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Perturbation theory of impurity diffusion

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A derived generalized Langevin equation for classical impurity diffusion in a lattice is studied in perturbation theory. Temperature dependence of the activation barrier to impurity motion is absent for an interaction Hamiltonian linear in phonon amplitudes, but appears for an interaction Hamiltonian including quadratic or higher orders in phonon amplitudes. The time integral of the memory function, known as the friction constant, separates into one-phonon and multiphonon contributions to dissipation. At low temperatures the friction constant becomes a power series in temperature. The coefficients of this power series are evaluated for a Gaussian impurity-lattice interaction potential. When the potential is short ranged, one-phonon acoustic umklapp processes dominate and the friction constant goes to a constant value as temperature vanishes; otherwise, umklapp processes can be ignored, and the leading term in the power series is the linear temperature coefficient which, in lowest order, is dominated by two-phonon normal quasielastic scattering process. Transverse modes in the two-phonon processes contribute significantly to the latter, but only when the interaction Hamiltonian contains terms of at least quadratic order in the phonon amplitudes. Due to the power series form of the friction constant and the temperature dependence of the activation energy, the diffusion constant obtained using Kramers's formulas assumes a generalized Arrhenius form.

I. INTRODUCTION

The theory of impurity diffusion in solids has received much attention in recent years because of the potential impact in areas of technological interest such as hydrogen diffusion and superionic conductors.[1] Experiments usually reveal that the impurity diffusion constant D has the pure Arrhenius form

$$D = D_0 e^{-E_a/k_B T} \tag{1}$$

for low temperatures $k_B T \ll E_a$, where E_a and D_0 are two experimentally fitted constants: the activation energy and Arrhenius prefactor, respectively.

There have been many theoretical attempts to explain the Arrhenius form. Transition-state theories[2,3] yield (1), where E_a coincides with a real energy barrier to impurity motion and D_0 is proportional to a jump "attempt" frequency. A microscopic determination of the latter generally meets with only order-of-magnitude success. This fact has led others to make more detailed investigations. Fokker-Planck transport theories[4,5] utilize generalizations of Brownian motion to include the effect of a periodic potential on a diffusing particle. In these theories E_a appears as a parameter along with the friction constant η. A more recent theory[6] along this line is an attempt to extend the usefulness of Kramers's formulas.[4] These theories contain no method for evaluating any dependence of E_a or η on temperature or potential parameters.

More realistic mode-coupling theories[7] have been advanced to analyze the effects of lattice vibrations on E_a and η, the diffusion constant, and other functions. Microscopic determinations of η have also been attempted using other methods including perturbation theory.[8,9] In a mode-coupling theory single-phonon and multiphonon processes are all hidden within a relaxation function that includes conservative and dissipative forces, so that no clear physical picture of the mechanics of diffusion emerges. Perturbation theory, on the other hand, yields a simple physical picture which readily segregates one-, two-, and higher-order phonon processes. The problem with perturbation theory, as clearly stated by Kleppman and Zeyher,[7] is that activated diffusion is ordinarily nonperturbative in nature requiring the use, for example, of a mode-coupling approach.

Munakata has solved this problem by separating the dissipative from conservative forces, thus providing a natural environment for the use of perturbation theory in a generalized Langevin approach.[9] The systematic dissipative term involves the memory function $\mathbf{K}(t)$ which is related to the fluctuation force through a fluctuation-dissipation relation. The friction constant η then becomes the time integral of the memory function. Both the memory function and its time integral are central quantities in diffusion calculations (cf. Refs. 10–12).

Munakata calculated E_a and normal (as distinguished from umklapp) one-phonon contributions to η and the memory function to lowest nonvanishing order for the traditionally analyzed impurity-lattice Hamiltonian. The latter consists of a harmonic lattice perturbed by an interaction Hamiltonian that retains only those terms that are linear in the phonon amplitudes. E_a in this approximation does not vary with temperature. The behavior of η to this order is a generalized Arrhenius form where the prefactor is proportional to $T^{-1/2}$. Using the low-friction Kramers's formula[4] (in which case the jump rate is proportional to η/T) Munakata obtained a form which deviates from the Arrhenius form (1) in that the prefactor is proportional to $T^{-3/2}$ and the activation energy is increased due to elastic forces by the amount $Mc_0^2/2$, where

c_0 is the sound speed and M is the impurity mass.

It was originally believed by the authors that the behavior of impurity diffusion exemplified by the pure Arrhenius form (1) was correctly induced from experiment and should be obtainable from multiphonon contributions which were ignored in Ref. 9. It is known that, to lowest nonvanishing order, classical two-phonon contributions to kink diffusion, obtained in a perturbation theory where one expands about free phonons and kinks, give rise to a linear variation of η with temperature;[10] presuming that Kramers's low-friction formula should apply at sufficiently low temperature, the two-phonon contributions should yield (1). The perturbation theory carried out in this paper suggests, however, that this picture is an oversimplification.

First, it is shown that when quadratic or higher orders of phonon amplitudes are retained in the interaction Hamiltonian, E_a becomes temperature dependent. The quadratic order generally smooths the effective periodic potential seen by the impurity, thus causing a decrease in the barrier height.

Second, it is shown that at low temperatures (i.e., where $k_B T \ll Mc_0^2$) one-phonon normal contributions to η are dominated by one-phonon umklapp and multiphonon contributions. The form of η becomes the power series

$$\eta = d_0 + d_1 k_B T + d_2 (k_B T)^2 + \cdots \ , \tag{2}$$

where the d_i are constants. "Low temperatures" include room temperatures for typical impurity-lattice system parameters.

The first term d_0 in (2) is entirely due to one-phonon acoustic umklapp processes. If the impurity-lattice interaction potential is short range (if the range of a Gaussian interaction potential is $\lesssim \frac{7}{8}$ of a lattice site), then one-phonon acoustic umklapp processes yield dominant contributions to all the d_i. Otherwise, umklapp processes can be ignored and multiphonon scattering dominates impurity diffusion. In the latter case the linear temperature coefficient d_1 is, to lowest order, dominated by two-phonon normal quasielastic scattering of the impurity; the d_i for $i \geq 2$ are then dominated by higher-order multiphonon contributions. When the low-temperature formula (2) along with the temperature-dependent E_a is used in Kramers's high- and low-friction rate-theory formulas,[4] a generalized version of (1) results where D_0 is allowed to vary with temperature and E_a takes on its zero-temperature relaxed value (the temperature-dependent part of E_a being collected into the prefactor).

The dominant two-phonon contributions to d_1 *do not* arise from interaction Hamiltonian terms which are linear in the phonon amplitudes—they arise from terms which are *quadratic* in the phonon amplitudes. The linear terms give rise to one-phonon contributions of order V^2, and two-phonon contributions of order V^4; the quadratic terms give rise to two-phonon contributions of order V^2 and higher. Inclusion of the quadratic phonon amplitudes in the interaction Hamiltonian yields a perturbation theory correct to order V^2. Although transverse modes always contribute to umklapp processes (and thus d_0), normal processes which contribute to d_1 do not contain transverse modes unless phonon amplitudes of *at least* quadratic order are included (in which case their contribution dominates longitudinal modes). This indicates that mode-coupling and other theories should retain in the interaction Hamiltonian higher orders than linear in the phonon amplitudes.

Interestingly, it is found that phonon-impurity interactions which contribute to dissipation obey a classical selection rule. In an interaction between the impurity and the lattice a net energy ΔE and net momentum $\Delta \mathbf{P}$ are transferred from the lattice to the impurity. It is shown in this paper that in any dissipative interaction the following equation is satisfied:

$$\mathbf{V}_I \cdot \Delta \mathbf{P} = \Delta E \ , \tag{3}$$

where $\mathbf{V}_I$ is the impurity velocity. The impurity velocities are distributed according to a Maxwellian so that the probability for a dissipative interaction is maximized when the speed V_I is small. The dominance in dissipation of multiphonon processes and of one-phonon umklapp processes at low temperatures is attributable to the fact that both can take place at any value of V_I including $V_I = 0$, whereas normal one-phonon processes (treated, for example, by Munakata[9]) are likely only when the impurity travels near the speed of sound.

The paper is organized as follows. In Sec. II the Hamiltonian and generalized Langevin formulation derived by Munakata[9] is stated and generalized to nonlinear Hamiltonians. In Sec. III the temperature dependence of the activation barrier is studied. In Sec. IV the memory function is described in terms of perturbation theory. In Sec. V terms calculated to order V^2 (the lowest nonvanishing order) are discussed, with emphasis on the calculation of the one-, two-, and three-phonon processes. The lowest-order contributions to η are also calculated here. Selection rules for classical phonon-impurity interactions are derived. A Gaussian interaction potential is introduced in order to evaluate the memory function and its associated friction constant. The low-temperature limit of η is discussed in general terms and studied in the Einstein and Debye approximations. Mass dependence is discussed. In Sec. VI is a discussion of higher-order effects. Three general theorems are stated regarding the perturbation theory of the temperature dependence of the memory function from which are deduced consequences at low temperatures. In Sec. VII the nature of the single-phonon and multiphonon contributions to the memory is discussed in quantum-mechanical terms using a classical impurity and quantum phonons. The quantum selection rules derived therein are shown to be an expression of energy and momentum conservation in interaction events. Section VIII contains conclusions.

II. THE HAMILTONIAN AND THE LANGEVIN EQUATION

Consider the Hamiltonian

$$H = H_0 + P^2/2M + H_I \ ,$$

where H_0 is the lattice Hamiltonian in absence of the impurity, P the magnitude of the impurity momentum $\mathbf{P}$, M the impurity mass, and H_I the interaction which couples the lattice to the impurity. The Hamiltonian is assumed to be purely classical. The interaction is assumed to occur via a pair potential

$$H_I = \sum_l V(\mathbf{r}_l) \ ,$$

where $\mathbf{r}_l = \mathbf{R}_l - \mathbf{X}$, where $\mathbf{R}_l$ and $\mathbf{X}$ denote the lth lattice atom and impurity positions, respectively. $V(\mathbf{r}_1)$ can be expanded about the lattice sites $\mathbf{x}_l = \sum_l a_{li}\mathbf{b}_i$ in small displacements $\mathbf{u}_l$ to yield a power series in the components of $\mathbf{u}_l$, where the $\mathbf{b}_i$ are the primitive lattice vectors and the a_{li} are integers.

The generalized Langevin equation for an impurity in a lattice is[9]

$$\dot{\mathbf{P}}(t) + \int_0^t ds\, \mathbf{K}(t-s)\cdot\mathbf{P}(t) = -\nabla_{\mathbf{X}} U + \sum_l \mathbf{f}_l(t) \ , \tag{4}$$

where $\mathbf{K}$ is the memory function (a matrix), $U(\mathbf{X})$ is the effective periodic potential seen by the impurity—it is obtained from the lattice at equilibrium with $\mathbf{X}$ held fixed,

$$e^{-\beta U(\mathbf{X})} = \frac{1}{Z} \int \prod_l d\mathbf{u}_l d\mathbf{p}_l e^{-\beta(H_0 + H_I)} \ , \tag{5}$$

where $\beta = 1/k_B T$, and Z is the partition function for the free-lattice atom coordinates and momenta; $\mathbf{f}_l(t)$ is the random force contributed by the lth atom; the memory function $\mathbf{K}(t)$ is related entirely to the random forces through the fluctuation-dissipation relation[11,12]

$$\mathbf{K}(t) = \frac{1}{M k_B T} \sum_{l,l'} \langle \mathbf{f}_l(t) \mathbf{f}_{l'} \rangle \ , \tag{6}$$

where $\langle\ \rangle$ denotes a canonical ensemble over the total system.

Equation (4) is approximate, where a small memory term in the periodic potential has been ignored. The approximate form has been proven only to second order in the interaction potential for an interaction Hamiltonian that is linear in the phonon amplitudes.[9] This approximation is generalizable to all orders for any Hamiltonian (see Appendix A).

III. THE TEMPERATURE DEPENDENCE OF $U(\mathbf{X})$ AND E_a

The temperature-dependent activation barrier may be obtained from (5). This is possible without resorting to perturbation theory by assuming that the lattice is harmonic and by truncating the interaction Hamiltonian to quadratic order in the phonon amplitudes. Using the standard normal-mode transformation,

$$\mathbf{u}_l = (Nm)^{-1/2} \sum_{\mathbf{q}j} \mathbf{e}_{\mathbf{q}j} Q_{\mathbf{q}j} e^{i\mathbf{q}\cdot\mathbf{x}_l} \ ,$$

where $\mathbf{e}_{\mathbf{q}j}$ is the normal-mode polarization vector with complex amplitude $Q_{\mathbf{q}j}$ for wave vector $\mathbf{q}$ and branch j, the lattice Hamiltonian becomes, in the harmonic approximation,

$$H_0 = \tfrac{1}{2} \sum_{\mathbf{q},j} (P_{\mathbf{q}j} P^*_{\mathbf{q}j} + \omega^2_{\mathbf{q}j} Q_{\mathbf{q}j} Q^*_{\mathbf{q}j}) \ , \tag{7}$$

where $P_{\mathbf{q}j} = \dot{Q}_{\mathbf{q}j}$ and $\omega_{\mathbf{q}j}$ are the eigenfrequencies of the lattice.

In order to perform the integration in (5) it is simpler to deal with matrices and vectors for terms involving $Q_{\mathbf{q}j}$. Thus, let the vector $\mathbf{Q}$ be constructed from elements $Q_{\mathbf{q}j}$. In order to deal with just $\mathbf{Q}$ in (5) rather than both $\mathbf{Q}$ and its complex conjugate, a matrix $\mathbf{B}_0$ is defined such that

$$\mathbf{Q}\cdot\mathbf{B}_0\cdot\mathbf{Q} \equiv \tfrac{1}{2} \sum_{\mathbf{q},j} \omega^2_{\mathbf{q}j} Q_{\mathbf{q}j} Q^*_{\mathbf{q}j} \ .$$

Noting that

$$Q^*_{\mathbf{q}j} = Q_{-\mathbf{q}j} \ ,$$

one can see that $\mathbf{B}_0$ is a rearrangement of the normal diagonalized form into an "antidiagonal" matrix of 3×3 diagonal submatrices with elements $\omega^2_{\mathbf{q}j}/2$, $j = 1,2,3$.

It is convenient to deal with the system at time $t = 0$. The interaction Hamiltonian then can be expressed as

$$\begin{aligned} H_I &= \sum_l V(\mathbf{x}_l - X_0) + \sum_l \left[\frac{\partial V}{\partial r_\alpha} \right]_{\mathbf{x}_l - \mathbf{X}_0} u_\alpha(l;0) \\ &\quad + \sum_l \left[\frac{1}{2} \frac{\partial^2 V}{\partial r_\alpha \partial r_\beta} \right]_{\mathbf{x}_l - \mathbf{X}_0} u_\alpha(l;0) u_\beta(l;0) + \cdots \\ &\equiv H_I^{(0)} + H_I^{(1)} + H_I^{(2)} + \cdots \ , \end{aligned}$$

where it has been assumed that $\mathbf{R}_l = \mathbf{x}_l + \mathbf{u}_l$, and the Cartesian component of $\mathbf{u}_l(t)$ is denoted by $u_\alpha(l;t)$. Einstein summation is assumed, but only in repeated *Greek* indices, where Greek characters are reserved to indicate Cartesian components and l, l', etc., are atomic indices.

By transforming into reciprocal space, the $H_I^{(i)}$ may be expressed in terms of reciprocal-lattice vectors $\mathbf{G}$ as

$$H_I^{(0)} = \frac{1}{v_0} \sum_{\mathbf{G}} \hat{V}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{X}_0} \ ,$$

$$H_I^{(1)} = -\sum_{\mathbf{q},j} \frac{i}{v_0 (Nm)^{1/2}} \sum_{\mathbf{G}} (\mathbf{q}+\mathbf{G})\cdot\mathbf{e}_{\mathbf{q}j} \hat{V}(\mathbf{q}+\mathbf{G}) e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{X}_0} Q_{\mathbf{q}j} \equiv \mathbf{C}\cdot\mathbf{Q} \ ,$$

$$H_I^{(2)} = -\sum_{\mathbf{q},j} \sum_{\mathbf{q}',j'} \frac{1}{v_0 (Nm)} \sum_{\mathbf{G}} (\mathbf{q}+\mathbf{q}'+\mathbf{G})\cdot\mathbf{e}_{\mathbf{q}j} (\mathbf{q}+\mathbf{q}'+\mathbf{G})\cdot\mathbf{e}_{\mathbf{q}'j'} \hat{V}(\mathbf{q}+\mathbf{q}'+\mathbf{G}) e^{i(\mathbf{q}+\mathbf{q}'+\mathbf{G})\cdot\mathbf{X}_0} Q_{\mathbf{q}j} Q_{\mathbf{q}'j'} \equiv -\mathbf{Q}\cdot\mathbf{B}_1\cdot\mathbf{Q} \ ,$$

where v_0 is the volume of the primitive cell, and the vector $\mathbf{C}$ and matrix $\mathbf{B}_1$ are defined by their respective equations.

