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Lattice Thermal Conductivity for a One-Dimensional, Harmonic, Isotopically Disordered Crystal*

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A formally exact expression for the Kubo thermal conductivity is obtained for an infinite, one-dimensional chain of atoms which are connected by nearest-neighbor, harmonic springs of equal strength, and which are of equal mass except within a finite section of the chain which contains disordered isotopic impurities. The two infinite, isotopically pure regions are used as high- and low-temperature reservoirs which cause an energy flow through the isotopically disordered region, whose thermal conductivity is calculated. It is found that the Kubo thermal conductivity for this model is always finite. Various approximations which allow explicit evaluation of the conductivity are discussed.

I. INTRODUCTION

ENERGY transport in a solid has experimentally been found to obey an equation[1] of the type

$$J=-K(dT/dx)\,, \tag{1}$$

where J is the energy per unit time per unit area flowing in the x direction, dT/dx is the temperature gradient, and K is the thermal conductivity. For solids which are electrical insulators, a theoretical calculation of K may be made in terms of phonon scattering by other phonons,[2–5] by lattice defects,[4,5] and by the crystal surface.[6] Although at high temperatures these calculations certainly yield valid results which may be fitted to the experimental data,[7] they all involve uncontrolled approximations of one type or another, and most involve the Boltzmann equation in the relaxation-time approximation. At high temperatures for which the lattice motion is anharmonic, these approximations are at present unavoidable. But at sufficiently low temperatures, the lattice motion is dominated by harmonic forces, and a first-principles calculation of the lattice thermal conductivity, though difficult, should be possible. We here attempt such a calculation of K for a simple-type harmonic system containing isotopic impurities. Before turning to this calculation, however, we must discuss several very basic difficulties which arise in using a harmonic system as a model for thermal conductivity.

First, in neglecting anharmonicity we have omitted not only the umklapp processes,[8] which are unimportant at low temperatures, but also the normal processes,[8] which are responsible for that energy exchange between normal modes which causes an approach to equilibrium. We overcome this difficulty by choosing the initial state of our harmonic system so that energy is correctly distributed among the various modes.[9] Second, the calculation of the thermal conductivity due to multiple phonon scattering from isotopes in three dimensions is a problem which can be treated at present only through perturbation theory, even for a harmonic system.[10] Thus we choose to attack the problem in one dimension, where one may obtain a formally exact solution to the multiple scattering problem.

Third, there is the problem of obtaining a finite thermal conductivity for a harmonic system whose only scattering mechanisms is isotopic impurities. In the usual derivation of the thermal conductivity,[11] the expression for the one-dimensional heat current J is written

$$J=\frac{1}{L}\sum_s N_s\hbar\omega_s v_s\,, \tag{2}$$

where L is the length of the sample, and where N_s, $\hbar\omega_s$, and v_s are the occupation number, energy, and group velocity for phonons of wave number s. The Boltzmann transport equation is then solved for N_s, using the relaxation-time approximation, yielding

$$N_s=N_s^0-\tau_s v_s(dN_s^0/dT)(dT/dx)\,, \tag{3}$$

where T is the absolute temperature and where τ_s and N_s^0 are the relaxation time and the equilibrium occupa-

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[11] See, e.g., P. Carruthers, Rev. Mod. Phys. **33**, 92 (1961).

tion number for phonons of wave number s. Combining Eqs. (2) and (3), one obtains

$$J=-\frac{1}{L}\sum_{s}\hbar\omega_s\tau_s(dN_s^0/dT)v_s^2(dT/dx), \tag{4}$$

with J being proportional to the temperature gradient in agreement with Eq. (1). If one considers a material whose only scattering mechanism is isotopic impurities, then one may show that τ_s becomes infinite as s tends to zero; hence Eq. (4) yields an infinite thermal conductivity for this case. However, one notes that as τ_s increases, Eq. (3) must, at some point, predict negative occupation numbers, which is physical nonsense. Thus the usual derivation is not internally consistent. We overcome this difficulty by observing that Eq. (4) cannot be strictly correct when only isotopic scattering is operative, since the low-frequency phonons are not sufficiently attenuated. The Kubo formalism[2] provides a systematic method for including the low-frequency phonons; using it we obtain a finite conductivity. We now turn to a discussion of our model.

