega_{\mathbf{k}}}$. The estimate (2.4) follows from a dimensional analysis of (A.2).

APPENDIX B. REDUCED DENSITY MATRIX AND INFLUENCE FUNCTIONAL

With a generalization of the "bra-ket" notations in (2.11) to the system of our particle plus phonons, we have in place of (2.12)

$$\frac{\partial}{\partial t}|\rho_{\rm tot}(t)\rangle = \mathscr{L}_{\rm tot}(t)\,|\rho_{\rm tot}(t)\rangle \tag{B.1}$$

where $\mathscr{L}_{\rm tot}(t)$ is the Liouvillian operator correspondings to $H_{\rm tot}(t)$ in (2.8). This is integrated with the initial condition $|\rho_{\rm tot}(t_0)\rangle = |z_0\rangle \otimes |\rho_{\rm ph}(t_0)\rangle$, where $|\rho_{\rm ph}(t_0)\rangle$ corresponds to the canonical distribution of phonons given in (2.7), yielding

$$\begin{aligned}|\rho_{\rm tot}(t)\rangle = \sum_{n=0}^{\infty} \int_{t_0}^{t} dt_n \int_{t_0}^{t_n} dt_{n-1} \cdots \int_{t_0}^{t_2} dt_1 \\ \times e^{(\mathscr{L}_s + \mathscr{L}_{IL})(t-t_0)}\, \hat{\mathscr{L}}_h(t_n)\, \hat{\mathscr{L}}_h(t_{n-1}) \cdots \hat{\mathscr{L}}_h(t_1)\, |z_0\rangle \otimes |\rho_{\rm ph}(t_0)\rangle\end{aligned} \tag{B.2}$$

where $\mathscr{L}_{IL}$ corresponds to $H_I + H_L$, and

$$\hat{\mathscr{L}}_h(t) = e^{-(\mathscr{L}_s + \mathscr{L}_{IL})(t-t_0)}\, \mathscr{L}_h(t)\, e^{(\mathscr{L}_s + \mathscr{L}_{IL})(t-t_0)} \tag{B.3}$$

with everything else defined as in the text. We can then insert in (B.2) the complete sets $\{|z_j\rangle\langle z_j|\}$ for the particle sector, and trace out the phonon degrees of freedom, yielding

$$\begin{aligned}&\langle z_f|\ {\rm tr}\ |\rho_{\rm tot}(t)\rangle \\ &= \sum_{n=0}^{\infty} \int_{t_0}^{t} dt_n \int_{t_0}^{t_n} dt_{n-1} \cdots \int_{t_0}^{t_2} dt_1 \sum_{\{z_j\}} \\ &\quad \times \langle z_f|\ \mathscr{L}_h(t_n)\ |z_{n-1}\rangle\langle z_{n-1}|\ \mathscr{L}_h(t_{n-1})\ |z_{n-2}\rangle \cdots \langle z_1|\ \mathscr{L}_h(t_1)\ |z_0\rangle \\ &\quad \times \exp\left\{\sum_{j=1}^{n} \lambda(z_j)(t_{j+1} - t_j)\right\} \\ &\quad \times {\rm tr}\{e^{\mathscr{L}_{IL}(z_f)(t-t_n)} e^{\mathscr{L}_{IL}(z_{n-1})(t_n - t_{n-1})} \cdots e^{\mathscr{L}_{IL}(z_0)(t_1 - t_0)}\, |\rho_{\rm ph}(t_0)\rangle\}\end{aligned} \tag{B.4}$$

where $\mathscr{L}_{IL}(z) = \langle z|\ \mathscr{L}_{IL}\ |z\rangle$ now acts only on the phonon degrees of freedom. In the above and hereafter, tr means tracing out of the phonon degrees of freedom. If the phonon coordinates are collectively denoted as R, then the phonon phase space is coordinated as (R, R'). The trace

operation in the "bra-ket" notation is simply, $\text{tr}\,|\rho\rangle = \sum_{R=R'} \langle R, R'|\rho\rangle$. Recall that the reduced density matrix is defined as

$$\rho(z_f, t) = \langle z_f|\,\text{tr}\,|\rho_{\text{tot}}(t)\rangle \tag{B.5}$$