Inserting the above expressions into Eq. (5) and integrating over the momenta yields

$$e^{-\beta U(\mathbf{X}_0)}=\frac{\int d\mathbf{Q}\, e^{-\beta[H_I^{(0)}+\mathbf{Q}\cdot(\mathbf{B}_0-\mathbf{B}_1)\cdot\mathbf{Q}+\mathbf{C}\cdot\mathbf{Q}]}}{\int d\mathbf{Q}\, e^{-\beta\mathbf{Q}\cdot\mathbf{B}_0\cdot\mathbf{Q}}}\ , \tag{8}$$

where $d\mathbf{Q}\equiv\prod_{\mathbf{q},j}dQ_{\mathbf{q}j}$. Equation (8) is just a Gaussian quadrature. The integration yields

$$e^{-\beta U(\mathbf{X}_0)}=e^{-\beta[U_R(\mathbf{X}_0)+k_BTU'(\mathbf{X}_0)]}\ , \tag{9a}$$

or

$$U(\mathbf{X}_0)=U_R(\mathbf{X}_0)+k_BTU'(\mathbf{X}_0)\ , \tag{9b}$$

where

$$U'(\mathbf{X}_0)=-\tfrac{1}{2}\ln(\det\mathbf{R}) \tag{10}$$

and

$$\mathbf{R}=(1-\mathbf{B}_0^{-1}\mathbf{B}_1)^{-1} \tag{11}$$

has elements $R_{\mathbf{q}j,\mathbf{q}'j'}$ (so there should be no confusion with the lattice atom position $\mathbf{R}_l$), and

$$U_R(\mathbf{X}_0)=H_I^{(0)}-\tfrac{1}{2}\sum_{\mathbf{q},j}\sum_{\mathbf{q}',j'}\frac{1}{\omega_{\mathbf{q}'j'}^2}C_{\mathbf{q}j}R_{\mathbf{q}j,\mathbf{q}'j'}C_{-\mathbf{q}'j'} \tag{12}$$

is the statically relaxed potential (temperature independent).

The activation barrier E_a is obtained by comparing the U at saddle-point position $\mathbf{Z}_0$ with the U at the minimum position $\mathbf{Y}_0$ [for a simple-cubic lattice $\mathbf{Z}_0=(b/2)(0,1,1)$, $\mathbf{Y}_0=(b/2)(1,1,1)$]. Thus, from (9)–(12) one obtains

$$E_a=U(\mathbf{Z}_0)-U(\mathbf{Y}_0)=E_a^0+k_BT\ln E_a'(T)\ , \tag{13}$$

where

$$E_a^0=U_R(\mathbf{Z}_0)-U_R(\mathbf{Y}_0)\ ,$$

$$\ln E_a'=U'(\mathbf{Z}_0)-U'(\mathbf{Y}_0)\ ,$$

where E_a' is nondimensional and, in general, a rational function of T. When the interaction Hamiltonian is linear in the phonon amplitudes, $\mathbf{B}_1=\mathbf{0}$. From (11), $\mathbf{R}=1$. Then, from (10), $U'=0$, so $E_a'=1$. Thus, in this case, $E_a=E_a^0$, which is a constant. E_a^0 is the statically relaxed value of E_a to this order (cf. Refs. 7 and 9). The temperature dependence of E_a comes in, therefore, through E_a', which requires phonon amplitudes of at least quadratic order in the interaction Hamiltonian.

One may in general expand U_R and U' in powers of the potential. For example, the quadratic interaction Hamiltonian yields

$$\begin{aligned}U'&=-\tfrac{1}{2}\mathrm{Tr}(\mathbf{B}_0^{-1}\mathbf{B}_1)+O(V^2)\\&=-\frac{1}{v_0Nm}\sum_{\mathbf{G}}\sum_{\mathbf{q},j}\frac{\mathbf{G}\cdot\mathbf{e}_{\mathbf{q}j}\mathbf{G}\cdot\mathbf{e}_{-\mathbf{q}j}}{\omega_{\mathbf{q}j}^2}\hat{V}(\mathbf{G})e^{i\mathbf{G}\cdot\mathbf{X}_0}+O(V^2)\ ,\end{aligned} \tag{14}$$

where Tr denotes the trace. This is just a constant, so that from (13) it can be seen that E_a is linear in T for the quadratic interaction Hamiltonian.

For acoustic phonons with $\omega_{\mathbf{q}j}=qc_j$ $(j=L,T)$ (L for longitudinal and T for transverse) in a simple-cubic lattice with lattice constant b, this can be simplified to

$$U'=\frac{1}{6\pi m}\left[\frac{1}{c_L^2}+\frac{2}{c_T^2}\right]b^2\nabla_{\mathbf{x}_0}^2H_I^{(0)}+O(V^2)\ .$$

Thus, the effect of U' is to increase the minima of U_R and not significantly alter U_R at the saddle point, unless in the neighborhood of the saddle point one constrains the impurity motion to move along a trajectory connecting the minimas (as in Ref. 3), in which case U' will also depress U_R significantly at the saddle point.

To estimate the extent of the deviation of E_a from E_a^0 take the first term of $H_I^{(0)}$ along a line connecting two energy minima; in this case the Laplacian of $H_I^{(0)}$ just becomes roughly the second derivative of the $E_a^0/2$ times the cosine of $2\pi\mathbf{X}_0/b$. Then, to lowest order $\ln E_a'\approx-2\pi E_a^0/mc_0^2$, where $c_0=c_L\cong c_T$ is assumed. Typical values (cf. Kleppman and Zeyher in Ref. 7) are $E_a^0\sim200$ K, and $mc_0^2\sim10^4$ K, which yields a linear temperature coefficient $\ln E_a'$ of ~0.12. For room temperature $k_BT\ln E_a'$ is ~36 K, which is roughly one-sixth of E_a^0. Since E_a, to this order, is linear in T, inserting E_a into (1) just rescales D_0 by the factor E_a'.

To include higher-order terms in H_I, it is best to find the true equilibrium positions $\mathbf{y}_l(\mathbf{X}_0)$ for each impurity position (e.g., numerically) and to expand the total Hamiltonian around such positions perturbation theoretically,

$$H=\sum_j H^{(j)}\ ,$$

$$H^{(j)}=\sum_{l_1,\ldots,l_j}\left[\frac{1}{j!}\frac{\partial^j(H_I+H_0)}{\partial R_{l_1\alpha_1}\cdots\partial R_{l_j\alpha_j}}\right]_{\mathbf{y}_l(\mathbf{X}_0)}\times\xi_{\alpha_1}(l_1;t;\mathbf{X}_0)\cdots\xi_{\alpha_j}(l_j;t;\mathbf{X}_0)\ .$$

By definition, around $\mathbf{y}_l$ there arises no linear term, i.e., $H^{(1)}=0$. Therefore, in Eq. (5), $\exp(-\beta H^{(3)}-\cdots)$ can be expanded into a power series in phonon amplitudes, leading to Gaussian integrals of polynomials. Every phonon amplitude introduces a factor $T^{1/2}$, so (9a) becomes multiplied with a power series in T which, at zero temperature, reduces to 1. Therefore, $U(\mathbf{X}_0)$ is of the form (9b), where U' is, in general, the logarithm of a power series in T. This makes E_a' a rational function of T.

It is interesting to note the implications that the temperature-dependent activation energy has regarding the form of (1). Inserting (13) in (1), one obtains

$$D=D_0E_a'(T)e^{-E_a^0/k_BT}\ . \tag{15}$$

Thus, the temperature dependence of E_a leads to a prefactor of D_0 multiplied by the temperature-dependent factor E_a' and an exponential factor where the activation barrier is the statically relaxed value E_a^0. For a linear interaction Hamiltonian there is no change from (1) (E_a' is unity); for a quadratic Hamiltonian the prefactor is simply rescaled

(E_a' is a constant); including higher orders introduces a temperature dependence into the prefactor—a rational function in T which multiplies D_0.

IV. THE MEMORY FUNCTION IN PERTURBATION THEORY

Normally the time integral of the memory function is used to calculate the diffusion constant directly.[10,11] However, the form of (4) is strongly suggestive of a Fokker-Planck approach (in the spirit of Kramers) where a Markov approximation yields a friction constant and the activation effects [e.g., the exponential factor in (1)] are extracted nonperturbatively. A perturbation theoretical calculation of a diffusion constant using Kramers's formulas [see (36)] must, therefore, exclude the nonperturbative effects of the activation barrier from a calculation of the friction constant [see (19)]. To be consistent with the Fokker-Planck approach the projection operator is ignored in the time propagator for time-evolving dynamical variables.[13] This approximation is tantamount to allowing, for example, the random force to evolve mechanically (see Appendix B). In fact, the perturbation theoretical calculation of (6) requires this in order to exclude nonperturbative activation effects (Appendix B).

At time $t=0$ the random forces have the periodic potential subtracted out and exactly satisfy

$$\sum_l \mathbf{f}_l = -\nabla_{\mathbf{X}_0}[H_I - U(\mathbf{X}_0)] \ , \tag{16}$$

where $\mathbf{X}_0$ is the initial impurity position; thus, the random forces are just due to lattice vibrations. In light of the preceding remarks, the time evolution of $\mathbf{f}_l$ is taken as

$$\mathbf{f}_l(t) = -\left\{ \left[\nabla_{\mathbf{X}} \left[\frac{\partial V}{\partial r_\alpha} \right]_{\mathbf{x}_l - \mathbf{X}(t)} \right] [u_\alpha(l;t) - \langle u_\alpha(l;t) \rangle_{\text{lattice}}] + \left[\nabla_{\mathbf{X}} \left[\frac{1}{2} \frac{\partial^2 V}{\partial r_\alpha \partial r_\beta} \right]_{\mathbf{x}_l - \mathbf{X}(t)} \right] [u_\alpha(l;t) u_\beta(l;t) - \langle u_\alpha(l;t) u_\beta(l;t) \rangle_{\text{lattice}}] + \cdots \right\} , \tag{17}$$

where

$$\langle A \rangle_{\text{lattice}} \equiv \frac{e^{\beta U(\mathbf{X})}}{Z} \int \prod_l d\mathbf{u}_l d\mathbf{p}_l e^{-\beta(H_0 + H_I)} A$$

are static terms due to the effective periodic potential.

Note that the static contributions (the averaged terms) are subtracted out and do not contribute to the dissipation, as only time correlations of $\mathbf{f}_l(t)$ are important in (6). These correlations contain the static contributions [cf. (C2)], so that the static contributions need not be retained explicitly. Thus, the fluctuating force is written as

$$\mathbf{f}_l(t) = -\nabla_{\mathbf{X}} \left[\left[\frac{\partial V}{\partial r_\alpha} \right]_{\mathbf{x}_l - \mathbf{X}(t)} u_\alpha(l;t) + \left[\frac{1}{2} \frac{\partial^2 V}{\partial r_\alpha \partial r_\beta} \right]_{\mathbf{x}_l - \mathbf{X}(t)} u_\alpha(l;t) u_\beta(l;t) + \cdots \right] . \tag{18}$$

The lattice is assumed to be isotropic, with lattice constant b. In this case, from (6) one can see that $\mathbf{K}$ is diagonal, all elements being equal. The time integral of these elements is termed the friction constant,

$$\eta = \int_0^\infty dt\, K(t), \quad K(t) \equiv \tfrac{1}{3} K_{\alpha\alpha}(t) \ , \tag{19}$$

where $K_{\alpha\beta}$ is an element of $\mathbf{K}$. This quantity is used in Sec. V to calculate the Fokker-Planck diffusion constant from Kramers's formulas.

At this point notation is introduced that will be used extensively below. Let $\gamma_i = 1,2,3$ denote a particular component of a vector, where i may take on any integer value. Then let

$$\begin{aligned} W_\alpha^{\gamma(n)}(l;t) &\equiv \frac{\partial}{\partial X_\alpha} \frac{1}{n!} \left[\frac{\partial^n V}{\partial r_{\gamma_1} \cdots \partial r_{\gamma_n}} \right]_{\mathbf{x}_l - \mathbf{X}(t)} \\ &\equiv \frac{\partial}{\partial X_\alpha} \frac{1}{n!} (V_{\gamma(n)})_{\mathbf{x}_l - \mathbf{X}(t)} \ . \end{aligned} \tag{20}$$

Letting $\gamma(n) = \gamma_1 \cdots \gamma_n$ in (20), a component of $\mathbf{f}_l$ in (18) may be written

$$f_{l\alpha} = -W_\alpha^\beta(l;t) u_\beta(l;t) - W_\alpha^{\beta\gamma}(l;t) u_\beta(l;t) u_\gamma(l;t) - \cdots \ . \tag{21}$$

From (4), (6), (20), and (21) one can see that the scalar quantity K in (19) is a sum of contributions of the form

$$\frac{1}{3Mk_BT} \sum_{l,l'} \langle W_\alpha^{\beta'(m)}(l';0) \mathbf{u}_{\beta'(m)}(l';0) W_\alpha^{\beta(n)}(l;t) \mathbf{u}_{\beta(n)}(l;t) \rangle \ ,$$

where the following shorthand notation has been used:

$$\mathbf{u}_{\beta(n)}(l;t) \equiv u_{\beta_l}(l;t) \cdots u_{\beta_n}(l;t) \ .$$

Note that $W_\alpha^{\beta(n)} \mathbf{u}_{\beta(n)}$ is contracted over all $\beta(n) = \beta_1, \ldots, \beta_n$ indices.

For any correlation function $\langle A_\alpha(t) A_\gamma(0) \rangle$, the canonical ensemble is

$$\langle A_\alpha(t)A_\gamma(0)\rangle=\frac{1}{Z}\int\frac{d\mathbf{X}_0}{Z_X}\int\frac{d\mathbf{P}}{Z_P}\int\prod_l d\mathbf{u}_l d\mathbf{p}_l \times e^{-\beta H}A_\gamma(0)e^{iLt}A_\alpha(0)\ , \tag{22}$$

where $\beta=1/k_BT$, Z_X and Z_P are the partition functions for the impurity coordinate and impurity momentum, and L is the Liouville operator.

To perform the perturbation expansion, first let $L=L_0+L_I$, where L_0 and L_I are the free and interaction Liouville operators, respectively. Expanding in orders j of L_I about L_0 gives rise to the following series:

$$e^{iLt}=\left[1+i\int_0^t d\tau L_I(\tau)+i^2\int_0^t d\tau L_I(\tau)\int_\tau^t d\tau' L_I(\tau') + \cdots\right]e^{iL_0t}$$
$$\equiv\left[\sum_{j=0}\Lambda_j(t)\right]e^{iL_0t}\ .$$

Now, let

$$A_\alpha(t)\rightarrow A_{l\alpha}^{(m)}(t)\equiv W_\alpha^{\gamma(m)}(l;t)\mathbf{u}_{\gamma(m)}(l;t)\ .$$

Then, (22) becomes

$$K(t)=\frac{1}{3Mk_BT}\sum_{l,l'}\sum_{m,n}\frac{\left\langle A_{l'\alpha}^{(m)}(0)e^{-\beta H_I}\mathbf{T}\exp\left[i\int_0^t d\tau L_I(\tau)\right]A_{l\alpha}^{(n)}(t)\right\rangle_{\text{free}}}{\langle e^{-\beta H_I}\rangle_{\text{free}}}\ , \tag{23}$$

where $\mathbf{T}$ is the time-ordering operator and the subscript "free" denotes an average taken about the free Hamiltonian and the motion obtained therefrom. The lowest nonvanishing order in perturbation theory is, therefore, V^2 (one power from each $A_{l\alpha}$). Expanding in powers of βH_I and in L_I yields higher powers in V. In general, the terms in (23) take the form

$$K_{mn}^{(jk)}(t)=\frac{1}{3Mk_BT}\times\sum_{l,l'}\left\langle A_{l'\alpha}^{(m)}(0)\frac{(-\beta H_I)^k\Lambda_j(t)}{k!}A_{l\alpha}^{(n)}(t)\right\rangle_{\text{free}}\ , \tag{24}$$

where now the average is taken over connected diagrams only (cf. Ref. 14). The $\Lambda_j(t)$ contribution represents dynamical processes which take place between time 0 and time t in (24), while the βH_I contributions represent only time-0 (static) quantities.

V. THE LOWEST NONVANISHING ORDER

A. The memory function and the friction constant

One goal of this paper is to calculate the various contributions to dissipation and thus the memory function. The number of genuine phonon contributions in (24) is determined by the number of time correlations in the displacements $\mathbf{u}_l$ that exist within the term. The time dependence arises from either Λ_j or directly from $\mathbf{u}_l(t)$ in (24). The simplest terms occur for $j=0$. It is instructive to look at the lowest nonvanishing order of these terms, i.e., $(jk)=(00)$. Suppressing the superscript for these terms, one may write

$$K_{mn}(t)=\frac{1}{3Mk_BT}\sum_{l,l'}\int\frac{d\mathbf{X}_0}{Z_X}\int\frac{d\mathbf{P}}{Z_P}e^{-\beta P^2/2M}W_\alpha^{\gamma(m)}(l';0)W_\alpha^{\gamma'(n)}(l;t)\langle\mathbf{u}_{\gamma(m)}(l';0)\mathbf{u}_{\gamma'(n)}(l;t)\rangle_0\ ,$$

and the $\langle\ \rangle_0$ denotes a canonical ensemble taken over the free lattice alone. Odd correlations in components of $\mathbf{u}_l$ vanish, so that only when $m+n$ is even do terms contribute.

The diagonal terms K_{nn} represent the lowest-order n-phonon contributions to the memory function $K(t)$. K_{11} is the lowest-order one-phonon contribution, which was calculated in Ref. 9. The off-diagonal terms (i.e., where $m\neq n$) are simply static corrections to the w-phonon process which multiply the diagonal ww term by a power of $T^{|m-n|/2}$, where w is the lesser of the two values m and n. The off-diagonal terms are "virtual" phonons (nonpropagating diagrams), whereas the diagonal terms belong to the set of "genuine" phonon processes (propagating diagrams).