In this paper, we choose to consider an infinite, one-dimensional chain of atoms connected by nearest-neighbor harmonic springs of equal strength. All atoms outside one finite section of the chain have mass m. Within this finite section there is a disordered mixture of two isotopes having mass m and M. Physically the two infinite, isotopically pure regions will be used to stimulate high- and low-temperature reservoirs which cause an energy flow through the isotopically disordered region whose thermal conductivity we intend to calculate.

In Sec. II we calculate a formally exact expression for the thermal conductivity for this model, using the Kubo method of correlation functions.[12,13] Our formal expression for the Kubo thermal conductivity is put into a form which relates it to some recent work by Rubin[14] on the transmission properties of one-dimensional isotopically disordered chains. Section II concludes with a discussion of the physical significance of the derived results. Section III then summarizes our paper.

The literature on this problem is extensive, and our list of references is not meant to be encyclopedic. This paper was initially motivated by the work of Kashiwamura and Teramoto,[15] who calculated a temperature drop across a single impurity and by the work of Rubin,[16] who made computer studies of the energy flow in small isotopically disordered systems. In concluding this section, let us note that the primary motivation of this paper is not that of fitting theory to experimental data; rather, we seek to expose a model whose solution may be used to explore the theoretical problems of nonequilibrium processes.

II. THERMAL CONDUCTIVITY

In this section we use the Kubo formalism in order to calculate the thermal conductivity of our model. Before turning to this, however, we shall very briefly outline the transformation to the phonon representation. We do this primarily to define the notation which we shall use through the remainder of this paper.

The Hamiltonian for our system is given by

$$H=\sum_{j}(p_j^2/2m_j)+\tfrac{1}{2}\sum_{j,k}\phi_{j,k}u_ju_k, \tag{5}$$

where p_j is the momentum of particle j, m_j its mass, u_j its displacement from equilibrium, and $\phi_{j,k}$ the nearest-neighbor harmonic-force constants. Equation (5) can be reduced to the form[17,18]

$$H=\frac{L}{2\pi}\int\hbar\omega(s)[a^\dagger(s)a(s)+\tfrac{1}{2}]ds \tag{6}$$

by the transformation

$$u_j=\frac{L}{2\pi}\int[\hbar/2m_j\omega(s)]^{1/2}[B_j(s)a(s)+B_j^*(s)a^\dagger(s)]ds \tag{7}$$

and

$$p_j=-i\frac{L}{2\pi}\int[\tfrac{1}{2}\hbar m_j\omega(s)]^{1/2}\times[B_j(s)a(s)-B_j^*(s)a^\dagger(s)]ds. \tag{8}$$

Here the $a^\dagger(s)$ and $a(s)$ are, respectively, creation and destruction operators for phonons with wave number s, $\omega(s)$ is the frequency of a phonon with wave number s, $\hbar$ is Planck's constant divided by 2π, a is the equilibrium lattice spacing, and L is the total length of the chain which is to be made infinite in the final formulas. The $B_j(s)$ satisfy the equation

$$\sum_{k}[\phi_{j,k}/(m_jm_k)^{1/2}]B_k(s)=\omega^2(s)B_j(s), \tag{9}$$

and are normalized so that they satisfy the equation

$$\sum_{j}B_j(s)B_j^*(s')=(2\pi/L)\delta(s-s'), \tag{10}$$

where δ is the Dirac δ function. For our model with nearest-neighbor harmonic forces, $\phi_{j,k}$ is given:

$$\phi_{j,k}=-\gamma(\delta_{j,k-1}-2\delta_{j,k}+\delta_{j,k+1}), \tag{11}$$

where γ is the strength of the harmonic force.