The expression (B.4) is just (2.17) with

$$\exp(\Phi[z]) = \text{tr}\{e^{\mathscr{L}_{IL}(z_f)(t-t_n)} e^{\mathscr{L}_{IL}(z_{n-1})(t_n-t_{n-1})} \cdots z^{\mathscr{L}_{IL}(z_0)(t_1-t_0)}\,|\rho_{\text{ph}}(t_0)\rangle\} \tag{B.6}$$

The usual definition for the influence functional is, in our language,

$$\exp(\Phi[z]) = \text{tr}\,|\rho_{\text{ph}}([z], t)\rangle \tag{B.7}$$

where

$$\frac{\partial}{\partial\tau}|\rho_{\text{ph}}([z], \tau)\rangle = \mathscr{L}_{IL}(z_\tau)\,|\rho_{\text{ph}}([z], \tau)\rangle \tag{B.8}$$

The two definitions are the same, if we make the recognition of z_τ as defined in (2.16). Finally, the expression (2.18) for the influence functional has been calculated in ref. 15.

APPENDIX C. EVALUATING THE INFLUENCE FUNCTIONAL

For a particular path of n jumps, we can use (2.16) to carry out the double-time integral in (2.18). The result is a sum over contributions from the pieces of the τ–s plane partitioned by the times $\{t_j\}$.[19] After some rearrangements, we have

$$\begin{aligned}
\Phi[z] &= -\sum_{\mathbf{k}} J(\mathbf{k})[\coth(\beta\hbar\omega_{\mathbf{k}}/2)F_1 - iF_2] \\
F_1 &= \sum_{j=0}^{n} (U_j U_j^* - U_j U_{j-1}^*) \\
&\quad + \sum_{j=0}^{n} \sum_{r=0}^{j} \cos\omega_{\mathbf{k}}\,(t_{j+1} - t_{j-r})(U_{j+1} - U_j)(U_{j-r}^* - U_{j-r-1}^*) \qquad \text{(C.1)} \\
F_2 &= \sum_{j=0}^{n} U_j V_j^* \omega_{\mathbf{k}}(t_{j+1} - t_j) \\
&\quad + \sum_{j=0}^{n} \sum_{r=0}^{j} \sin\omega_{\mathbf{k}}\,(t_{j+1} - t_{j-r})(U_{j+1} - U_j)(V_{j-r}^* - V_{j-r-1}^*)
\end{aligned}$$

where $J(\mathbf{k})$ and the U's and V's are defined in (2.21).

A number of simplifications are in order. First, since $|g(\mathbf{k})|$ and $\omega_{\mathbf{k}}$ are invariant under $\mathbf{k} \to -\mathbf{k}$, the first sum in the expression for F_1 can be replaced by

$$\frac{1}{2}\sum_{j=1}^{n} |U_j - U_{j-1}|^2 + \frac{1}{2}|U_0|^2 + \frac{1}{2}|U_n|^2 \tag{C.2}$$

and the first sum in F_2 can be replaced by zero. These replacements do not change the value of $\Phi[z]$. Second, since $\mathscr{L}_h(t_j) = 0$ for $t_j < 0$, we can replace the lower limit t_0 of the multiple integrals over $\{t_j\}$ in (2.17) by zero. Third, since z_0 and $z_n = z_f$ are diagonal, i.e., $\mathbf{y}_0 = \mathbf{x}_0$ and $\mathbf{y}_n = \mathbf{x}_n$, we have $U_0 = U_n = 0$. We can therefore write

$$\begin{aligned} F_1 &= \frac{1}{2}\sum_{j=0}^{n} |U_j - U_{j-1}|^2 \\ &\quad + \sum_{j=1}^{n-1}\sum_{r=0}^{j-1} \cos\omega_{\mathbf{k}}(t_{j+1} - t_{j-r})(U_{j+1} - U_j)(U^*_{j-r} - U^*_{j-r-1}) \\ F_2 &= \sum_{j=1}^{n-1}\sum_{r=0}^{j-1} \sin\omega_{\mathbf{k}}(t_{j+1} - t_{j-r})(U_{j+1} - U_j)(V^*_{j-r} - V^*_{j-r-1}) \\ &\quad + \sum_{j=0}^{n-1} \sin\omega_{\mathbf{k}}(t_{j+1} - t_0)(U_{j+1} - U_j)V_0^* \end{aligned} \tag{C.3}$$