Virtual-phonon contributions are uninteresting at low temperatures as they are dominated by the genuine phonon contributions. Thus, the only terms considered in lowest order here are the diagonal terms, which may be written with a single subscript

$$K_n(t)\equiv\frac{1}{3Mk_BT}\sum_{l,l}\int\frac{d\mathbf{X}_0}{Z_X}\int\frac{d\mathbf{P}}{Z_P}e^{-\beta P^2/2M}W_\alpha^{\gamma(n)}(l;0)W_\alpha^{\gamma'(n)}(l';t)\langle\mathbf{u}_{\gamma(n)}(l;0)\mathbf{u}_{\gamma'(n)}(l';t)\rangle_0\ . \tag{25}$$

In three dimensions $Z_X=Nv_0$, where N is the number of particles in the lattice, and $Z_P=(2\pi Mk_BT)^{3/2}$. Now, (21) becomes, in lowest order,

$$\eta=\sum_n\eta_n\equiv\sum_n\int_0^\infty K_n(t)\ . \tag{26}$$

The most interesting results of this paper are found when the interaction Hamiltonian is limited to quadratic order in the phonon amplitudes; thus, anharmonicity in H_0 (i.e., higher orders than quadratic) is neglected. Using the argument in Appendix C, the one-, two-, and three-phonon memory functions can be written

$$K_1(t)=\frac{1}{3M}\frac{1}{(K_0^3v_0)^2}\frac{1}{Nm}\sum_{\mathbf{q},j}\sum_{\mathbf{G}}|\hat{W}_\alpha^\gamma[\mathbf{Q}_1/K_0]\hat{W}_\alpha^\delta[\mathbf{Q}_1/K_0]|\,e^{-t^2Q_1^2k_BT/2M}\frac{\Psi_{\gamma\delta}(\mathbf{q}j)}{\omega_{\mathbf{q}j}^2}\cos(\Omega_1t)\ , \tag{27}$$

$$K_2(t)=\frac{k_BT}{3M}\frac{1}{(K_0^3v_0)^2}\frac{1}{(Nm)^2}\sum_{\mathbf{q},j}\sum_{\mathbf{q}',j'}\sum_{\mathbf{G}}|\hat{W}_\alpha^{\gamma\delta}[\mathbf{Q}_2/K_0]\hat{W}_\alpha^{\gamma'\delta'}[\mathbf{Q}_2/K_0]|\,e^{-t^2Q_2^2k_BT/2M}\frac{\Psi_{\gamma\gamma'}(\mathbf{q}j)\Psi_{\delta\delta'}(\mathbf{q}'j')}{\omega_{\mathbf{q}j}^2\omega_{\mathbf{q}'j'}^2}\sum_{\Omega_2}\cos(\Omega_2t)\ , \tag{28}$$

$$K_3(t)=\frac{(k_bT)^2}{3M}\frac{1}{(K_0^3v_0)^2}\frac{1}{(Nm)^3}\sum_{\mathbf{q},j}\sum_{\mathbf{q}',j'}\sum_{\mathbf{q}'',j''}\sum_{\mathbf{G}}|\hat{W}_\alpha^{\gamma\delta\lambda}[\mathbf{Q}_3/K_0]\hat{W}_\alpha^{\gamma'\delta'\lambda'}[\mathbf{Q}_3/K_0]|$$

$$\times e^{-t^2Q_3^2k_BT/2M}\frac{\Psi_{\gamma\gamma'}(\mathbf{q}j)\Psi_{\delta\delta'}(\mathbf{q}'j')\Psi_{\lambda\lambda'}(\mathbf{q}''j'')}{\omega_{\mathbf{q}j}^2\omega_{\mathbf{q}'j'}^2\omega_{\mathbf{q}''j''}^2}\tfrac{3}{2}\sum_{\Omega_3}\cos(\Omega_3t)\ , \tag{29}$$

where $\omega_{\mathbf{q}j}$ is the jth branch of the dispersion relation for the lattice vibrations in the harmonic approximation, $\hat{W}$ is the Fourier transform of W [cf. (D1) and (D2)], K_0 is a parameter used later in the evaluation of a Gaussian interaction potential,

$$\Psi_{\alpha\beta}(\mathbf{q}L)=q_\alpha q_\beta/q^2,\quad \Psi_{\alpha\beta}(\mathbf{q}T)=\delta_{\alpha\beta}-\Psi_{\alpha\beta}(\mathbf{q}L)$$

are the longitudinal (L) and transverse (T) contributions from the polarization vectors in an isotropic lattice ($\delta_{\alpha\beta}$ is the Kronecker delta), and

$$\Omega_1=\omega_{\mathbf{q}j},\quad \Omega_2=\omega_{\mathbf{q}j}\pm\omega_{\mathbf{q}'j'},\quad \Omega_3=\omega_{\mathbf{q}j}\pm\omega_{\mathbf{q}'j'}\pm\omega_{\mathbf{q}''j''},\ \ldots$$

$$\mathbf{Q}_1=\mathbf{q}+\mathbf{G},\quad \mathbf{Q}_2=\mathbf{q}+\mathbf{q}'+\mathbf{G},\quad \mathbf{Q}_3=\mathbf{q}+\mathbf{q}'+\mathbf{q}''+\mathbf{G},\ \ldots$$

where $\mathbf{G}$ is a reciprocal-lattice vector and the ± is taken over all possible combinations (note that the sum $\mathbf{Q}_n$ of wave vectors or its magnitude Q_n should not be confused with the vector $\mathbf{Q}$ or its normal mode elements $Q_{\mathbf{q}j}$ used in Sec. III). In deriving Eqs. (27)–(29) it has been assumed that $V(r)$ is an even function, and (29) is obtained by using the symmetric properties of the sum over $\mathbf{q},\mathbf{q}',\mathbf{q}''$ and ignoring the virtual-phonon corrections to K_1 that arise from the first term in (C3).

Thus, to lowest order, the memory function consists of a sum over types of impurity-phonon interaction "events" whose memories oscillate in time with frequency Ω_n and are damped by Gaussians of variance $2M/(Q_n^2k_BT)$. The oscillatory nature arises directly from the sinusoidal variation of the phonon correlation functions. The Gaussian form of the damping arises from the expansion about the free motion of the impurity. Later, the time dependence of the K_n will be analyzed for a particular model to reveal the long-time inverse-power-law behavior of both K_1 and K_2.

At high temperature the variance of the Gaussians are small. This maximizes the relative contribution of high frequencies Ω_n, because at lower temperatures the sum over these rapidly varying processes tend to cancel so that low-frequency processes dominate. Note from the definitions of Ω_n that "low frequency" does not necessarily mean low $\omega_{\mathbf{q}j}$ (except for $n=1$). In the two-phonon process, for example, it may mean low $|\omega_{\mathbf{q}j}-\omega_{\mathbf{q}'j'}|$.

The n-phonon contributions to the friction constant η may be evaluated from (27)–(29), yielding, for example,

$$\eta_1=\left[\frac{\pi}{2M}\right]^{1/2}\frac{1}{3(K_0^3v_0)^2}\frac{(k_BT)^{-1/2}}{Nm}\sum_{\mathbf{q},j}\sum_{\mathbf{G}}\frac{|\hat{W}_\alpha^\gamma[\mathbf{Q}_1/K_0]\hat{W}_\alpha^\delta[\mathbf{Q}_1/K_0]|}{|\mathbf{Q}_1|}\frac{\Psi_{\gamma\delta}(\mathbf{q}j)}{\omega_{\mathbf{q}j}^2}e^{-E_1/k_BT}\ , \tag{30}$$

$$\eta_2=\left[\frac{\pi}{2M}\right]^{1/2}\frac{1}{3(K_0^3v_0)^2}\frac{(k_BT)^{1/2}}{(Nm)^2}\sum_{\mathbf{q},j}\sum_{\mathbf{q}',j'}\sum_{\mathbf{G}}\frac{|\hat{W}_\alpha^{\gamma\delta}[\mathbf{Q}_2/K_0]\hat{W}_\alpha^{\gamma'\delta'}[\mathbf{Q}_2/K_0]|}{|\mathbf{Q}_2|}\frac{\Psi_{\gamma\gamma'}(\mathbf{q}j)\Psi_{\delta\delta'}(\mathbf{q}'j')}{\omega_{\mathbf{q}j}^2\omega_{\mathbf{q}'j'}^2}\sum_{E_2}e^{-E_2/k_BT}\ , \tag{31}$$

$$\eta_3=\left[\frac{\pi}{2M}\right]^{1/2}\frac{1}{3(K_0^3v_0)^2}\frac{(k_BT)^{3/2}}{(Nm)^3}\sum_{\mathbf{q},j}\sum_{\mathbf{q}',j'}\sum_{\mathbf{q}'',j''}\sum_{\mathbf{G}}\frac{|\hat{W}_\alpha^{\gamma\delta\lambda}[\mathbf{Q}_3/K_0]\hat{W}_\alpha^{\gamma'\delta'\lambda'}[\mathbf{Q}_3/K_0]|}{|\mathbf{Q}_3|}$$

$$\times\frac{\Psi_{\gamma\gamma'}(\mathbf{q}j)\Psi_{\delta\delta'}(\mathbf{q}'j')\Psi_{\lambda\lambda'}(\mathbf{q}''j'')}{\omega_{\mathbf{q}j}^2\omega_{\mathbf{q}'j'}^2\omega_{\mathbf{q}''j''}^2}\tfrac{3}{2}\sum_{E_3}e^{-E_3/k_BT}\ , \tag{32}$$

where

$$E_n \equiv \tfrac{1}{2} M \left[\frac{\Omega_n}{Q_n} \right]^2 .$$

The form of (30)–(32) is that of a sum over scattering form factors multiplied by Arrhenius "activation" factors, whose "energy barriers" are E_n. The Arrhenius factors tend to make the largest contributions to impurity scattering when the E_n are smallest. This corresponds to the vanishing of the oscillatory nature of the contribution to the memory function.

As of yet, the power-series formula (2) for η is not readily apparent. The form of (2) emerges upon upon consideration of low temperatures, which is found in subsection C.

A more revealing method of calculating (30)–(32) is to integrate over time *before* integrating over momentum (see Appendix D). This method yields the selection rule

$$\mathbf{V}_I \cdot \mathbf{Q}_n = \Omega_n \ . \tag{33}$$

This is a generalization of one-phonon selection rules for the excitation of phonons by dislocations and kinks.[15] Later, in Sec. VII, (33) will be shown to be equivalent to (3).

Note that since Ω_n and $\mathbf{Q}_n$ involve sums of n frequencies and wave numbers, respectively, the interaction between phonons characterized by these properties can only take place with an impurity traveling at speed V_I calculable from (33) as Ω_n divided by the component of $\mathbf{Q}_n$ parallel to $\mathbf{V}_I$. Examination of (31) in light of a Debye approximation reveals that both normal and umklapp multiphonon events can readily take place when $V_I=0$; one-phonon normal events (30) can take place only at high impurity speeds (near c_0, the sound speed), whereas one-phonon umklapp events can take place when $V_I=0$. For choices of the impurity-lattice and lattice atom–lattice atom interaction potentials which make E_a small compared to the impurity-lattice interaction potential height V_0, there is a range of temperature for which one-phonon umklapp effects will be damped out (see Sec. V C 3). In this case, one expects multiphonon processes to dominate disspation unless the thermal velocity of the impurity $(k_B T/M)^{1/2} \sim c_0$.

In cases where one may ignore the one-phonon umklapp effects, multiphonon effects generally dominate. For example, if one takes T_R as the ratio of the actual temperature to room temperature, and M_R as the ratio of the impurity mass to the *electron* mass, $c_0 \sim 10^5$ cm/s requires $M_R \sim 4.5 \times 10^3 T_R$ for one-phonon processes to be important. This requires an atom the size of helium at room temperature, or nitrogen at 5 times room temperature.

B. The Gaussian potential

Evaluation of (27)–(32) requires the specification of the interaction potential V. One of the simplest forms for V is a Gaussian, and since it is also used in other theories (cf. Refs. 7 and 9) it will be used here. Thus, let

$$V(\mathbf{r}) = V_0 e^{-K_0^2 r^2} \tag{34}$$

Then it may be shown that

$$| \hat{W}_\alpha^{\gamma(n)}[\mathbf{Q}_n/K_0] | = \frac{\pi^{3/2}}{n!} V_0 Q_n^\alpha \mathbf{Q}_n^{\gamma(n)} e^{-Q_n^2/4K_0^2} , \tag{35}$$

where

$$\mathbf{Q}_n^{\gamma(n)} \equiv Q_n^{\gamma_1} \cdots Q_n^{\gamma_n}$$

in the same manner as $\mathbf{u}_{\gamma(n)}$ was defined previously, with $Q_n^{\gamma_i}$ taken as the γ_i component of $\mathbf{Q}_n$.

C. The low-temperature limit

Equations (30)–(32) can be evaluated numerically for any given dispersion relation $\omega_{\mathbf{q}j}$ and for any temperature; however, analysis leads to interesting results in the Debye and Einstein models, especially at low temperature. In particular, it is shown that for low temperatures η takes the form of the power series (2) in temperature.

In the Debye model the transverse dispersion relations are taken as $\omega_{\mathbf{q}T} = c_T |\mathbf{q}|$, and the longitudinal as $\omega_{\mathbf{q}L} = c_L |\mathbf{q}|$, whereas in the Einstein model $\omega_{\mathbf{q}j} = \omega_0$, $j=T,L$, where c_T and c_L are the transverse and longitudinal sound speeds in the lattice, respectively.

By making a Markoff approximation of (4), Kramers's high- and low-fiction formulas for the jump rate[4] over an activation barrier may be used to yield the diffusion constant

$$D_{\text{high}\,\eta} = z b^2 \frac{\omega_A \omega_B}{2\pi\eta} e^{-E_a/k_B T}, \quad \eta \gg 2\omega_B \tag{36a}$$

$$D_{\text{low}\,\eta} = z b^2 \frac{\eta E_a}{k_B T} e^{-E_a/k_B T}, \quad \eta \ll 2\omega_A \tag{36b}$$

where z is a geometrical factor and ω_A and ω_B are frequencies characteristic of the curvatures of the minimum and maximum of the periodic potential, respectively. Since the solid considered here is isotropic, Eqs. (36a) and (36b) apply in three dimensions as long as E_a is measured from the saddle-point configuration.

Of course, Kramers's formulas were derived for a fixed periodic potential, i.e., where E_a, ω_A, and ω_B are constants. In light of Sec. III this constraint should be relaxed. Thus, although their values may be well approximated by their zero-temperature relaxed values, they should be allowed to vary with temperature.

1. The one-phonon normal processes

When (35) is inserted in (30), the Debye model yields, for the first Brillouin zone (see subsection C 3 for a discussion of umklapp processes),

$$\eta_1 = \left[\frac{\pi}{2M} \right]^{1/2} \frac{\pi V_0^2}{3K_0^2 v_0 m c_L^2} \frac{e^{-M c_L^2/2k_B T}}{\sqrt{k_B T}} \times \left[\frac{1}{8\pi K_0^4} \int_{\text{1st BZ}} d\mathbf{q}\, |\mathbf{q}|\, e^{-q^2/2K_0^2} \right] . \tag{37}$$

The last term in large parentheses is equal to 1 if the integration limits are extended to infinity. In this case the result is the same as Munakata's acoustic-phonon[9] result, except for a factor of 4 that resulted from an erroneous factor $\frac{1}{2}$ in his Fourier transform of the Gaussian potential.[16]

The Einstein model yields, after extending the first Brillouin zone to infinity,

$$\eta_1^{\text{Einstein}}=\frac{1}{3}\left[\frac{\pi^3}{2}\right]\frac{V_0^2\omega_0}{K_0^3 v_0}\frac{M}{m}\frac{1}{(k_B T)^2}\Phi_3\left[\frac{\omega_0}{K_0}\sqrt{M/k_B T}\right], \tag{38}$$

where Φ_ν is the modified Bessel function (K_ν in Abromowitz and Stegun[17]) of order ν.