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[12] H. Mori, I. Oppenheim, and J. Ross, in *Studies in Statistical Mechanics*, edited by J. DeBoer and G. E. Uhlenbeck (Interscience Publishers, Inc., New York, 1962), Vol. I.

[13] J. A. McLennan, in *Advances in Chemical Physics*, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1963), Vol. V.

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[17] T. A. Bak, *Phonons and Phonon Interactions* (W. A. Benjamin Co., Inc., New York, 1964).

[18] All integrals over s are from $-\pi/a$ to π/a unless otherwise noted.

It might at first be surprising to see modes of well-defined wave vector employed in a defect calculation. The justification for this is the fact that for this model one obtains eigenfunctions which are plane waves outside of the region of impurities. Furthermore, these plane waves may be put in one to one correspondence with the modes of a simple monatomic chain as L becomes infinite. An exception to this occurs when the impurity mass is less than host mass. If the impurity mass is less than the host mass, then, in addition to those modes included in Eqs. (6)–(8), one obtains a finite number of so-called localized modes for which s is complex. The localized modes, however, do not contribute to the heat current and are therefore neglected. (For further discussion of these points, see Appendix A.)

Solving Eq. (9) for the $B_k(s)$ is the crux of performing this transformation; and for this model, a procedure which yields formally exact solutions to Eq. (9) can be obtained. However, the discussion of this procedure is relegated to an appendix in order not to detract from the central purpose of this paper, which is the calculation of the thermal conductivity.

The Kubo expression for the thermal conductivity K is given in this case by

$$K=(L_0/T)\int_0^{\tau_0=\infty} dt\int_0^{\beta} d\lambda\langle J(0)J(t+i\lambda\hbar)\rangle_0, \qquad (12)$$

where J is the local heat flux operator averaged over the impurity bearing region of the chain of length L_0 [see Eq. (6.92) in Ref. 12]. Here t is a parameter with units of time and the upper limit of the time integration τ_0 can be taken as infinite since the entire system is infinite, λ is a parameter with units $(\text{energy})^{-1}\,\beta=1/kT$, where k is the Boltzmann constant, and

$$\langle J(0)J(t+i\lambda\hbar)\rangle_0 = \mathrm{Tr}[J(0)J(t+i\lambda\hbar)e^{-\beta H}]/\mathrm{Tr}[e^{-\beta H}]. \qquad (13)$$

The operator $J(t+i\lambda\hbar)$ is given by

$$J(t+i\lambda\hbar)=e^{iHt/\hbar}e^{-\lambda H}J(0)e^{\lambda H}e^{-iHt/\hbar}. \qquad (14)$$

From this point on we shall drop the argument of $J(0)$. It is to be understood that in subsequent equations J is calculated at $t=0$.

If we now write Eq. (12) in occupation-number representation using Dirac bra and ket notation, where $|l\rangle$ is a normalized eigenstate of the Hamiltonian with energy E_l, then, since K is real, we can write

$$K=\tfrac{1}{2}(K+K^*)=\frac{\pi L_0}{kT^2}\sum_{l,n}\delta\left(\frac{E_n-E_l}{\hbar}\right) \times\langle l|J|n\rangle\langle n|J|l\rangle\rho_l, \qquad (15)$$

where

$$\rho_l=e^{-\beta E_l}/\sum_l e^{-\beta E_l}, \qquad (16)$$

and we have used

$$\int_{-\infty}^{\infty} dt\, e^{it(E_n-E_l)/\hbar}=2\pi\delta\left(\frac{E_n-E_l}{\hbar}\right). \qquad (17)$$

It is not necessary to write $K=\frac{1}{2}(K+K^*)$, but since K is real we may do so, and this provides a convenient expression for the rest of the paper.