Finally, we let $t_0 \to -\infty$. This now only affects the last sum in F_2 in the above expressions, whose contribution to $\Phi[z]$ approaches zero, because

$$\sum_{\mathbf{k}} J(\mathbf{k})(U_{j+1} - U_j)\, V_0^* \delta(\omega - \omega_{\mathbf{k}}) \tag{C.4}$$

does not have sharp peaks as a function of frequency ω. In fact, for any finite time t, $(\mathbf{x}_j, \mathbf{y}_j)$ are at finite distances from $\mathbf{x}_0$. Therefore, $(U_{j+1} - U_j)V_0$ is a smooth function of $\mathbf{k}$ and vanishes quadraticcally with $\mathbf{k}$ as $\mathbf{k} \to 0$. According to discussions in Section 1, the quantity (C.4) should behave smoothly near $\omega = 0$. Finally, since $J(\mathbf{k})$ does not have sharp peaks away from $\mathbf{k} = 0$, we expect the quantity (C.4) to have no sharp peaks in ω.

With all these simplifications, we can now rewrite (2.17) as

$$\begin{aligned} \langle z_f | \rho(t) \rangle = \sum_{n=0}^{\infty} \int_0^t dt_n \int_0^{t_n} dt_{n-1} \cdots \int_0^{t_2} dt_1 \sum_{\{z_j\}} \\ \times \langle z_f | \mathscr{L}_h | z_{n-1} \rangle \langle z_{n-1} | \mathscr{L}_h | z_{n-2} \rangle \cdots \langle z_1 | \mathscr{L}_h | z_0 \rangle \\ \times \exp\left\{ \lambda(z_0) t_1 + \sum_{j=1}^{n} \lambda(z_j)(t_{j+1} - t_j) \right\} \exp(\Phi_0[z]) \exp(\Phi_1[z]) \end{aligned} \tag{C.5}$$

where

$$\Phi_0[z] = -\frac{1}{2}\sum_{j=1}^{n}\sum_{\mathbf{k}} J(\mathbf{k}) \coth\left(\frac{\beta\hbar\omega_{\mathbf{k}}}{2}\right) |U_j - U_{j-1}|^2$$

$$\Phi_1[z] = \sum_{j=1}^{n-1}\sum_{t=0}^{j-1} f(t_{j+1} - t_{j-r}; z_{j+1}, z_j, z_{j-r}, z_{j-r-1})$$

$$\begin{aligned} f(\cdots) = -\sum_{\mathbf{k}} J(\mathbf{k}) \Bigg\{ & \coth\left(\frac{\beta\hbar\omega_{\mathbf{k}}}{2}\right) \cos\omega_{\mathbf{k}}(t_{j+1} - t_{j-r}) \\ & \times (U_{j+1} - U_j)(U^*_{j-r} - U^*_{j-r-1}) \\ & - i \sin\omega_{\mathbf{k}}(t_{j+1} - t_{j-r})(U_{j+1} - U_j)(V^*_{j-r} - V^*_{j-r-1}) \Bigg\} \end{aligned} \quad \text{(C.6)}$$

The factor $\exp(\Phi_1[z])$ is just the product of $F_{jj'}$ in (2.19).

Finally, the time-independent factor $\exp(\Phi_0[z])$ can be absorbed into the hopping matrix elements as

$$\langle z|\, \mathscr{L}_h\, |z'\rangle \to \langle z|\, \bar{\mathscr{L}}_h\, |z'\rangle$$

$$\equiv \langle z|\, \mathscr{L}_h\, |z'\rangle \exp\left[-\frac{1}{2}\sum_{\mathbf{k}} J(\mathbf{k}) \coth\left(\frac{\beta\hbar\omega_{\mathbf{k}}}{2}\right) |U - U'|^2 \right] \quad \text{(C.7)}$$