Taking the low-temperature limit does not change (37), but (38) becomes

$$\lim_{T\to 0}\eta_1^{\text{Einstein}}=\frac{\pi^2}{6}\frac{(K_0\omega_0)^{1/2}}{K_0^3 v_0}\frac{M^{3/4}}{m}\frac{V_0^2}{(k_B T)^{7/4}} \times e^{-(\omega_0/K_0)\sqrt{M/k_B T}} .$$

Thus, in both the Debye and Einstein models the transverse modes do not contribute, which is, as will be seen in subsections 2 and 3, a peculiarity of the single-phonon normal process. Also, in both models, the one-phonon term decreases more strongly than a power of T. The Debye model yields an additional activation energy $Mc_L^2/2$ when η_1 is inserted into (36b), as has been noted elsewhere.[9]

2. The two-phonon term

The low-temperature behavior of the two-phonon term is surprisingly different in the classical low-temperature regime and dominates the normal one-phonon behavior (37). This is due to the fact that the phonon-scattering "activation" energies $E_2\propto(\omega_{\mathbf{q}j}-\omega_{\mathbf{q}'j'})^2$ vanish rapidly as $q'j'\to\pm qj$ giving rise to strong scattering in processes which involve two phonons with nearly identical energies. To see the results of this, use (35) in (31) to obtain

$$\begin{aligned}\eta_2^{\text{Debye}}&=\frac{\pi^3}{12}\left[\frac{\pi k_B T}{2M}\right]^{1/2}\frac{1}{(K_0^3 v_0)^2}\frac{V_0^2}{(Nm)^2}\sum_{\mathbf{q},j}\sum_{\mathbf{q}',j'}\sum_{\mathbf{G}}|\mathbf{Q}_2|\,e^{-Q_2^2/2K_0^2}\frac{[\mathbf{Q}_2\cdot\boldsymbol{\Psi}(\mathbf{q}j)\cdot\mathbf{Q}_2][\mathbf{Q}_2\cdot\boldsymbol{\Psi}(\mathbf{q}'j')\cdot\mathbf{Q}_2]}{c_j^2q^2c_{j'}^2q'^2}\sum_{E_2}e^{-E_2/k_BT} ,\\ \eta_2^{\text{Einstein}}&=\frac{\pi^3}{12}\left[\frac{\pi k_B T}{2M}\right]^{1/2}\frac{1}{(K_0^3 v_0)^2}\frac{V_0^2}{(Nm\omega_0^2)^2}\sum_{\mathbf{q},j}\sum_{\mathbf{q}',j'}\sum_{\mathbf{G}}|\mathbf{Q}_2|^5 e^{-Q_2^2/2K_0^2}(e^{-2M\omega_0^2/Q_2^2k_BT}+1) ,\end{aligned} \tag{39}$$

where in Eq. (39) Ψ is the matrix composed of the components $\Psi_{\alpha\beta}$. In the low-temperature limit one can see that the exponential dependence on temperature vanishes compared to 1 in the Einstein model, and that

$$\lim_{T\to 0}\eta_2^{\text{Einstein}}\sim T^{1/2} . \tag{40}$$

The Einstein result is, however, somewhat misleading. To see this, consider the even-valued frequency dispersion

$$\omega_{\mathbf{q}j}^2=\omega_0^2+c_j^2q^2+\cdots ,$$

which approaches the Einstein model in the limit where $c_j\to 0$. Then note that one of the two temperature-dependent exponentials in (31) dominates the other one when $\omega_{\mathbf{q}j}\approx\omega_{\mathbf{q}'j'}$, so let $\epsilon\equiv\omega_{\mathbf{q}j}-\omega_{\mathbf{q}'j'}$ with $\epsilon\to 0$. The exponential in (28) is approximately equal to 1 in this case. Performing the time integration of (28) yields

$$\lim_{T\to 0}\eta_2=d_1^{\text{two}}k_BT=\left[\frac{\pi^4}{12M}\frac{V_0^2}{(Nm)^2(K_0^3v_0)^2}\sum_{\mathbf{q},j}\sum_{\mathbf{q}',j'}\sum_{\mathbf{G}}Q_2^2e^{-Q_2^2/2K_0^2}\frac{[\mathbf{Q}_2\cdot\boldsymbol{\Psi}(\mathbf{q}j)\cdot\mathbf{Q}_2][\mathbf{Q}_2\cdot\boldsymbol{\Psi}(\mathbf{q}'j')\cdot\mathbf{Q}_2]}{\omega_{\mathbf{q}j}^2\omega_{\mathbf{q}'j'}^2}\sum_{\Omega_2}\delta(\Omega_2)\right]k_BT , \tag{41}$$

where d_1^{two} is the two-phonon contribution (in lowest order) to the linear temperature coefficient d_1 in (2). Note that (41) is entirely proportional to T. The apparent contradiction between (40) and (41) is resolved by noting that the low-T behavior of (41) is approached only when $k_BT\lesssim Mc_j^2$; when c_j is exactly zero the low-T limit of (41) is never reached, and only then does (40) hold. It can be deduced that $k_BT\ll Mc_0^2$ at room temperature for sound velocities $c_0\approx 10^5$ cm/s and for impurities of $M\gtrsim 20$ amu, so practically speaking (41) is the interesting result.

The linear variation of η_2 with T dominates the one-phonon normal term as well as higher-order terms for weak coupling (see below). This seems to imply pure Arrhenius behavior in the low-friction limit [insert (41) into (36b)] or non-Arrhenius behavior in the high-friction limit [insert (41) into (36a)]. This conclusion must be reevaluated in light of the one-phonon umklapp contributions discussed in subsection C 3.

Note that (41) consists of umklapp and normal contributions. Ignoring the umklapp contributions, the Debye limit of (41) yields the following approximate contribution from the quasielastic normal two-phonon processes:

$$d_1^{\text{two}}\cong\frac{1}{48}\left[\frac{\pi}{2}\right]^{1/2}\frac{V_0^2}{m^2}\frac{K_0}{M}\left[\frac{8}{c_T^5}+\frac{7}{c_L^5}\right] . \tag{42}$$

Note that the transverse modes yield the term $8/c_T^5$ in (42), which is normally larger than the longitudinal contribution $7/c_L^5$. That transverse modes contribute to the dissipation is a property of interaction Hamiltonians that retain higher orders than linear in the phonon amplitudes; as will be seen in Sec. VI, transverse modes do not contribute to normal processes at any order of perturbation theory for interaction Hamiltonians that are linear in the phonon amplitudes.

3. *One-phonon umklapp terms*

In subsection C 1 it is shown that the normal one-phonon contribution is exponentially damped with temperature at low temperatures. This is not the case for umklapp processes. Indeed, it turns out that they dominate diffusion for sufficiently low temperature.

Analogously to Eq. (41), one obtains, as the low-temperature limit for the Gaussian potential (34),

$$\lim_{T\to 0}\eta_1=\frac{\pi^4}{3M}\frac{V_0^2}{(K_0^3v_0)^2Nm}\sum_{\mathbf{q},j}\sum_{\mathbf{G}}Q_1^2e^{-Q_1^2/2K_0^2}\frac{\mathbf{Q}_1\cdot\boldsymbol{\Psi}(\mathbf{q}j)\cdot\mathbf{Q}_1}{\omega_{\mathbf{q}j}^2}\left[1+\frac{Q_1^2k_BT}{2M}\frac{\partial^2}{\partial\omega_{\mathbf{q}j}^2}\right]\delta(\omega_{\mathbf{q}j})\equiv d_0+d_1^{\text{one}}k_BT\ , \tag{43}$$

where d_0 is the leading term of (2) and d_1^{one} is the one-phonon umklapp contribution to d_1 in (2). Evaluations of the various terms are made to yield

$$d_0\simeq\frac{\pi^2V_0^2}{18K_0^6v_0Mm}\left[\frac{1}{c_T^3}+\frac{1}{2c_L^3}\right]\sum_{\mathbf{G}}(G^2)^2e^{-G^2/2K_0^2}\ . \tag{44}$$

Note that transverse modes do contribute to umklapp processes. In a similar manner, the one-phonon umklapp contribution d_1^{one} may be calculated. d_1^{one} is calculated for the special case $c_L\approx c_T=c_0$ as only the order of magnitude will be of interest:

$$d_1^{\text{one}}\simeq\frac{d_0}{2Mc_0^2}\frac{\sum_{\mathbf{G}}G^4\left[14-5\frac{G^2}{K_0^2}+\frac{1}{3}\frac{G^4}{K_0^4}\right]e^{-G^2/2K_0^2}}{\sum_{\mathbf{G}}G^4e^{-G^2/2K_0^2}}\ .$$

Note that the power expansion (43) in T is only valid for

$$k_BT<<\tfrac{1}{2}Mc_j^2\left[\frac{K_0b}{2\pi}\right]^2\ .$$

For impurities of $M\gtrsim 50$ amu, sound velocities $c_j\gtrsim 3\times 10^5$ cm/s, and $K_0b\gtrsim 1$, this inequality is always fulfilled at room temperature, but for smaller impurity masses one has to determine more carefully when the power-series expansion in (43) breaks down.

From (41) and (43), it may be noted that the linear temperature coefficient d_1 consists of one- and two-phonon contributions, so

$$d_1=d_1^{\text{one}}+d_1^{\text{two}}\ ,$$

and (2) becomes

$$\eta=d_0+(d_1^{\text{one}}+d_1^{\text{two}})k_BT+\cdots\ .$$

The importance of one-phonon umklapp relative to two-phonon contributions to the linear temperature coefficient is measured by the ratio $\tilde r=d_1^{\text{one}}/d_1^{\text{two}}$. The ratio $\tilde r$ decreases rapidly with increasing range,

$$\delta r\equiv 1/K_0\ ,$$

and varies linearly with m/M when two-phonon umklapp processes are neglected. For example, assuming $c_L\approx c_T=c_0$ one has $\tilde r\approx 0.085(m/M)$ for $\delta r=0.9b$, whereas $\tilde r\approx 0.009(m/M)$ for $\delta r=b$.

The ratio $d_0/d_1^{\text{two}}k_BT$ determines the overall importance of one-phonon umklapp processes relative to two-phonon normal processes in impurity diffusion. From (44) and (42) one may write

$$\frac{d_0}{d_1^{\text{two}}k_BT}\simeq\frac{\pi(2\pi)^{1/2}}{3k_BT}\frac{m}{K_0^3v_0}\frac{1/c_T^3+\frac{1}{2}c_L^3}{1/c_T^5+\frac{7}{8}c_L^5}\sum_{\mathbf{G}}\frac{G^4}{K_0^4}e^{-G^2/2K_0^2}\ .$$

For $\delta r\gtrsim 0.5b$ one can neglect reciprocal-lattice vectors of length $G>2\pi/b$, simplifying the ratio to

$$\frac{d_0}{d_1^{\text{two}}k_BT}\simeq\frac{m}{k_BT}\frac{1/c_T^3+\frac{1}{2}c_L^3}{1/c_T^5+\frac{7}{8}c_L^5}\frac{(2\pi)^{11/2}}{(K_0b)^7}e^{-(2\pi/K_0b)^2/2}\ ,\qquad \delta r\gtrsim 0.5b\ . \tag{45}$$

This ratio is very sensitive to δr. Setting $c_L\approx c_T=c_0$ the ratio in (45) is equal to $A\times mc_0^2/k_BT$, with $A\approx 1.1$ for $\delta r=0.5b$, $A\approx 0.18$ for $\delta r=0.67b$, $A\approx 0.002$ for $\delta r=0.88b$, and $A\approx 0.000\,05$ for $\delta r=b$. At room temperature, therefore, one-phonon umklapp processes dominate the two-phonon contributions for short-range impurity-lattice interactions, i.e., for $\delta r\lesssim 0.88b$. For longer ranges, i.e., $\delta r\gtrsim 0.88b$, the two-phonon contribution becomes dominant.

One may also note that, if one neglects lattice relaxation effects, the right-hand side of (45) is proportional to $E_a^2/(V_0^2K_0b)$, so that for values of activation energies large compared to V_0 umklapp processes dominate.

4. *The mass dependence of the diffusion constant*

From (42) and (44) it is clear that, to order V^2 d_0 and d_1^{two} both vary as $1/M$. When they are inserted into (26) and (36a) and (36b), assuming ω_A and ω_B are $\sim 1/\sqrt{M}$, then $D_{\text{high}\,\eta}$ does not vary with M and $D_{\text{low}\,\eta}\sim 1/M$. An "intermediate-friction" system presumably interpolates between this constant and $1/M$ behavior, which may be interpreted, over a limited parameter range, as being consistent with $1/\sqrt{M}$ behavior characteristic of the transition-state theory. It turns out that higher-order corrections cause d_1 to have a more complex (and stronger) variation with mass, so that the diffusion constant has a correspondingly complex mass dependence (cf. Sec. VI B).

5. The time dependence of K_1 and K_2

From Eqs. (27) and (28) it is immediately seen that the long-time behavior of K_1 and K_2 is dominated by contributions from the first Brillouin zone. Only the Debye model will be considered here, as the Einstein model does not seem to be of relevance at low temperatures. For analysis the summations in (27) and (28) are transformed to integrals over $\mathbf{q}$ (large-N approximation). Through rescaling of the integration variables $\mathbf{q}\rightarrow\mathbf{y}=t\mathbf{q}$ in Eqs. (27) and (28), the large time dependence is readily obtained. Asymptotically, $K_1(t)$ behaves as t^{-5} and $K_2(t)$ as t^{-8}. More explicit formulas can be obtained. Using (35) in (27), the Debye approximation yields 4 times Munakata's result [formula (47) in Ref. 9], the factor of 4 being of the same origin as in Eq. (37). The time dependence of $K_2(t)$ is more involved. For the sake of simplicity it is assumed that transverse and longitudinal sound velocities are the same: $c_T=c_L\equiv c_0$. Let

$$a\equiv\frac{1}{2}\left[t^2\frac{k_BT}{M}+\frac{1}{K_0^2}\right] . \tag{46}$$

At low temperatures the main contribution to $K_2(t)$ at large times comes from the integration region where $\omega_{\mathbf{q}}\approx\omega_{\mathbf{q}'}$. Using

$$\begin{aligned}\cos(\Omega t)&=\frac{1}{2\pi i}\int_{\epsilon-i\infty}^{\epsilon+i\infty}ds\,\exp(s\,|\,\Omega\,|\,)\frac{s}{s^2+t^2}\rightarrow\frac{1}{2\pi}\int_{-\infty}^{\infty}dx\,\exp(ix\,|\,\Omega\,|\,)\frac{ix}{t^2}(1+x^2/t^2+\cdots)\\&=\frac{1}{t^2}\left[1-\frac{1}{t^2}\frac{\partial^2}{\partial\,|\,\Omega\,|^2}+\cdots\right]\delta'(\,|\,\Omega\,|\,),\quad t\rightarrow\infty\end{aligned} \tag{47}$$

where $\delta'(\,|\,\Omega\,|\,)$ is the derivative of the δ function, one obtains, in the Debye limit for $K_2(t)$,

$$K_2(t)\sim-\frac{1}{8\pi}\frac{V_0^2k_BT}{M(mc_0^2)^2K_0^6c_0^2t^2}\left[\frac{\partial}{\partial a}\right]^3\int_{-1}^{1}dz\int_0^\infty dq\int_0^\infty dq'\delta(q'-q)\left[1-\frac{1}{c_0^2t^2}\frac{\partial^2}{\partial q'^2}+\cdots\right]\frac{\partial}{\partial q'}e^{-a(q^2+2zqq'+q'^2)} . \tag{48}$$

It follows that only the seventh and higher derivatives contribute in (48), with the result

$$K_2(t)=-\frac{k_BT}{t^8}\left[\frac{264V_0^2}{\pi m^2MK_0^6c_0^{12}}+O\left[\frac{a}{c_0^2t^2}\right]\right] . \tag{49}$$

Equation (49) gives the coefficient of the t^{-8} term only up to the first power in T. There are corrections with higher powers in a.

VI. HIGHER-ORDER CONTRIBUTIONS

A. General results

The higher-order contributions $[(jk)\neq(00)]$ contribute significantly to diffusion, especially at high temperatures. It will be seen in this section, however, that their contribution to low-temperature behavior can also be significant, especially when $V/mc_0^2\sim1$.

The interaction Hamiltonian, and therefore also the corresponding Liouville operator, consists of a Taylor series expanded about $X(t)$,

$$H_I=\sum_{j=0}H_I^{(j)} .$$

Thus, for example, $H_I^{(0)}$ is the washboard potential, followed by terms linear and quadratic in the components of $\mathbf{u}_l$, etc., as in (6). Let

$$\eta_{mn}^{(r)}\equiv\int_0^\infty dt\,K_{mn}^{(r)},\quad K_{mn}^{(r)}\equiv\sum_{\substack{j,k\\(j+k=r)}}K_{mn}^{(jk)}(t) .$$

From perturbation theory three theorems can be proven (see Appendix E).

Theorem 1: If only $H_I^{(1)}$ is taken into account for higher-order contributions in the βH_I and Λ_j terms in (24), disregarding also contributions of $H_I^{(1)}$ to $\mathrm{U}(\mathbf{X}_0)$ as in (12), the low-temperature behavior of $K_{mn}^{(r)}$ and $\eta_{mn}^{(r)}$ goes as T^α, where $\alpha=|\,m+n-r-2\,|/2$, and where $m+n+r$ has to be even (otherwise, $K_{mn}^{(r)}=\eta_{mn}^{(r)}=0$). When umklapp processes are neglected, the following special cases arise at low T: $\eta_{mn}^{(m+n-2)}\sim T$, with the exception $\eta_{11}^{(0)}\equiv\eta_1$, which vanishes exponentially in T.

Corollary: In the special case where the total interaction Hamiltonian is linear in the phonon amplitudes (i.e., where H_I contains only $H_I^{(0)}$ and $H_I^{(1)}$), and contributions from $U(\mathbf{X}_0)$ and $L_I^{(0)}$ are neglected, then, at low temperatures,

$$K_{11}^{(r)}\sim T^{r/2}\ \text{for } r \text{ even} .$$

As an example to make the corollary of theorem 1 more concrete, one might note that for the Gaussian interaction potential the $r=0$ contribution, when integrated over time, yields $\eta_1 = d_0 + d_1^{\text{one}} k_B T$ in (43). For the special case in the corollary, the $r=2$ contribution, when integrated over time is—apart from d_1^{one}—the *only* contribution to d_1 in (2) [the lowest-order processes described by (41) occur only for interaction Hamiltonians that include phonon amplitudes to quadratic order].

Theorem 2: The higher-order contributions of any finite sum in the interaction Hamiltonian with $H_I^{(0)}$ excluded and effects from $U(\mathbf{X}_0)$ neglected yield the following low-temperature behavior for the memory function and the friction constant,

$$K_{mn}^{(r)} \sim \sum_{\alpha\,(=0)} A_\alpha T^\alpha, \quad \eta_{mn}^{(r)} \sim \sum_{\alpha\,(=0)} B_\alpha T^\alpha ,$$

where genuine n-phonon processes contribute to constants A_α and B_α with $\alpha \geq n-1$. Although genuine one-phonon normal processes contribute to all of the A_α, they do not contribute to any coefficient B_α; the genuine one-phonon normal contribution decays exponentially at low T as in (37).