We must now express the average heat-flux operator J in terms of the p_j and u_j. This expression has been derived by Hardy[19] and is given by

$$J=\frac{1}{2L_0}\sum_{j=-L_0/2a}^{L_0/2a}\{[p_j^2/2m_j+V_j](p_j/m_j) +\sum_k (i\hbar)^{-1}[p_j^2/2m_j,V_k](r_j-r_k)+\text{H.c.}\}, \qquad (18)$$

where H.c. stands for Hermitian conjugate,

$$V_j=\tfrac{1}{2}\sum_k \phi_{j,k}u_ju_k, \qquad (19)$$

and

$$r_j=ja+u_j. \qquad (20)$$

Using Eqs. (18)–(20) and the commutation relations

$$[u_j,p_k]=i\hbar\delta_{j,k}, \qquad (21)$$

the expression for the average heat-flux operator becomes

$$J=\frac{1}{2L_0}\sum_{j=-L_0/2a}^{L_0/2a}\{[p_j^2/2m_j+V_j](p_j/m_j) +\sum_k \phi_{k,j}u_k(p_j/m_j)[(k-j)a+(u_k-u_j)]+\text{H.c.}\}. \qquad (22)$$

Equation (22) contains terms which are cubic in the operators u_j and p_j, and one term which is quadratic. At low temperatures, when the oscillations are of small amplitude, the only significant contribution to J comes from the quadratic term.[19] We thus approximate the average heat-flux operator, with the help of Eq. (11) for $\phi_{k,j}$, as

$$J=(\gamma a/2L_0)\sum_{j=-L_0/2a}^{L_0/2a}(u_{j-1}-u_{j+1})(p_j/m_j). \qquad (23)$$

In terms of the $B_j(s)$, J is given by

$$J=-\frac{i\hbar\gamma a}{4L_0}\left(\frac{L}{2\pi}\right)^2\sum_{j=-L_0/2a}^{L_0/2a}\int\int\left(\frac{\omega(s')}{\omega(s)}\right)^{1/2} \times\left[\left(\frac{B_{j-1}(s)}{m_{j-1}{}^{1/2}}-\frac{B_{j+1}(s)}{m_{j+1}{}^{1/2}}\right)a(s)+\left(\frac{B_{j-1}{}^*(s)}{m_{j-1}{}^{1/2}} -\frac{B_{j+1}{}^*(s)}{m_{j+1}{}^{1/2}}\right)a^\dagger(s)\right]\left[\frac{B_j(s')}{m_j{}^{1/2}}a(s')-\frac{B_j{}^*(s')}{m_j{}^{1/2}}a^\dagger(s')\right]dsds'. \qquad (24)$$

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[19] R. J. Hardy, Phys. Rev. **132**, 168 (1963).

We note that it is the matrix elements $\langle l|J|n\rangle$, where $E_l=E_n$, which are needed in Eq. (15). After some straightforward but tedious manipulations it is found that if $E_n=E_l$, then

$$\langle l|J|n\rangle=\frac{-i\hbar\gamma a}{4L_0}\left(\frac{L}{2\pi}\right)^2\int\int G(s,s')\times\langle l|a^\dagger(s)a(s')|n\rangle ds\,ds', \tag{25}$$

where

$$G(s,s')=\sum_{j=-L_0/2a}^{L_0/2a}\left\{\left(\frac{B_{j-1}{}^*(s)}{m_{j-1}{}^{1/2}}-\frac{B_{j+1}{}^*(s)}{m_{j+1}{}^{1/2}}\right)\frac{B_j(s')}{m_j{}^{1/2}}-\left(\frac{B_{j-1}(s')}{m_{j-1}{}^{1/2}}-\frac{B_{j+1}(s')}{m_{j+1}{}^{1/2}}\right)\frac{B_j{}^*(s)}{m_j{}^{1/2}}\right\}. \tag{26}$$

If Eq. (25) is now inserted into Eq. (15) we obtain

$$K=-\frac{\hbar^2\gamma^2a^2\pi}{16L_0kT^2}\left(\frac{L}{2\pi}\right)^4\int\int\int\int\delta[\omega(s'')-\omega(s''')]\times G(s,s')G(s'',s''')\sum_{l,n}\langle l|a^\dagger(s)a(s')|n\rangle\times\langle n|a^\dagger(s'')a(s''')|l\rangle\rho_l ds\,ds'\,ds''\,ds'''. \tag{27}$$