Written explicitly, we have

$$\begin{aligned} &\langle \mathbf{x}, \mathbf{y}|\, \bar{\mathscr{L}}_h\, |\mathbf{x}', \mathbf{y}'\rangle \\ &= \frac{\Delta}{i\hbar}\sum_{\boldsymbol{l}} \Bigg\{ \langle \mathbf{x}|\, \mathbf{x}' + \boldsymbol{l}\rangle\langle \mathbf{y}'|\, \mathbf{y}\rangle \exp\left[-\frac{1}{2}\sum_{\mathbf{k}} J(\mathbf{k}) \coth\left(\frac{\beta\hbar\omega_{\mathbf{k}}}{2}\right) |e^{i\mathbf{k}\mathbf{x}} - e^{i\mathbf{k}\mathbf{x}'}|^2 \right] \\ &\quad - \langle \mathbf{x}|\, \mathbf{x}'\rangle\langle \mathbf{y}'|\, \mathbf{y} + \boldsymbol{l}\rangle \exp\left[-\frac{1}{2}\sum_{\mathbf{k}} J(\mathbf{k}) \coth\left(\frac{\beta\hbar\omega_{\mathbf{k}}}{2}\right) |e^{i\mathbf{k}\mathbf{y}} - e^{i\mathbf{k}\mathbf{y}'}|^2 \right] \Bigg\} \\ &= \frac{\Delta}{i\hbar}\sum_{\boldsymbol{l}} \{ \langle \mathbf{x}|\, \mathbf{x}' + \boldsymbol{l}\rangle\langle \mathbf{y}'|\, \mathbf{y}\rangle - \langle \mathbf{x}|\, \mathbf{x}'\rangle\langle \mathbf{y}'|\, \mathbf{y} + \boldsymbol{l}\rangle \} \\ &\quad \times \exp\left[-\frac{1}{2}\sum_{\mathbf{k}} J(\mathbf{k}) \coth\left(\frac{\beta\hbar\omega_{\mathbf{k}}}{2}\right) |1 - e^{i\mathbf{k}\boldsymbol{l}}|^2 \right] \end{aligned} \quad \text{(C.8)}$$

where we have used the constraints implied by $\langle \mathbf{x}|\, \mathbf{x}' + \boldsymbol{l}\rangle$ and so forth. For an atomic lattice of cubic symmetry, the exponential in the last line of the above equations is independent of the direction of the nearest neighbor lattice vector $\boldsymbol{l}$, and can be factored out as in (2.20). These arguments are still valid even if the particle is restricted to a subset of the sites (potential wells).

APPENDIX D. THE DOUBLE-LEVEL TRANSITION PROBABILITY

In order to find the probability $P(\mathbf{x}_f, \mathbf{x}_0, \lambda)$ in (3.15), we need to know $\Sigma_1(\lambda)$, which is the Laplace transform of $\Sigma_1(t)$ given by

$$\begin{aligned}\langle z|\, \Sigma_1(t)\, |z'\rangle = \sum_{z_1 z_1'} [F(t, z, z_1, z_1', z') - 1] \\ \times \langle z|\, \bar{\mathscr{P}}_h\, |z_1\rangle\langle z_1|\, e^{\mathscr{P}_P t}\, |z_1'\rangle\langle z_1'|\, \bar{\mathscr{P}}_h\, |z'\rangle \end{aligned} \tag{D.1}$$

where z now stands for the pair (x, y). The Liouvillian operators are given by

$$\begin{aligned}\bar{\mathscr{P}}_P &= \bar{\mathscr{P}}_h + \mathscr{P}_s \\ \bar{\mathscr{P}}_h\, |x, y\rangle &= \frac{\bar{\Delta}}{i\hbar}(|\bar{x}, y\rangle - |x, \bar{y}\rangle) \\ \mathscr{P}_s |x, y\rangle &= \frac{\varepsilon}{i\hbar}(x - y)\, |x, y\rangle \end{aligned} \tag{D.2}$$

where $\bar{x} = -x$, $\bar{y} = -y$, and εx is the site energy of the site $\mathbf{x} = x\mathbf{l}_1/2$. Therefore,

$$\begin{aligned}\langle z|\, \bar{\mathscr{P}}_h\, |z_1\rangle\langle z_1| &= \frac{\bar{\Delta}}{i\hbar}(\langle \bar{x}, y|\, \delta_{x_1\bar{x}}\delta_{y_1 y} - \langle x, \bar{y}|\, \delta_{x_1 x}\delta_{y_1\bar{y}}) \\ |z_1'\rangle\langle z_1'|\, \bar{\mathscr{P}}_h\, |z'\rangle &= \frac{\bar{\Delta}}{i\hbar}(|\bar{x}', y'\rangle\, \delta_{x_1'\bar{x}'}\delta_{y_1' y'} - |x', \bar{y}'\rangle\, \delta_{x_1' x'}\delta_{y_1'\bar{y}'}) \end{aligned} \tag{D.3}$$