Theorem 3: Inclusion of $U(\mathbf{X}_0)$ and higher orders of $L_I^{(0)}$ does not destroy the dominant behavior of $K_{mn}^{(r)}(t)$ and $\eta_{mn}^{(r)}$ at low T. All higher-order corrections from $\exp[-\beta U(\mathbf{X}_0)]$ take a simple form at low temperatures and do not change the power laws of theorems 1 and 2. The higher-order corrections from the Liouville operator $L_I^{(0)}$ vanish at least linearly in T at low T, regardless of the number of involved genuine phonons, and resulting deviations from the power laws in theorem 1 and 2 are of the order $\hat{V}(\mathbf{G})/V_0 v_0$, where $\mathbf{G} \neq \mathbf{0}$ is a reciprocal-lattice vector, and powers thereof.

These theorems yield rich information about the low-temperature behavior of $K(t)$ and η. Consider, for example, H_I truncated to linear order in the phonon amplitudes as in the corollary of theorem 1. Aside from one-phonon umklapp processes and corrections from $U(\mathbf{X}_0)$ and $L_I^{(0)}$, the low-temperature behavior of η is dominated by the single linear temperature ($\alpha=1$) term $\eta_{11}^{(2)}$. This term is of fourth order in V. Still disregarding $U(\mathbf{X}_0)$ and $L_I^{(0)}$, but including single-phonon umklapp processes, the friction constant becomes dominated at low temperature by the behavior of the single contribution $\eta_1 = \eta_{11}^{(00)}$, which does not vary with temperature [thus, is the main contribution to d_0, given by (44) for the Gaussian interaction potential] and is second order in V. When the full interaction Hamiltonian without effects from $U(\mathbf{X}_0)$ and $L_I^{(0)}$ is considered, theorem 2 tells us that, disregarding single-phonon umklapp processes, there is an *infinite* number of higher-order processes contributing to linear T behavior (i.e., to the linear temperature coefficient d_1), each of which involves a genuine two-phonon process with virtual-phonon corrections of order V_0/mc_0^2. All higher-order genuine multiphonon processes contribute only terms with higher powers in T. Considering also higher-order single-phonon umklapp processes, infinitely many corrections to d_0 of (44) are introduced through the nonlinear, especially the quadratic, terms of the interaction Hamiltonian. Finally, if the corrections from $U(\mathbf{X}_0)$ and $L_I^{(0)}$ are also taken into account, then according to theorem 3, there are infinitely many additional contributions to d_1 coming from all kinds of single-phonon and multiphonon process, each of which are of order $\hat{V}(\mathbf{G})/V_0 v_0$ and which multiply together to yield a power series in $\hat{V}(\mathbf{G})/V_0 v_0$. It should be noted that contributions to d_0 come only from the static part $\exp[-\beta U(\mathbf{X}_0)]$ and not from the Liouville operator $L_I^{(0)}$, contrary to what one might expect. Further, these static contributions can be easily calculated at low temperatures, according to Eqs. (E10)–(E13). One consequence is that for traditionally studied purely linear interaction Hamiltonians the expression (44) for d_0 is readily generalized to a form valid to all orders of perturbation theory:

$$d_0 = \frac{\pi^2 V_0^2}{18 K_0^6 v_0 M m} \left[\frac{1}{c_T^3} + \frac{1}{2c_L^3} \right] \times \sum_{\mathbf{G}_1, \mathbf{G}_2} (-1)^{\mathbf{G}\cdot\mathbf{Y}_0/\pi} (\mathbf{G}_1 \cdot \mathbf{G}_2)^2 e^{-(G_1^2 + G_2^2)/4K_0^2} ,$$

where $\mathbf{G} = \mathbf{G}_1 - \mathbf{G}_2$ and $\mathbf{Y}_0 = (b/2)(1,1,1)$. Note that although d_0 appears to be from terms limited to order V_0^2, it includes contributions from all orders of the static part $\exp[-\beta U(\mathbf{X}_0)]$, which gives rise to the double sum over reciprocal-lattice vectors. The static part leads to higher orders in V_0 only in the coefficients d_1, d_2, etc. Other higher-order corrections to d_0 can only arise through a quadratic term in the Hamiltonian.

For $V_0/mc_0^2 \ll 1$ and $E_a \ll V_0$ the main contribution to η at low temperature comes from normal genuine two-phonon processes with zero virtual phonons, i.e.,

$$\eta \sim \eta_{11}^{(2)} + \eta_{12}^{(1)} + \eta_{21}^{(1)} + \eta_{22}^{(00)} .$$

Using the methods in Appendix D the following formulas may be derived,[18] neglecting umklapp contributions,

$$\eta_{11}^{(2)} = \left[\frac{\pi M k_B T}{2} \right]^{1/2} \frac{1}{72 M^3 v_0^4} \frac{1}{(Nm)^2} \sum_{\mathbf{q},\mathbf{q}'} \frac{q^2 (\mathbf{q}\cdot\mathbf{q}')^2 q'^2 \, |\mathbf{q}+\mathbf{q}'|}{\omega_{\mathbf{q}L}^2 \omega_{\mathbf{q}'L}^2} |\hat{V}(\mathbf{q})|^2 |\hat{V}(\mathbf{q}')|^2 \sum_{\pm} \mathrm{Re} \left[\int_0^\infty dy\, y^3 \exp[A_\pm] \right] , \tag{50}$$

$$\eta_{12}^{(1)} = \eta_{21}^{(1)} = \left[\frac{\pi M k_B T}{2} \right]^{1/2} \frac{1}{12 M^2 v_0^3} \frac{1}{(Nm)^2} \sum_{\mathbf{q},\mathbf{q}'} \frac{(\mathbf{q}+\mathbf{q}')\cdot\mathbf{q}(\mathbf{q}\cdot\mathbf{q}')(\mathbf{q}+\mathbf{q}')\cdot\mathbf{q}' \, |\mathbf{q}+\mathbf{q}'|}{\omega_{\mathbf{q}L}^2 \omega_{\mathbf{q}'L}^2} \times \hat{V}(\mathbf{q}+\mathbf{q}') \hat{V}(-\mathbf{q}) \hat{V}(-\mathbf{q}') \sum_{\pm} \mathrm{Re} \left[\int_0^\infty dy\, y\, \mathrm{Re}[A_\pm] \right] , \tag{51}$$

$$\eta_{22}^{(0)} = \eta_2 \text{ [cf. Eq. (31)]} , \tag{52}$$

where

$$A_{\pm}=-\frac{1}{(\mathbf{q}+\mathbf{q}')^2}\left[y^2\frac{k_BT}{2M}\,|\,\mathbf{q}\times\mathbf{q}'\,|^2+iy(\mathbf{q}+\mathbf{q}')\cdot[\mathbf{q}'\omega_{\mathbf{q}L}\mp\mathbf{q}\omega_{\mathbf{q}'L}]+\frac{M}{2k_BT}[\omega_{\mathbf{q}'L}\pm\omega_{\mathbf{q}L}]^2\right] .$$

Note that $\eta_{mn}=\eta_{nm}$, in general. Furthermore, although there are apparently resonant contributions in $\eta_{11}^{(2)}$ and $\eta_{12}^{(1)}$, when $\mathbf{q}$ and $\mathbf{q}'$ are parallel (divergent contributions are cancelled by genuine one-phonon processes), they do not contribute to the low-temperature behavior. Also, even though $\eta_{12}^{(1)}$ is negative it will be shown below that at least at low temperatures the sum $\eta_0+\eta_{11}^{(2)}+2\eta_{12}^{(1)}+\eta_2$ is always positive. Finally, note that for normal processes in $\eta_{11}^{(2)}$ and $\eta_{12}^{(1)}$ only the longitudinal modes contribute. This is due to the fact that all the involved phonons originate from or end at vertices described by the linear Hamiltonian $H_I^{(1)}$. This leads to the following conclusion: *For an iteration Hamiltonian which is linear in the phonon amplitudes the transverse modes do not contribute to the friction constant in the first Brillouin zone to any order of perturbation theory.* This statement is inclusive of a similar conclusion of Munakata's which is limited to the lowest nonvanishing order.[9] For interaction Hamiltonians that include terms at least quadratic in the phonon amplitudes, the case is quite different, as the lowest-order result (42) has indicated.

B. The low-temperature limit in the Debye model

In addition to η_2 which varies linearly with T in the low temperature limit, $\eta_{11}^{(1)}$ and $\eta_{12}^{(1)}$ also vary linearly with T, thus also contribute to d_1. In particular,

$$\lim_{T\to 0}\eta_{11}^{(2)}=k_BT\frac{1}{72\pi^3M^3m^2v_0^2}\int_0^\infty dq\frac{q^{14}\,|\,\hat V(q)\,|^4}{\omega_q^8\,|\,d\omega_q/dq\,|} ,$$

$$\lim_{T\to 0}\eta_{12}^{(1)}=-k_BT\frac{1}{48\pi^3M^2m^2v_0}\int_0^\infty dq\frac{q^{12}\hat V^2(q)}{\omega_q^6\,|\,d\omega_q/dq\,|}\int_{-1}^{1}dz\,z(1+z)^3\hat V(q\sqrt{2[1+z]}) ,$$

where the substitutions $\hat V(\mathbf{q})\to\hat V(q)$ and $\omega_{\mathbf{q}L}\to\omega_q$ have been made. For the Gaussian potential

$$\hat V(q)=\left[\frac{\pi}{K_0^2}\right]^{3/2}V_0e^{-q^2/4K_0^2} ,$$

and for the Debye limit $\omega_q=c_Lq$. Then,

$$\lim_{\substack{T\to 0\\ \text{Debye}}}\eta_{11}^{(2)}=\frac{30\sqrt{2}}{7}\eta_2^{(L)}\alpha^2 ,$$

$$\lim_{\substack{T\to 0\\ \text{Debye}}}\eta_{12}^{(1)}=-\tfrac{128}{7}(11\sqrt{3}-19)\eta_2^{(L)}\alpha ,$$

where

$$\eta_2^{(L)}\equiv\frac{7}{48}\left[\frac{\pi}{2}\right]^{1/2}\frac{V_0^2}{m^2}\frac{K_0}{M}\frac{1}{c_L^5}k_BT ,$$

$$\alpha=\frac{1}{4}\left[\frac{\pi^3}{3}\right]^{1/2}\frac{V_0}{Mc_L^2}\frac{1}{K_0^3v_0} .$$

Thus, $\eta_2^{(L)}$ is the longitudinal-mode contribution to η_2^{Debye} in (42). Therefore,

$$\eta_2^{(L)}+\lim_{\substack{T\to 0\\ \text{Debye}}}(\eta_{12}^{(1)}+\eta_{21}^{(1)}+\eta_{11}^{(2)})$$

$$=\eta_2^{(L)}\left[1-\tfrac{256}{7}(11\sqrt{3}-19)\alpha+\frac{30\sqrt{2}}{7}\alpha^2\right]>0 .$$

α is a measure for the importance of higher orders due to the linear term compared to the quadratic term in the interaction Hamiltonian. If $K_0^3v_0\sim 1$ and $M\sim m$, it is clear from the condition $V_0\ll mc_0^2$ that the quadratic term yields the dominant contribution, whereas for $M\ll m$ it is the linear term that dominates. Both cases lead to different impurity-mass dependences of the prefactor D_0.

C. The long-time behavior of $K_{11}^{(2)}$ and $K_{12}^{(1)}$

The long-time behavior of $K_{11}^{(2)}$ and $K_{12}^{(1)}$ can be evaluated exactly as for K_2 and one readily obtains

$$K_{11}^{(2)}(t)+2K_{12}^{(1)}(t)+K_2(t)\sim K_2(t)(C_1\alpha^2-C_2\alpha+1) ,$$

with some positive numbers C_1 and C_2. The situation is therefore similar as at low temperature.

VII. A CLASSICAL IMPURITY IN A QUANTUM LATTICE—A DISCUSSION

A rigorous quantum-mechanical treatment is not appropriate here. It is expected that the most interesting quantum effect is the tunneling of small-mass impurities, an issue of quite a different nature than the scattering effects of concern here (for a treatment of quantum tunneling of an impurity, see Ref. 19). Nevertheless, for pedagogical purposes, one can formally quantize the phonon coordinates and momenta and use them to calculate the memory function from (20) for a classical impurity. The classical picture is naturally recovered in the limit as $\hbar\to 0$, but, more importantly, the physics of the dissipation process becomes clear. Phonon quasiparticles collide with the impurity, being scattered, emitted, or absorbed, and conservation equations for energy and momentum can be written to describe the kinematics. This quasiparticle picture reveals the collision events which contribute most to the memory function. In particular, it is found that two-phonon processes which classically yield d_1 are actually due to quasielastic scattering events that nearly conserve the phonon energy from $\hbar\omega_{\mathbf{q}j}$ to $\hbar\omega_{\mathbf{q}'j'}$.

As is normal in the quantum treatment of lattice vibrations, one defines the phonon creation and annihilation operators $a^{\dagger}_{\mathbf{q}j}$ and $a_{\mathbf{q}j}$, respectively, in terms of the normal coordinates. Then, following the procedure of Appendix C, the correlation functions corresponding to (27)–(29) can be written and the dissipation can be evaluated for equations corresponding to (30)–(32).

The quantum selection rule can be derived in an analogous manner to the classical selection rule (33). Letting $\Delta E=\hbar\Omega_n$ and $\Delta P=|\Delta\mathbf{P}|=|\hbar\mathbf{Q}_n|$, one obtains

$$\mathbf{V}_I\cdot\Delta\mathbf{P}=\Delta E-\frac{\Delta P^2}{2M}\ . \qquad (53)$$

By dividing (53) by $\hbar$ and letting $\hbar\to 0$, the classical selection rule (33) is obtained, which is equal to (3). This implies that in (3) the term $\Delta P^2/2M$ is neglected.

ΔE and $\Delta\mathbf{P}$ are the energy and momentum transfer to the impurity, respectively. To see this, consider the kinematics of the impurity-phonon interaction. The equation for the conservation of energy is

$$\frac{P_i^2}{2M}+\sum_{\text{initial}}^{L}\hbar\omega_{\mathbf{q}_{\text{in}}j_{\text{in}}}=\frac{P_f^2}{2M}+\sum_{\text{final}}^{L'}\hbar\omega_{\mathbf{q}_{\text{out}}j_{\text{out}}}\ .$$

The equation for the conservation of impurity and "crystal" momentum is

$$\mathbf{P}_i+\sum_{\text{initial}}^{L}\hbar\mathbf{q}_{\text{in}}=\mathbf{P}_f+\sum_{\text{final}}^{L'}\hbar\mathbf{q}_{\text{out}}+\hbar\mathbf{G}\ ,$$

where $\mathbf{P}_i$ and $\mathbf{P}_f$ are the impurity momenta before and after interaction, respectively, and the sums are taken over initial and final phonon states with wave vectors $\mathbf{q}_{\text{in}}$ and $\mathbf{q}_{\text{out}}$, respectively. There are L phonons going in and L' phonons coming out of the interaction, and $L+L'=n$ in an n-phonon process. Then,

$$\frac{P_f^2}{2M}-\frac{P_i^2}{2M}=\sum_{\text{initial}}^{L}\hbar\omega_{\mathbf{q}_{\text{in}}j_{\text{in}}}-\sum_{\text{final}}^{L'}\hbar\omega_{\mathbf{q}_{\text{out}}j_{\text{out}}}\equiv\hbar\Omega_n\ ,$$

$$\mathbf{P}_f-\mathbf{P}_i=\sum_{\text{initial}}^{L}\hbar\mathbf{q}_{\text{in}}-\sum_{\text{final}}^{L'}\hbar\mathbf{q}_{\text{out}}-\hbar\mathbf{G}\equiv\hbar\mathbf{Q}_n\ ,$$

which are, respectively, the energy transfer and momentum transfer to (i.e., recoil of) the impurity. Then, $\Delta P^2/2M$ in (53), absent in the classical equation (3), can be identified as the recoil energy. The recoil energy is lost whenever inherently quantum-mechanical scattering events are approximated by a classical scattering treatment, and can often be added on as a quantum correction to the classical result (cf. Ref. 20).

To illustrate, consider the one-phonon process in which the two types of interactions for a given wave vector $\mathbf{q}$ are phonon absorption ($L=1$ and $L'=0$, $\mathbf{q}_{\text{in}}=\mathbf{q}$) and phonon emission ($L=0$ and $L'=1$; $\mathbf{q}_{\text{out}}=\mathbf{q}$). In the two-phonon process the four types of interactions for a given pair of wave vectors $\mathbf{q},\mathbf{q}'$ are two-phonon absorption ($L=2$ and $L'=0$; both $\mathbf{q}$ and $\mathbf{q}'$ are $\mathbf{q}_{\text{in}}$), two-phonon emission ($L=0$ and $L'=2$; both $\mathbf{q}$ and $\mathbf{q}'$ are $\mathbf{q}_{\text{out}}$), and two scattering processes, one equivalent to absorption then emission ($L=1$ and $L'=1$; $\mathbf{q}_{\text{in}}=\mathbf{q}$, $\mathbf{q}_{\text{out}}=\mathbf{q}'$), and the other to emission then absorption ($L=1$ and $L'=1$; $\mathbf{q}_{\text{out}}=\mathbf{q}$, $\mathbf{q}_{\text{in}}=\mathbf{q}'$). Similar explanations can be made for higher orders.