Substituting the above relations into (D.1), we have

$$\begin{aligned}\langle z|\, \Sigma_1(t)\, |z'\rangle = \left(\frac{\bar{\Delta}}{\hbar}\right)^2 \{ &- \langle \bar{x}, y|\, e^{\mathscr{P}_P t}\, |\bar{x}', y'\rangle (e^{xx'g(t + i\hbar\beta/2)} - 1) \\ &- \langle x, \bar{y}|\, e^{\mathscr{P}_P t}\, |x', \bar{y}'\rangle (e^{yy'g(t - i\hbar\beta/2)} - 1) \\ &+ \langle \bar{x}, y|\, e^{\mathscr{P}_P t}\, |x', \bar{y}'\rangle (e^{-xy'g(t - i\hbar\beta/2)} - 1) \\ &+ \langle x, \bar{y}|\, e^{\mathscr{P}_P t}\, |\bar{x}', y'\rangle (e^{-yx'g(t + i\hbar\beta/2)} - 1)\} \end{aligned} \tag{D.4}$$

where $g(t)$ is given in (4.9) and we have used the following relation:

$$g\left(t \pm \frac{i\hbar\beta}{2}\right) = 4\int_0^\infty \frac{d\omega}{\omega^2} J(\omega)\left[\coth\left(\frac{\beta\hbar\omega}{2}\right)\cos(\omega t) \mp i \sin(\omega t)\right] \tag{D.5}$$

Using the Pauli matrices (4.6), one can write the particle Liouvillian $\bar{\mathscr{L}}_P$ as

$$\bar{\mathscr{L}}_P = \frac{1}{i\hbar}\left[(\bar{\Delta}\sigma_1 + \varepsilon\sigma_3) - (\bar{\Delta}\sigma_1' + \varepsilon\sigma_3')\right] \tag{D.6}$$

It can then be shown that

$$\begin{aligned}\Sigma_1(t) = (\bar{\Delta}/\hbar)^2\{&-\sigma_1 e^{\bar{\mathscr{L}}_P t}\sigma_1 C(t + i\hbar\beta/2) - \sigma_3\sigma_1 e^{\bar{\mathscr{L}}_P t}\sigma_1\sigma_3 S(t + i\hbar\beta/2)\\ &- \sigma_1' e^{\bar{\mathscr{L}}_P t}\sigma_1' C(t - i\hbar\beta/2) - \sigma_3'\sigma_1' e^{\bar{\mathscr{L}}_P t}\sigma_1'\sigma_3' S(t - i\hbar\beta/2)\\ &+ \sigma_1 e^{\bar{\mathscr{L}}_P t}\sigma_1' C(t - i\hbar\beta/2) - \sigma_3\sigma_1 e^{\bar{\mathscr{L}}_P t}\sigma_1'\sigma_3' S(t - i\hbar\beta/2)\\ &+ \sigma_1' e^{\bar{\mathscr{L}}_P t}\sigma_1 C(t + i\hbar\beta/2) - \sigma_3'\sigma_1' e^{\bar{\mathscr{L}}_P t}\sigma_1\sigma_3 S(t + i\hbar\beta/2)\}\end{aligned} \tag{D.7}$$

where $C(t) = \cosh[g(t)] - 1$ and $S(t) = \sinh[g(t)]$.

The operator $\bar{\mathscr{L}}_P$ is diagonalized by the following transformation:

$$e^{+i\theta(\sigma_2 + \sigma_2')}\bar{\mathscr{L}}_P e^{-i\theta(\sigma_2 + \sigma_2')} = \frac{\Omega}{i\hbar}(\sigma_3 - \sigma_3') \tag{D.8}$$

where $\Omega = (\bar{\Delta}^2 + \varepsilon^2)^{1/2}$ and $\theta = (1/2)\tan^{-1}(\bar{\Delta}/\varepsilon)$. Under the same transformation, the self-energy operator $\Sigma_1(\lambda)$ becomes $\tilde{\Sigma}_1(\lambda)$ as is given in (4.8)–(4.10) in the text.