The selection rule for normal one-phonon processes is

$$\mathbf{V}_I\cdot\hbar\mathbf{q}=\hbar\omega_{\mathbf{q}j}\pm\frac{\hbar^2q^2}{2M}\ .$$

So, for the Debye approximation, V_I obtained from this equation deviates only slightly from the classical result [obtained from (33)].

The selection rule for normal two-phonon scattering events, where $\mathbf{q}_{\text{in}}=\mathbf{q}$ and $\mathbf{q}_{\text{out}}=-\mathbf{q}'$, yields

$$\mathbf{V}_I\cdot(\hbar\mathbf{q}+\hbar\mathbf{q}')=[\hbar\omega_{\mathbf{q}j}-\hbar\omega_{\mathbf{q}'j'}]-\frac{\hbar^2|\mathbf{q}+\mathbf{q}'|^2}{2M}\ .$$

For $j=j'$ these events become elastic in the limit that $|\mathbf{q}|=|\mathbf{q}'|$, in which case the momentum transfer can be maximized at $2\hbar\mathbf{q}$. Classically, $V_I\to 0$ for $|\mathbf{q}|=|\mathbf{q}'|$, which is a maximum likelihood event, *at any temperature*. An analogous situation exists for all higher-order multiphonon contributions.

VIII. SUMMARY AND CONCLUSIONS

The results of a classical perturbation-theory analysis reveals that activated diffusion is not necessarily of the pure Arrhenius form. The prefactor must be generalized to vary with temperature. The need to generalize the Arrhenius form arises from the evaluation of the friction constant in perturbation theory, and its use in Kramers's high- and low-friction formulas.[4] Using the perturbation-theory formula (2) (truncated to linear order in T) in Kramers's formulas (36a) and (36b) yields

$$D_{\text{high}\,\eta}=zb^2\frac{\omega_A\omega_B}{2\pi(d_0+d_1k_BT)}e^{-E_a/k_BT},\quad \eta\gg 2\omega_B \qquad (54)$$

$$D_{\text{low}\,\eta}=zb^2\frac{(d_0+d_1k_BT)E_a}{k_BT}e^{-E_a/k_BT},\quad \eta\ll 2\omega_A \qquad (55)$$

where the values of d_0 and d_1 are calculated from perturbation theory [cf. (41) and (43)] and E_a is determined from (13). This result is valid when $k_BT\ll Mc_0^2$. For long-range interactions (larger than $\frac{7}{8}$ of a lattice site for a Gaussian interaction) multiphonon effects dominate diffusion so that d_0 and umklapp contributions to d_1 can be ignored. Otherwise, the more general forms (54) and (55) obtain.

It should be noted that E_a is a temperature-dependent quantity whose zero-temperature value is the statically relaxed value E_a^0 [see (13)]. The static value is obtainable from the linear interaction Hamiltonian, the linear temperature coefficient from the quadratic interactions, and so on. To retain a temperature-independent parameter in the exponential of (54) or (55), one may collect the temperature-dependent part of E_a into the prefactor as in (15); but as the linear temperature coefficient of E_a is typically ~ 0.1, then except for very high temperatures (many times room temperature) one may safely ignore the temperature variations due to higher orders than quadratic in the interaction Hamiltonian, thereby taking into account only the rescaling of the prefactor that the linear temperature coefficient introduces.

Although formally the generalized Arrhenius forms (54) and (55) differ significantly from the pure Arrhenius form (1), it should be emphasized that when (1) and (54) or (55) are plotted on the same graph on a logarithmic scale over a temperature range limited to 1 and 2 orders of magnitude the curves can be made to look virtually identical by allowing the activation energy in (1) to differ from the activation energy used in (54) or (55). Thus, if one uses the pure form of (1) to fit data instead of one of the generalized forms, erroneous estimates of the activation energy may result. One can satisfy oneself that fitting an Arrhenius form with a constant prefactor is indistinguishable, for limited ranges of temperature, from fitting an Arrhenius form with a temperature-dependent prefactor by simply adjusting the parameters (including, for example, E_a). It is estimated that errors of the order of 10% in E_a may be incurred by fitting to the wrong form.

The perturbation theory has provided much insight into the physics of dissipation. Selection rules are found to place constraints on which impurity-lattice interactions may contribute to dissipation. The most significant two-phonon effects, as well as higher-order one-phonon umklapp effects, are found to arise from an interaction Hamiltonian which includes terms quadratic in the phonon amplitudes. In addition, as soon as one includes these terms, and/or umklapp process, transverse modes are found to contribute significantly to dissipation. A consideration that should not be overlooked, is that a diffusion-constant calculation using the theory outlined in this paper is significantly simpler and more straightforward than a mode-coupling calculation which typically requires a numerically intensive iteration procedure.

There are obvious drawbacks to a perturbation-theory calculation, mostly having to do with the complexity of higher-order calculation. This is especially true when one considers orders higher than quadratic in phonon amplitudes in the impurity-lattice interaction since, in order to make a consistent perturbation theory, one must include anharmonicities in the lattice Hamiltonian of at least the same order as in the interaction Hamiltonian; lattice anharmonicity is not a critical issue in this paper since the main results arise from interaction terms which are only up to quadratic order. When complexity of calculation becomes prohibitively different (beyond the lowest orders calculated here) mode-coupling theory with (at least) a quadratic interaction Hamiltonian may provide better results, especially at higher temperatures. The latter is particularly valid when $V_0 \gtrsim mc_0^2$, where perturbation theory converges extremely slowly or not at all. A calculation of a spatially varying friction constant was not attempted here for similar reasons. A translationally invariant friction constant is a somewhat restrictive assumption for this problem (cf. Ref. 7).

In spite of these limitations, however, it would be interesting to compare the results of the perturbation theory and mode-coupling theory against simulation results utilizing the Gaussian interaction potential. This would be a test of the accuracy and usefulness of the relatively simple perturbation theory of Arrhenius diffusion described here.

APPENDIX A: GENERALIZATION OF THE LANGEVIN EQUATION

In Ref. 9 a linear Hamiltonian has been assumed and (4) of the text was shown to be valid only up to second order in the potential. This result may be generalized, making (4) correct to within the approximation described by Munakata[9] to any order of perturbation theory and for any Hamiltonian. The notation in this appendix largely follows that of Ref. 9.

Equations (14), (16), (20), (22), and (23) of Ref. 9 are valid generally. Equation (16) of Ref. 9 is simply a statement that $\gamma(\mathbf{G})$ is the Fourier coefficient of $\exp[-\beta U(\mathbf{X})]$. Because of the periodicity it is assumed that the integration over the impurity coordinate runs only over the primitive cell. The crucial point for the generalization is to find the inverse of the matrix $\alpha(\mathbf{G},\mathbf{G}')$. The inverse is

$$\alpha^{-1}(\mathbf{G},\mathbf{G}')=n^2\left[\int d\mathbf{X}_0 e^{-\beta U(\mathbf{X}_0)}\right] \times \int d\mathbf{X}_0 e^{\beta U(\mathbf{X}_0)} e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{X}_0} .$$

Together with (20) and (22) of Ref. 9, it is now easy to show that $(i\hat{\omega}\cdot\mathbf{A})_{\mathbf{P}_I}=-\nabla_{\mathbf{X}_0}U(\mathbf{X}_0)$. Since this does not involve truncation or any assumption about H_I, (4) of the text is valid generally aside from the neglected retarded periodic force term [cf. (28) of Ref. 9].

APPENDIX B. THE TIME EVOLUTION OF THE RANDOM FORCES

The time evolution of the random forces in (4), which is used in the calculation of the memory matrix from (6), is correctly obtained from its initial value using the propagator $\exp(i\Pi L t)$, where L is the Liouville operator,and where Π is the projection operator which projects any dynamical variable onto the space orthogonal to the vector $\mathbf{A}$ used, for example, in Ref. 9. In (17) and (18) of the text, however, it has been assumed implicitly that the time evolution of $\mathbf{f}_l$ is described by the mechanical propagator $\exp(iLt)$. It is the purpose of this appendix to comment on this approximation. The notation of Ref. 9 is used in part.

Let the correlation matrices be defined as

$$\begin{aligned}\boldsymbol{\Psi}(t)&=\langle\, \mathbf{A}(t)\,\mathbf{A}^*(0)\rangle\cdot\mathbf{N}^{-1} ,\\ \boldsymbol{\Theta}(t)&=\langle\, \dot{\mathbf{A}}(t)\,\mathbf{A}^*(0)\rangle\cdot\mathbf{N}^{-1} ,\end{aligned} \tag{B1a}$$

$$\begin{aligned}\boldsymbol{\Phi}(t)&=\langle\, \dot{\mathbf{A}}(t)\,\dot{\mathbf{A}}^*(0)\rangle\cdot\mathbf{N}^{-1} ,\\ \mathbf{K}(t)&=\langle[\Pi\,\dot{\mathbf{A}}](t)[\Pi\,\dot{\mathbf{A}}]^*(0)\rangle\cdot\mathbf{N}^{-1} ,\end{aligned} \tag{B1b}$$

where the correlation functions are normalized by the matrix

$$\mathbf{N}\equiv\langle\, \mathbf{A}(0)\,\mathbf{A}^*(0)\rangle$$

and where the dynamical variables $\mathbf{A}$ are the vectors of Ref. 9.

The quantity of central importance in the generalized Langevin equation is the memory matrix $\mathbf{M}$ (cf. Refs. 11 and 12), which fulfills

$$[s-\boldsymbol{\Theta}(0)+\hat{\mathbf{M}}(s)]\cdot\hat{\boldsymbol{\Psi}}(s)=\mathbf{1}\ , \tag{B2}$$

where $\hat{\phi}(s)$ denotes the Laplace transform of a matrix $\phi(t)$. The direct calculation of $\hat{\mathbf{M}}(0)$ to obtain the diffusion constant in the impurity diffusion problem [cf. (B6) below] is nonperturbative in nature due to the activation effect of the periodic potential seen by the impurity. Any successful perturbation-theoretical approach must separate this effect out from the dissipative effects that are perturbative in nature.

To accomplish this separation Munakata[9] splits $\mathbf{A}$ into two contributions: the impurity momentum $\mathbf{P}$ and the impurity density vector $\mathbf{A}_{\mathbf{G}}$, where $\mathbf{G}$ are nonzero reciprocal-lattice vectors and the mean value (due to the periodic potential) is subtracted out. Thus, all the correlation functions [for example, those in (B1a) and (B1b)] take the form of

$$\Xi\equiv\begin{bmatrix}\Xi^{(PP)} & \Xi^{(PG)}\\ \Xi^{(GP)} & \Xi^{(GG)}\end{bmatrix},$$

$$\Xi^{P}\equiv\begin{bmatrix}\Xi^{(PP)} & 0_{3\times\infty}\\ 0_{\infty\times 3} & 0_{\infty\times\infty}\end{bmatrix},$$

$$\Xi^{G}\equiv\begin{bmatrix}0_{3\times 3} & 0_{3\times\infty}\\ 0_{\infty\times 3} & \Xi^{(GG)}\end{bmatrix},$$

where $0_{3\times 3}$, $0_{3\times\infty}$, $0_{\infty\times 3}$, and $0_{\infty\times\infty}$ are zero matrices of dimensions 3×3, $3\times\infty$, $\infty\times 3$, and $\infty\times\infty$, respectively. The submatrices $\Xi^{(PP)}$ and $\Xi^{(GG)}$ on the diagonal of Ξ are real symmetric matrices. The off-diagonal submatrices $\Xi^{(PG)}$ and $\Xi^{(GP)}$ of Ξ are purely imaginary. One can define the real matrix $\Xi^{D}\equiv\frac{1}{2}(\Xi+\Xi^{+})=\Xi^{P}+\Xi^{G}$ consisting of the diagonal submatrices and the imaginary matrix $\Xi^{\mathrm{OD}}\equiv\frac{1}{2}(\Xi-\Xi^{+})=\Xi-\Xi^{D}$ consisting of the off-diagonal submatrices.

From Appendix A and Ref. 9, it can be noted that

$$[\Pi\,\dot{\mathbf{A}}]_{\mathbf{P}}-[\,\dot{\mathbf{A}}-i\hat{\boldsymbol{\omega}}\cdot\mathbf{A}\,]_{\mathbf{P}}=-\nabla_{\mathbf{X}_0}[H_I-U(\mathbf{X}_0)]\ .$$

Thus, in (16) the effective periodic potential is subtracted out from the impurity-lattice interaction. What remains at time $t=0$ is just the random force which is $[\Pi\,\dot{\mathbf{A}}]_{\mathbf{P}}$. Noting the form of $\mathbf{K}(0)$ from (B1b), one can write

$$\mathbf{K}^{(PP)}(0)=\langle[\Pi\,\dot{\mathbf{A}}(0)]_{\mathbf{P}}[\Pi\,\dot{\mathbf{A}}(0)]_{\mathbf{P}}\rangle\cdot\mathbf{N}^{-1} \tag{B3}$$

$$=\sum_{l,l'}\langle\mathbf{f}_l\mathbf{f}_{l'}\rangle\cdot\mathbf{N}^{-1}\ . \tag{B4}$$

Now, if one forms the time correlation function of (B3) by just inserting the mechanical propagator into (B3) and (B4), one can identify $\mathbf{K}^{(PP)}(t)$ as the correlation function calculated in the text from (6).

Consider now the memory matrix $\mathbf{M}$. It turns out that $\mathbf{M}$ can be written[12] as

$$\mathbf{M}(t)=\langle[e^{i\Pi Lt}\Pi\,\dot{\mathbf{A}}(0)][\Pi\,\dot{\mathbf{A}}(0)]\rangle\cdot\mathbf{N}^{-1}\ . \tag{B5}$$

The relationship of $\mathbf{K}$ to $\mathbf{M}$ then becomes clear: neglecting Π in the propagator in (B5) is tantamount to replacing $\mathbf{M}(t)$ with $\mathbf{K}(t)$. In other words, by subtracting the periodic potential from the initial interaction [e.g., as in (16)] and propagating the random forces forward mechanically in time, the memory term $\mathbf{K}$ is extracted from $\mathbf{M}$. Arguments are given below to show that the perturbation theoretical treatment of $\hat{\mathbf{K}}^{(PP)}(0)$ can be used to evaluate a friction constant appropriate for use in Kramers's formulas.

First, in the text it is shown that the perturbation-theoretical (PT) value $\hat{\mathbf{K}}^{(PP)}_{\mathrm{PT}}(0)$ for $\hat{\mathbf{K}}^{(PP)}(0)$ has a low-temperature behavior that is convergent in all orders of the lattice-impurity interaction Hamiltonian due to the exclusion of the conservative periodic force from the random forces [cf. (4)–(6) of the text]. Perturbation-theoretical values for the other correlation functions, (B1a) and (B1b), all have time integrals that diverge at low temperatures, so $\hat{\mathbf{M}}^{(PP)}_{\mathrm{PT}}(0)$ will also diverge [consider, for example, (B8) below]; this occurs, however, only at higher orders as $\mathbf{K}^{(PP)}_{\mathrm{PT}}$ and $\mathbf{M}^{(PP)}_{\mathrm{PT}}$ are equivalent up to the lowest nonvanishing order.

Second, in the exact theory, the real part of $\hat{\boldsymbol{\Psi}}(0)\cdot\mathbf{N}/M^2$ is the diffusion constant matrix $\mathbf{D}$, where M is the impurity mass. Noting $\mathbf{N}=\mathbf{N}^{D}$, then $\mathbf{D}=\hat{\boldsymbol{\Psi}}^{D}(0)\cdot\mathbf{N}/M^2$. By letting $s=0$ in (B2), the following can be written:

$$\mathbf{D}=[(\hat{\mathbf{M}}(0)-\boldsymbol{\Theta}(0))^{-1}]^{D}\cdot\frac{\mathbf{N}}{M^2}\ . \tag{B6}$$

$\hat{\mathbf{M}}(0)$ contains all the information for the diffusion constant. For impurity diffusion, therefore,

$$\hat{\mathbf{M}}^{(PP)}(0)\sim\mathbf{F}(T)\exp(E_a/k_BT)$$

at low T, where $\mathbf{F}(T)$ is some rational matrix function of T. Thus, $\hat{\mathbf{M}}^{(PP)}(0)$ contains information about the activation barrier which should be excluded from a friction constant to be used in Kramers's formula (where the effect of the periodic potential has already been extracted).