APPENDIX E. EVALUATING THE DIFFUSION POLE

As $\mathbf{u} \to 0$, the drift term can be treated as a small perturbation. We first symmetrize the collision kernel by writing

$$\psi(\mathbf{v}) = e^{-\beta\varepsilon_{\mathbf{v}}/2}\phi(\mathbf{v}) \tag{E.1}$$

Then $\phi(\mathbf{v})$ satisfies the equation

$$\lambda\phi(\mathbf{v}) = Q_0\phi(\mathbf{v}) + Q_1\phi(\mathbf{v}) \tag{E.2}$$

where

$$\begin{aligned}Q_0\phi(\mathbf{v}) &= \sum_{\mathbf{v}'} W_{\mathbf{v}\mathbf{v}'}[\phi(\mathbf{v}') - e^{\beta(\varepsilon_{\mathbf{v}} - \varepsilon_{\mathbf{v}'})/2}\phi(\mathbf{v})]\\ Q_1\phi(\mathbf{v}) &= \mathbf{u}\frac{\partial\varepsilon_{\mathbf{v}}}{i\hbar}\phi(\mathbf{v})\end{aligned} \tag{E.3}$$

We now apply the Lanczos iterative method to evaluate $\lambda(\mathbf{u})$.[38] We

take $\phi_0(\mathbf{v}) = e^{-\beta\varepsilon_\mathbf{v}/2}$ as the starting state. We first calculate $Q\phi_0$, project it onto ϕ_0, and call the remainder ϕ_1. We thus have

$$\lambda\phi_0 = a\phi_0 + \phi_1 \tag{E.4}$$

where by definition

$$a = \sum_\mathbf{v} \phi_0(\mathbf{v})\, Q\phi_0(\mathbf{v}) \Big/ \sum_\mathbf{v} \phi_0(\mathbf{v})\, \phi_0(\mathbf{v}) \tag{E.5}$$

The coefficient a is actually zero, because ϕ_0 is a zero mode of Q_0 and the thermal average of $Q_1 = \mathbf{u}\,\partial\varepsilon_\mathbf{v}/i\hbar$ is zero. Next, we calculate $Q\phi_1(\mathbf{v})$, project it onto ϕ_0 and ϕ_1, and call the remainder ϕ_2. Therefore

$$\lambda\phi_1 = b\phi_0 + c\phi_1 + \phi_2 \tag{E.6}$$

where

$$\begin{aligned} b &= \sum_\mathbf{v} \phi_0(\mathbf{v})\, Q_1^2\phi_0(\mathbf{v}) \Big/ \sum_\mathbf{v} \phi_0(\mathbf{v})\, \phi_0(\mathbf{v}) \\ c &= \sum_\mathbf{v} \phi_0(\mathbf{v})\, Q_1 Q_0 Q_1 \phi_0(\mathbf{v}) \Big/ \sum_\mathbf{v} \phi_0(\mathbf{v})\, Q_1^2\phi_0(\mathbf{v}) \end{aligned} \tag{E.7}$$

Note that while b goes to zero quadratically with $\mathbf{u}$, c approaches a finite constant.

If we ignore ϕ_2 in (E.6), we then have a two-dimensional eigenvalue problem (E.4) and (E.6) to solve. The eigenvalues are easily found to be

$$\begin{aligned} \lambda(\mathbf{u}) &= \tfrac{1}{2}[c \pm (c^2 + 4b)^{1/2}] \\ &\approx \tfrac{1}{2}[c \pm c(1 + 2b/c^2)] \end{aligned} \tag{E.8}$$

where in the second step we have used the fact that $b \ll c^2$ as $\mathbf{u}$ goes to zero. The solution with the negative sign in (E.8) goes continuously to zero as $\mathbf{u} \to 0$, and corresponds to the diffusion mode. We thus take $\lambda(\mathbf{u}) = -b/c$. The expressions (6.4) and (6.14) in the text then follow from (E.7). D is isotropic because of the cubic symmetry of the lattice.

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