Third, note that the formal relation between $\mathbf{K}$ and $\mathbf{M}$ is[12]

$$\hat{\mathbf{K}}(s)=\hat{\mathbf{M}}(s)-\hat{\mathbf{M}}(s)\cdot\hat{\boldsymbol{\Psi}}(s)\cdot\hat{\mathbf{M}}(s)\ . \tag{B7}$$

This can be rewritten by using (B2) in the second term on the right-hand side of (B4) to obtain

$$\hat{\mathbf{K}}(s)=\hat{\mathbf{M}}(s)\cdot[1+\hat{\boldsymbol{\Theta}}(s)-\hat{\boldsymbol{\Psi}}(s)\cdot\boldsymbol{\Theta}(0)]\ . \tag{B8}$$

Then, from (B2) and (B8) evaluated at $s=0$, and using the fact that $1+\hat{\boldsymbol{\Theta}}(0)=0$, one obtains

$$\hat{\mathbf{K}}(0)=-\boldsymbol{\Theta}(0)-\boldsymbol{\Theta}(0)\cdot\hat{\boldsymbol{\Psi}}(0)\cdot\boldsymbol{\Theta}(0)\ . \tag{B9}$$

Computing the submatrix $\hat{\mathbf{K}}^{(PP)}(0)$ then yields

$$\begin{aligned}\hat{\mathbf{K}}^{(PP)}(0)&=-\boldsymbol{\Theta}^{(PG)}(0)\cdot\hat{\boldsymbol{\Psi}}^{(GG)}(0)\cdot\boldsymbol{\Theta}^{(GP)}(0)\\&=\frac{\beta}{M}\int_0^\infty dt\,\langle\nabla U(\mathbf{X}_0)e^{iLt}\nabla U(\mathbf{X}_0)\rangle\\&=\frac{1}{M}\int_0^\infty dt\int\frac{d\mathbf{P}}{Z_P}e^{-\beta(P^2/2M)}\\&\qquad\times\int\frac{d\mathbf{X}_0}{Z_X}e^{-\beta U(\mathbf{X}_0)}\nabla e^{i\tilde{L}t}\nabla U(\mathbf{X}_0)\ ,\end{aligned} \tag{B10}$$

where Z_P and Z_X are the partition functions of the impurity coordinate and impurity, respectively, and where $\tilde{L}$ is defined by $e^{i\tilde{L}t}=\langle e^{iLt}\rangle_{\text{lattice}}$. If only the free part of $\tilde{L}$ is retained, one obtains a $\hat{\mathbf{K}}^{(PP)}(0)$ which diverges at low T and which contains contributions from the periodic potential. Of course, this is precisely what one does not want to do for low temperatures [i.e., the diffusion constant calculated using $\hat{\mathbf{K}}^{(PP)}(0)$ just becomes a power series in temperature and one loses the exponential activation effect—this is due to expanding about a free motion when the impurity is basically trapped at low temperatures]. This approach may be used somewhat more effectively, however, for $k_BT \gtrsim E_a$, where the impurity moves more freely through the lattice (cf. Ref. 10). On the other hand, the text shows that the perturbation-theoretical calculation of $\hat{\mathbf{K}}_{\text{PT}}^{(PP)}(0)$ directly from the definition in (B1b) does not diverge at low T. Therefore, $\mathbf{K}_{\text{PT}}(t)$ has different long-time properties than the exact correlation function $\mathbf{K}(t)$, i.e., in $\mathbf{K}_{\text{PT}}(t)$ the nonperturbative effects of activation are separated out (cf. theorem 3 in Sec. VI).

Finally, in the derivation of (4) of the text, the submatrix $\mathbf{M}^{(PG)}$ has been neglected.[9] The neglected part is a memory effect due to the periodic potential. Omission of this term in (B8) and the off-diagonal part $\hat{\mathbf{\Psi}}^{(PG)}(0)$ leads to

$$\hat{\mathbf{K}}^{(PP)}(0)=\hat{\mathbf{M}}^{(PP)}(0)\cdot[1+\hat{\Theta}^{(PP)}(0)]\ . \tag{B11}$$

In the text the dominant contributions to $\hat{\mathbf{K}}_{\text{PT}}(0)$ come from processes which fulfill the selection rule (3). Inclusion of $\hat{\Theta}_{\text{PT}}^{(PP)}(0)$ causes the violation of the selection rules due to contributions of virtual processes.[21,22] This is unphysical for low temperatures as phonons have perfectly well-defined energies and momenta, and impurity-phonon collisions should conserve energy and momentum. In a perturbative treatment, therefore, these terms should be ignored.

Summarizing, in this work the friction-constant matrix obtained in the Markov approximation of (4) is $\hat{\mathbf{K}}^{(PP)}(0)$. A perturbative treatment works because it does not contain nonperturbative activation effects. This makes it a suitable choice for calculating a friction constant to be used in Kramers's formulas. In another context (soliton diffusion in nonlinear Klein-Gordon theories[21]) it has also been shown that in perturbation theory $\hat{\mathbf{K}}(0)$ is the appropriate friction constant. Note that the second and third points above show that in the exact theory of impurity diffusion neither $\hat{\mathbf{K}}(0)$ nor $\hat{\mathbf{M}}(0)$ can be used as friction constants in Kramers's formula, as they contain too much information about the activation barrier. In Sec. 3 of Ref. 12 one finds a discussion of the differences between $\mathbf{M}$ and $\mathbf{K}$ in the exact theory (denoted in Ref. 12 by ϕ and Φ, respectively).

APPENDIX C: DERIVATION OF THE MEMORY FUNCTION

For simplicity anharmonicity in H_0 is neglected. In this case small fluctuations are linear, and the phonon correlation function in (25) for $n=1$ becomes

$$\langle u_\alpha(l;t)u_\gamma(l';0)\rangle_0=\frac{k_BT}{Nm}\sum_{\mathbf{q},j}\Psi_{\alpha\gamma}(\mathbf{q}j)\frac{\cos(\omega_{\mathbf{q}j}t)}{\omega_{\mathbf{q}j}^2}e^{-i\mathbf{q}(\mathbf{x}_l-\mathbf{x}_{l'})}\ . \tag{C1}$$

Higher-order correlations are treated in the normal way. Thus, for example,

$$\langle u_{\alpha_1}(l;t)u_{\alpha_2}(l;t)u_{\gamma_1}(l';0)u_{\gamma_2}(l';0)\rangle_0\simeq\sum_{j=1,2}\langle u_{\alpha_j}(l;t)u_{\gamma_1}(l';0)\rangle_0\langle u_{\alpha_{3-j}}(l;t)u_{\gamma_2}(l';0)\rangle_0\ , \tag{C2}$$

$$\begin{aligned}\left\langle\prod_{j=1}^{3}u_{\alpha_j}(l;t)u_{\gamma_j}(l';0)\right\rangle_0\simeq&\sum_{9}\langle u_{\alpha_1}(l;t)u_{\alpha_2}(l';t)\rangle_0\langle u_{\gamma_1}(l;0)u_{\gamma_2}(l';0)\rangle_0\langle u_{\alpha_3}(l;t)u_{\gamma_3}(l';0)\rangle_0\\&+\sum_{6}\langle u_{\alpha_1}(l;t)u_{\gamma_1}(l';0)\rangle_0\langle u_{\alpha_2}(l;t)u_{\gamma_2}(l';0)\rangle_0\langle u_{\alpha_3}(l;t)u_{\gamma_3}(l';0)\rangle_0\ ,\end{aligned} \tag{C3}$$

where $\sum_k$ indicates that there are k similar terms obtained by combining the α's with different γ's and the static correction term in (C2) has been omitted [see (17) and discussion in text].

To be consistent in the perturbation theory (which is to order V^2—weak impurity-phonon coupling), it is assumed that $X\approx X_0+(\mathbf{P}/M)t$ in (25), so the following change of variables is made:

$$\boldsymbol{\mu}=K_0(\mathbf{x}_l-\mathbf{X}_0),\quad d\mathbf{X}_0=-d\boldsymbol{\mu}/K_0^3\ ,$$

$$\xi=K_0\left[\mathbf{x}_{l'}-\mathbf{X}_0-\frac{P}{M}t\right],\quad d\mathbf{P}=-d\xi\left[\frac{M}{K_0t}\right]^3 .$$

Note that $1/K_0$ is the length scale of the potential. It is assumed that $V(\mathbf{r})=V[\zeta]$, where $\zeta\equiv K_0\mathbf{r}$, so that $W(l;t)\to W[\zeta]$. The inclusion of K_0 facilitates the evaluation of the memory function and the friction constant. For example, explicit evaluation of the η_i is made in the text for the Gaussian potential $V_0\exp(-K_0^2r^2)$.

Now, (25) may be written

$$K_n(t)=\frac{1}{3Mk_BT}\frac{1}{Z_XZ_PK_0^6}\left[\frac{M}{t}\right]^3\int d\xi\,W_\alpha^{\gamma(n)}[\xi]\int d\boldsymbol{\mu}\,W_\alpha^{\gamma'(n)}[\boldsymbol{\mu}]\sum_{l,l'}e^{-\beta z_{l,l'}^2M/2t^2}\langle\mathbf{u}_{\gamma(n)}(l;t)\mathbf{u}_{\gamma'(n)}(l';0)\rangle_0\ , \tag{C4}$$

where

$$\mathbf{z}_{l,l'}=\mathbf{x}_{l'}-\mathbf{x}_l+\frac{\boldsymbol{\mu}-\boldsymbol{\xi}}{K_0}\ ,$$
$$W_\alpha^{\gamma(n)}[\boldsymbol{\mu}]\equiv[W_\alpha^{\gamma(n)}(l;t)]_{\mathbf{x}_l-\mathbf{X}=\boldsymbol{\mu}/K_0}\ . \tag{C5}$$

Now, using the following formula,

$$e^{-x^2/4a}=(a/\pi)^{3/2}\int d\mathbf{r}\,e^{-i\mathbf{r}\cdot\mathbf{z}}e^{-ar^2}\ , \tag{C6}$$

and the fact that

$$\sum_{l,l'}e^{-i(\mathbf{r}-\mathbf{q})\cdot(\mathbf{x}_l-\mathbf{x}_{l'})}=(2\pi)^3\frac{N}{v_0}\sum_{\mathbf{G}}\delta(\mathbf{r}-\mathbf{q}-\mathbf{G})\ , \tag{C7}$$

where the sum runs over all reciprocal-lattice vectors **G**, Eqs. (C6) and (C7) can be inserted in (C4) to yield the one-phonon contribution (27) of the text. This method was devised to study kink transport in the ϕ^4 theory.[10] In a similar fashion, the two- and three-phonon memories can be obtained using (C2) and (C3), respectively, to obtain (28) and (29) of the text.

APPENDIX D: DERIVATION OF THE SELECTION RULES

The basic method outlined here has been used to study kink diffusion in polyacetylene and can be found in Ref. 22. First compute $K_1(t)$. Start from (C5) and define

$$[W_\alpha^{\gamma(n)}(l;t)]_{\mathbf{x}_l-\mathbf{X}=\boldsymbol{\zeta}/K_0}\equiv W_\alpha^{\gamma(n)}[\boldsymbol{\zeta}]$$
$$=\frac{1}{(2\pi)^3}\int d\mathbf{r}\,e^{-i\mathbf{r}\cdot\boldsymbol{\zeta}}\hat{W}_\alpha^{\gamma(n)}[\mathbf{r}]\ , \tag{D1}$$

where $\hat{W}$ is the inverse Fourier transform

$$\hat{W}_\alpha^{\gamma(n)}[\mathbf{r}]=\int d\boldsymbol{\zeta}\,e^{i\mathbf{r}\cdot\boldsymbol{\zeta}}W_\alpha^{\gamma(n)}[\boldsymbol{\zeta}]\ . \tag{D2}$$

This yields

$$K_1(t)=\frac{1}{3Mk_BT}\frac{1}{Z_XZ_P}\frac{1}{(2\pi)^6}\sum_{l,l'}\int d\mathbf{X}_0\int d\mathbf{P}\,e^{-\beta P^2/2M}$$
$$\times\int d\mathbf{r}_1\hat{W}_\alpha^{\gamma_1}[\mathbf{r}_1]e^{-i\mathbf{r}_1\cdot\boldsymbol{\zeta}_1(t)}\int d\mathbf{r}_2\hat{W}_\alpha^{\gamma_2}[\mathbf{r}_2]e^{-i\mathbf{r}_2\cdot\boldsymbol{\zeta}_2(0)}$$
$$\times\frac{k_BT}{Nm}\sum_{\mathbf{q},j}\Psi_{\gamma_1\gamma_2}(\mathbf{q}j)\frac{\cos(\omega_{\mathbf{q}j}t)}{\omega_{\mathbf{q}j}^2}e^{-i\mathbf{q}\cdot(\mathbf{x}_l-\mathbf{x}_{l'})}\ . \tag{D3}$$

Note that in (D3) $\boldsymbol{\zeta}_1(t)\equiv K_0(\mathbf{x}_l-\mathbf{X}(t))$, and $\boldsymbol{\zeta}_2(0)=K_0(\mathbf{x}_{l'}-\mathbf{X}_0)$. When the sum over l,l' is performed, one obtains two sums over reciprocal-lattice vectors,

$$\frac{(2\pi)^3}{v_0}\sum_{\mathbf{G}_{1,2}}\delta(K_0\mathbf{r}_{1,2}\pm(\mathbf{q}+\mathbf{G}_{1,2}))\ ,$$

where the ± is taken for $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively. Expand $\cos(\omega_{\mathbf{q}j}t)$ into exponentials, use the perturbation approximation $\mathbf{X}(t)\cong\mathbf{X}_0+t\mathbf{P}/M$, perform the integral over $\mathbf{X}_0$ yielding the equality of the $\mathbf{G}_{1,2}$ vectors, and take the real part of the time integral of the result to obtain

$$\eta_1=\mathrm{Re}\left[\int_0^\infty dt\,K_1(t)\right]=\frac{\pi}{3M}\frac{1}{Z_P}\frac{1}{NmK_0^6v_0^2}\int d\mathbf{P}\,e^{-\beta P^2/2M}\sum_{\mathbf{q},j}\sum_{\mathbf{G}}\left|\hat{W}_\alpha^{\gamma_1}\left[\frac{\mathbf{q}+\mathbf{G}}{K_0}\right]\hat{W}_\alpha^{\gamma_2}\left[\frac{\mathbf{q}+\mathbf{G}}{K_0}\right]\right|$$
$$\times\frac{\Psi_{\gamma_1\gamma_2}(\mathbf{q}j)}{2\omega_{\mathbf{q}j}^2}\left[\delta\left[\omega_{\mathbf{q}j}+\frac{\mathbf{P}}{M}\cdot(\mathbf{q}+\mathbf{G})\right]+\delta\left[\omega_{\mathbf{q}j}-\frac{\mathbf{P}}{M}\cdot(\mathbf{q}+\mathbf{G})\right]\right]\ ,$$

where δ is the Dirac delta function. This yields the selection rule (33) in the text, and upon integrating over momentum yields (30) of the text. Similar treatments yield the selection rule for the multiphonon interactions.

APPENDIX E: PROOFS OF HIGHER-ORDER THEOREMS 1, 2, AND 3

1. Proof of theorem 1

The object is to prove that the low-temperature behavior of the higher-order terms,

$$K_{mn}^{(r)}\equiv\sum_{\substack{j,k\\(j+k=r)}}K_{mn}^{(jk)}\ , \tag{E1}$$

obeys the power law in T indicated in the text when only the linear term in the interaction Hamiltonian is considered. Thus, the evaluation of the behavior of the operator

$$[-\beta H_I(0)]^k\Lambda_j(t)$$

needs to be made, for $j+k=r$ [see (24) in text]. This will be done below for $r=2$ as an example.

First, note that $H_I^{(j)}$, $j\geq 1$, consists of products of the jth derivative of the potential (the potential part) and the jth power in the components of the displacements $\mathbf{u}_l$ (the phonon part). Then, the Liouville operators in Eq. (E1) are expressed as a sum of two operators,

$$L_I^{(j)}(\tau)=\hat{L}_I^{(j)}(\tau)+\bar{L}_I^{(j)}(\tau)\ , \tag{E2}$$

where $\hat{L}_I^{(j)}(\tau)$ involves the Poisson bracket of the potential part of $H_I^{(j)}(\tau)$ with the potential part of H_I at other times, and $\bar{L}_I^{(j)}(\tau)$ involves the Poisson bracket of the phonon part of $H_I^{(j)}(\tau)$ with the phonon part of H_I at other times; all cross terms in potential parts and phonon parts vanish. For convenience, make the following definition:

$$\Gamma_r \equiv \sum_{\substack{j,k \\ (j+k=r)}} \frac{[-\beta H_I(0)]^k}{k!} \Lambda_j(t) .$$

Then, for $r=2$ the following is true:

$$\Gamma_2 = \int_0^t d\tau\, iL_I^{(1)}(\tau) \int_\tau^t d\tau' iL_I^{(1)}(\tau') - \beta H_I^{(1)}(0) \int_0^t d\tau\, iL_I^{(1)}(\tau) + \frac{\beta^2}{2}[H_I^{(1)}(0)]^2$$

$$= \int_0^t d\tau\, i\hat{L}_I^{(1)}(\tau) \int_\tau^t d\tau' iL_I^{(1)}(\tau') - \beta \int_0^t d\tau \sum_l V_\gamma[\mathbf{x}_l - \mathbf{X}(\tau)]\{\dot{u}_\gamma(l;\tau)\}_R \int_\tau^t d\tau' iL_I^{(1)}(\tau')$$

$$- \beta H_I^{(1)}(0) \int_0^t d\tau\, iL_I^{(1)}(\tau) + \frac{\beta^2}{2}[H_I^{(1)}(0)]^2 ,$$

where the decomposition (E2) has been used, $V_\gamma[\mathbf{x}_L - \mathbf{X}(\tau)]$ denotes the partial derivative of V with respect to $u_\gamma(l)$, and the notation $\{\ \}_{R,L}$ is used to signify that the phonon amplitudes within the curly braces should be correlated only with phonon amplitudes to its right (R) or left (L). Use has been made of formula (13) in Ref. 13 which introduces the time derivative [i.e., $\dot{u}_\gamma(l)$]. Partial integration yields

$$\Gamma_2 = \int_0^t d\tau\, i\hat{L}_I^{(1)}(\tau) \int_\tau^t d\tau' iL_I^{(1)}(\tau') + \beta \int_0^t d\tau \sum_l \{u_\gamma(l;\tau)\}_R \frac{\partial}{\partial \tau} \left[V_\gamma[\mathbf{x}_l - \mathbf{X}(\tau)] \int_\tau^t d\tau' iL_I^{(1)}(\tau') \right]$$

$$- \beta\{H_I^{(1)}(0)\}_L \int_0^t d\tau\, iL_I^{(1)}(\tau) + \frac{\beta^2}{2}[H_I^{(1)}(0)]^2 .$$

By executing the derivatives with respect to τ, the derivative of the potential yields a factor of $-\beta\mathbf{P}/M$, which results equivalently from

$$\nabla_{\mathbf{P}} e^{-\beta P^2/2M} ,$$

and this fact can be used to write

$$\Gamma_2 = \int_0^t d\tau\, i\hat{L}_I^{(1)}(\tau) \int_\tau^t d\tau' iL_1^{(1)}(\tau') - \frac{\partial}{\partial P_\delta} \int_0^t d\tau \sum_l \{u_\gamma(l;\tau)\}_R V_{\gamma\delta}[\mathbf{x}_l - \mathbf{X}(\tau)] \int_\tau^t d\tau' iL_1^{(1)}(\tau')$$

$$- \beta\{H_I^{(1)}(0)\}_L \int_0^t d\tau\, iL_I^{(1)}(\tau) - \beta \int_0^t d\tau \{H_I^{(1)}(\tau)\}_R iL_I^{(1)}(\tau) + \frac{\beta^2}{2}[H_I^{(1)}(0)]^2 .$$

The same procedure can now be applied to the second Liouville operator. It has to be noted that if one replaces the factor $-\beta\mathbf{P}/M$ by the derivative of the exponential $\exp(-\beta P^2/2M)$, one has to take care because of the noncommutativity of $\mathbf{P}$ with the Liouville operators and with the derivative $\nabla_{\mathbf{P}}$. But these contributions cancel each other.

This method works to every order of r. The general result is

$$K_{mn}^{(r)} = \frac{\beta}{3M} \int \frac{d\mathbf{X}_0 d\mathbf{P}}{Z_X Z_P} e^{-\beta P^2/2M} \sum_{l,l'} \langle W_\alpha^{\gamma(n)}(l;0) \mathbf{u}_{\gamma(n)}(l;0) \mathbf{I} W_\alpha^{\gamma'(m)}(l';t) \mathbf{u}_{\gamma'(m)}(l';t) \rangle_{\text{free}} , \tag{E3}$$

where $\mathbf{I}$ is the following operator:

$$\mathbf{I} \equiv \sum_{\substack{j,k \\ (j+k \le r)}} \frac{1}{j!}(-\beta\{H_I^{(1)}(0)\}_L)^j I^{r-(j+k)} \frac{1}{k!}(-\beta\{H_I^{(1)}(t)\}_R)^k , \tag{E4}$$

where $I^{(M)}=1$ for $M=0$, and otherwise is the sum of time-ordered terms,

$$I^{(M)} = \frac{1}{M!} \mathbf{T} \sum_{m=0}^{M} \left[-\frac{\partial^m}{\partial \mathbf{P}_{\gamma(m)}} \right] \left[\int_0^t d\tau\, i\hat{L}_1^{(1)}(\tau) \right]^{M-m} \prod_{j=1}^{m} \sum_l \int_0^t d\tau \{u_\delta(l;\tau)\}_R V_{\delta\gamma_j}[\mathbf{x}_l - \mathbf{X}(\tau)] , \tag{E5}$$

for $M \ge 1$, where $\mathbf{T}$ is the time-ordering operator and where

$$\partial \mathbf{P}_{\gamma(n)} \equiv \partial P_{\gamma_1} \cdots \partial P_{\gamma_n} ,$$

in a manner similar to $\mathbf{u}_{\gamma(n)}$ and $\mathbf{Q}_l^{\gamma(n)}$ in the text. Equations (E3)–(E5) can be used in actual calculations, and are the main results of this Appendix.

Theorem 1 is a simple corollary of (E4) and (E5). First, note that correlations among $\beta H_I^{(1)}(0)$ factors in (E4) are terms coming from $\exp[-\beta U(\mathbf{X}_0)]$ and are excluded. Further, the result of contracting the terms $W_\alpha^{\gamma(n)}(l';0)\mathbf{u}_{\gamma(n)}(l';0)$ and $W_\alpha^{\gamma'(m)}(l;t)\mathbf{u}_{\gamma'(m)}(l;t)$ completely with $\beta H_I^{(1)}$ factors, as in

$$\langle W_\alpha^{\gamma(m)}(l;0)\mathbf{u}_{\gamma(m)}(l;0)[-\beta H_I^{(1)}(0)]^m\rangle ,$$

has also to be excluded for all $m \geq 1$, because such static contributions are also included in the periodic potential $U(\mathbf{X})$. Assume now that $r \geq m+n-2$. Then, the low-temperature behavior is dominated by the terms

$$K_{mn}^{(r)} = \frac{\beta}{3M}\int \frac{dX_0 d\mathbf{P}}{Z_X Z_P} e^{-\beta P^2/2M} \times \sum_{l,l'} \Big\langle W_\alpha^{\gamma(n)}(l';0)\mathbf{u}_{\gamma(n)}(l';0)\frac{1}{(n-1)!}(-\beta\{H_I^{(1)}(0)\}_L)^{n-1} \times I^{(r+2-m-n)}\frac{1}{(m-1)!}(-\beta\{H_I^{(1)}(t)\}_R)^{m-1} W_\alpha^{\gamma'(m)}(l;t)\mathbf{u}_{\gamma'(m)}(l;t)\Big\rangle_{\text{free}} , \tag{E6}$$

which, at low temperatures, behave as

$$T^{|r+2-m-n|/2} .$$

In the special case $m+n=r+2$, the above contribution gives rise to a genuine one-phonon process which, in the first Brillouin zone, yields a friction constant which is exponentially damped at low temperature. Therefore, disregarding umklapp processes, the main contribution comes from at least one correlation with $\beta H_I^{(1)}$ less leading to linear-T behavior from a genuine two-phonon process.

If $r < m+n-2$, then it is even simpler, since correlating the phonon fields from the border terms $W_\alpha^{\gamma(n)}(l';0)\mathbf{u}_{\gamma(n)}(l';0)$ and $W_\alpha^{\gamma'(m)}(l;t)\mathbf{u}_{\gamma'(m)}(l;t)$ with r phonon fields from $\beta H_I^{(1)}(0)_L$ and $\beta H_I^{(1)}(t)_R$ with $m+n-r$ phonon fields remaining yields a dependence

$$T^{|m+n-r-2|/2} .$$

2. Proof of theorem 2

The goal of this section is to prove the power-law behavior in T of the memory function for a *general* interaction Hamiltonian at low temperatures. The low-temperature behavior of $K_{mn}^{(r)}$ is dominated by the contributions from the linear term $H_L^{(1)}$ and the quadratic term $H_I^{(2)}$ since the higher orders introduce more than three phonon fields which do not bring the behavior of η below the linear dependence upon T. This is in spite of the prefactor of β multiplying $H_I^{(j)}$, $j \geq 3$, which is overcome by the phonon fields that introduce factors which vary at least as $\beta^{-3/2}$.

From the proof of theorem 1 it should be clear that the main contribution at low temperature for $r \geq m+n-2$ is from terms like (E6), where the operator I which includes only linear terms $H_I^{(1)}$ is replaced by an operator J, say, which includes all orders of H_I. For $r < m+n-2$ the dominant contributions come from terms where as many phonon fields as possible are correlated with phonon fields from the $\beta H_I^{(1)}$ factors; in this case the operator $J=1$, and comes within the bounds of theorem 1.

In the case where $r \geq m+n-2$ the operator $J^{(r+2-m-n)}$ involves at least $r+2-m-n$ "internal" phonon fields which have to be correlated among themselves and with the two remaining "external" phonon fields from the border terms $W_\alpha^{\gamma(n)}(l';0)\mathbf{u}_{\gamma(n)}(l';0)$ and $W_\alpha^{\gamma'(m)}(l;t)\mathbf{u}_{\gamma'(m)}(l;t)$ in (E3). The internal phonon fields come from Liouville operators $iL_I^{(k)}$, and from $\beta H_I^{(k)}$, $k \geq 1$. If $k \geq 2$, then one does not miss any inverse powers of T by counting the contribution as $T^{k/2-1}$ (-1 from β and $k/2$ from the phonon fields). If $k=1$ still no inverse power of T is introduced because such inverse powers can only arise from terms coming from $\exp[-\beta U(\mathbf{X}_0)]$ which are excluded. This shows that the operator J in the worst case gives rise to a constant at low temperature. It remains to show that genuine n-phonon processes always reduce at least $n-1$ factors of β, leading to T^{n-1} behavior of $K_{mn}^{(r)}$ at low T.

The origins at time 0 of additional genuine phonons are either the border term or $\beta H_I^{(j)}$ factors, or they come from the lower integration limits of the Liouville operators $iL_I^{(k)}$. There might be some intermediate scattering with other phonons, but the ultimate origins are always the border term or a $\beta H_I^{(i)}$ factor and a Liouville operator $iL_I^{(1)}$ in both of which all the phonon fields have to be correlated to the right. In the first case there is one $\beta H_I^{(1)}$ factor less and therefore one power of T more. In the second case the β factor can again be reduced quite in analogy to the proof of theorem 1. Although one deals here with different kinds of Liouville operators, not just with $iL_I^{(1)}$, the cancellation mechanism works by summing over all possible orderings of these Liouville operators, due to the following commutation property.

Let in both $H_I^{(j)}(0)$ and in the corresponding Liouville operator $iL_I^{(j)}(\tau)$ all j phonon fields be correlated with phonon fields at later times. Then by using formula (13) of Ref. 13 and by performing partial integration as in the proof of theorem 1, one obtains, for a typical combination with some other Liouville operator $L_I^{(k)}$, $k \geq 1$,

$$\int_{\tau_1}^{t} d\tau\, i\bar{L}_I^{(j)}(\tau) \int_{\tau}^{t} d\tau' iL_I^{(k)}(\tau') - \beta H_I^{(j)}(\tau_1) \int_{\tau_1}^{t} d\tau' iL_I^{(k)}(\tau') = \beta \int_{\tau_1}^{t} d\tau \sum_{l} \mathbf{u}_{\gamma(j)}(l;\tau) \frac{\partial}{\partial\tau} \left[V_{\gamma(j)}[\mathbf{x}_l - \mathbf{X}(\tau)] \int_{\tau}^{t} d\tau' iL_I^{(k)}(\tau') \cdots \right] . \tag{E7}$$

where $V_{\gamma(n)}$ is given in (6) of the text. The derivative of the potential leads to a term proportional to **P** which can be reduced to a derivative with respect to **P** without the β factor in front, as in the proof of theorem 1. The derivative of the integral yields a term like

$$-\beta \int_{\tau_1}^{t} d\tau\, H_I^{(j)}(\tau) iL_I^{(k)}(\tau) , \tag{E8}$$

which cancels against a term from the commuted version of the first term in (E7),

$$\int_{\tau_1}^{t} d\tau\, iL_I^{(k)}(\tau) \int_{\tau}^{t} d\tau' i\bar{L}_I^{(j)}(\tau') = \beta \int_{\tau_1}^{t} d\tau\, iL_I^{(k)}(\tau) H_I^{(j)}(\tau) - \beta \int_{\tau_1}^{t} d\tau\, iL_I^{(k)}(\tau) H_I^{(j)}(t) \cdots \Big|_{\tau'=t} + \cdots , \tag{E9}$$

where the last term again involves derivatives with respect to τ' of the potential and of integrals having τ' as integration limits. The factor $\beta\mathbf{P}/m$ coming from the derivative of the potential can be commuted through $L_I^{(k)}$ and reduced to a derivative with respect to **P**. The contribution from the commutator can be cancelled by applying the same procedure to $L_I^{(k)}$, again similar to the proof of theorem 1.

Finally, if several genuine phonons have the same ultimate origin, then interaction Hamiltonians $H_I^{(k)}$ with $k \geq 3$ are involved, giving the appropriate power in T.

3. Proof of theorem 3

Equation (23) of the text can be written in the form

$$K(t) = \frac{\int d\mathbf{X}_0 e^{-\beta U(\mathbf{X}_0)} B(\mathbf{X}_0)}{\langle e^{-\beta H_I} \rangle_{\text{free}}} , \tag{E10}$$

where $B(\mathbf{X}_0)$ comes from the sum of contributions as in Eq. (24) and is a periodic function of the lattice. It can therefore be represented as a Fourier sum over the reciprocal-lattice vectors:

$$B(\mathbf{X}_0) = \sum_{\mathbf{G}} \hat{B}(\mathbf{G}) \exp(i\mathbf{G}\cdot\mathbf{X}_0) . \tag{E11}$$

$U(\mathbf{X}_0)$ itself is, of course, also such a Fourier sum,

$$U(\mathbf{X}_0) = \frac{1}{v_0} \sum_{\mathbf{G}} \hat{U}(\mathbf{G}) \exp(i\mathbf{G}\cdot\mathbf{X}_0) , \tag{E12}$$

where $\hat{U}(\mathbf{q})$ is the Fourier transform of the effective potential in Sec. III. At low temperatures the dominant contribution comes from $\mathbf{X}_0 = \mathbf{Y}_0 \equiv (b/2)(1,1,1)$ in the middle between two lattice sites in each direction, where $\exp(i\mathbf{G}\cdot\mathbf{X}_0) = (-1)^n$, $n = \mathbf{G}\cdot\mathbf{Y}_0/\pi$, so that

$$K(t) = \sum_{\mathbf{G}} \hat{B}(\mathbf{G})(-1)^{\mathbf{G}\cdot\mathbf{Y}_0/\pi} . \tag{E13}$$

As an illustration, assume that the dominant contributions to $U(\mathbf{X}_0)$ come from the boundary of the first Brillouin zone:

$$H_I^{(0)} = \frac{1}{b}\hat{U}(0) + \frac{2}{v_0} \sum_{i=1}^{3} \hat{U}(\mathbf{G}_i) \cos(\mathbf{G}_i\cdot\mathbf{X}_0) , \tag{E14}$$

where $\mathbf{G}_i$ is a reciprocal-lattice vector in the ith direction of length $|\mathbf{G}_i| = 2\pi/b$. Then,

$$K(t) = \sum_{\mathbf{G}} \hat{B}(\mathbf{G})(-1)^{\mathbf{G}\cdot\mathbf{Y}_0/\pi} \prod_{i=1}^{3} \frac{I_{n_i}\left[\frac{2}{v_0}\beta\hat{U}(\mathbf{G}_i)\right]}{I_0\left[\frac{2}{v_0}\beta\hat{U}(\mathbf{G}_i)\right]} , \tag{E15}$$

where the n_i $(i=1,2,3)$ are determined from $\mathbf{G} = (2\pi/b)(n_1,n_2,n_3)$, and the I_n are modified Bessel functions.[17] As these functions have the same asymptotic behavior for larger arguments irrespective of the order, the same result as before is obtained for low temperature.

It remains to show that the inclusion of the Liouville operators $iL_I^{(0)}$ does not affect the linear low-temperature behavior of terms as in Eq. (24). Because of Poisson brackets derivatives of $H_I^{(0)}$ will be taken and powers in the reciprocal-lattice vectors will appear. If one considers only normal (as opposed to umklapp) processes, one does not get any contributions from such Liouville operators and, therefore, any changes in the temperature behavior will be proportional to $\hat{V}(\mathbf{G})/V_0 v_0$, where $\mathbf{G} \neq \mathbf{0}$ is a reciprocal-lattice vector, or products of such elements. After performing all Poisson brackets, the low-temperature limit can be obtained by setting the impurity position $\mathbf{X}_0$ everywhere equal to $\mathbf{Y}_0$, except in $\exp[-\beta U(\mathbf{X}_0)]$, and the momentum **P** everywhere equal to zero, except in $\exp(-\beta P^2/2M)$. This procedure will neglect single-phonon normal processes which vanish exponentially at low T, but the indicated limit will at least take care of the dominant low-temperature behavior of single-phonon umklapp and multiphonon processes. Then, from the commutation property (E7)–(E9) proven in the proof of theorem 2, it is seen that $iL_I^{(0)}$ factors would not affect the low-temperature behavior at all unless they prohibit cancellation mechanisms which work without their inclusion. Unfortunately, this actually happens. Setting $k=0$ in (E7)–(E9) the emerging factor $\beta\mathbf{P}/M$ in (E9) gives as the argument of $L_I^{(0)}$ a contribution which does not get cancelled because the "partial-integration" procedure cannot be applied to $L_I^{(0)}$. What one can still assert is that in order to get a nonvanishing contribution in the low-temperature limit indicated above ($\mathbf{X}_0 \to \mathbf{Y}_0$, $\mathbf{P} \to \mathbf{0}$), some Poisson bracket has to be applied to the first appearing $L_I^{(0)}$ in Eq. (24) (otherwise, one would have a sum over an odd power of reciprocal-lattice vectors), reducing at least one β factor. Therefore all contributions vanish at least linearly in T at low T.

It can be noted that the effect of the time evolution due to $H_I^{(0)}$ can be taken into account by solving the equations of motion for such a potential iteratively and by replacing in Eq. (24) with all contributions from $L_I^{(0)}$ excluded the zero-order solutions $\mathbf{X}(\tau)=\mathbf{X}_0+\mathbf{P}\tau/M$ by these iterative solutions.

Also note, the generalization of the proofs for anharmonic effects of a lattice is trivial since there is no $\mathbf{X}$ dependence in the anharmonic terms (which may be gathered into H_I, for example), so that the proofs are quite general for any lattice Hamiltonian.

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