In Appendix A it is shown that

$$\omega(s)=2(\gamma/m)^{1/2}\sin|\tfrac{1}{2}sa|. \tag{28}$$

This result is to be expected for our model, since there are a finite number of impurities contained within an infinite chain (see Appendix A). By noting from Eq. (28) that $\omega(s'')=\omega(s''')$ if $s''=s'''$ or $s''=-s'''$, we can write

$$\delta[\omega(s'')-\omega(s''')]=[\delta(s''-s''')+\delta(s''+s''')]/|v(s'')|, \tag{29}$$

where $v(s'')$ is the group velocity of phonons with wave number s''. By using Eq. (29) in Eq. (27) and performing the integration over s''', we obtain

$$K=-\frac{\hbar^2\gamma^2a^2\pi}{16L_0kT^2}\left(\frac{L}{2\pi}\right)^4\int\int\int\int\{G(s,s')G(s'',s'')\times\sum_l\langle l|a^\dagger(s)a(s')|l\rangle n_l(s'')\rho_l+G(s,s')G(s'',-s'')\times\sum_{l,n}\langle l|a^\dagger(s)a(s')|n\rangle\langle n|a^\dagger(s'')a(-s'')|l\rangle\rho_l\}\times|v(s'')|^{-1}ds\,ds'\,ds'', \tag{30}$$

where $n_l(s'')$ is the number of phonons with wave number s'' in the state $|l\rangle$.

The statistical averages which appear in Eq. (30) are taken at complete thermal equilibrium, and thus we have

$$\sum_l\langle l|a^\dagger(s)a(s')|l\rangle n_l(s'')\rho_l=\left(\frac{2\pi}{L}\right)\delta(s-s')\times\left\{\frac{1}{(e^x-1)(e^{x''}-1)}+\left(\frac{2\pi}{L}\right)\delta(s-s'')\frac{e^x}{(e^x-1)^2}\right\}$$

and

$$\sum_{l,n}\langle l|a^\dagger(s)a(s')|n\rangle\langle n|a^\dagger(s'')a(-s'')|l\rangle\rho_l=\left(\frac{2\pi}{L}\right)\delta(s+s'')\delta(s'-s'')\frac{e^x}{(e^x-1)^2}, \tag{31}$$

where $x=\beta\hbar\omega(s)$. If we now use Eqs. (31) and Eq. (30), the thermal conductivity becomes

$$K=-\frac{\hbar^2\gamma^2a\pi}{16L_0kT^2}\left(\frac{L}{2\pi}\right)^2\left\{\left(\frac{L}{2\pi}\right)\int\int G(s,s)G(s'',s'')\times|v(s'')|^{-1}(e^x-1)^{-1}(e^{x''}-1)^{-1}ds\,ds''+\int[G^2(s,s)+G(s,-s)G(-s,s)]\times\frac{e^x}{(e^x-1)^2}|v(s)|^{-1}ds\right\}. \tag{32}$$

In Appendix B it is shown that $G(s,s)$ is antisymmetric in s, and thus the first term in Eq. (32) does not contribute. The thermal conductivity then becomes

$$K=-\frac{\hbar\gamma^2a^2\pi}{16L_0kT^2}\left(\frac{L}{2\pi}\right)^2\int[G^2(s,s)+G(s,-s)G(-s,s)]\times\frac{e^x}{(e^x-1)^2}|v(s)|^{-1}ds. \tag{33}$$

$G(s,s)$ and $G(s,-s)$ are calculated for this model in Appendix B, using the formal expression for the $B_j(s)$ derived in Appendix A. In calculating $G(s,s)$ and $G(s,-s)$ we show that one need know the values of the $B_j(s)$ only in the pure regions of the chain. If, thinking classically, one notes from Eqs. (9) that the $B_j(s)$ represent the shape of normal mode running waves, then one could write formal expressions for the $B_j(s)$ in the pure regions almost by inspection. For the sake of clarity in the remaining discussion, we now write these $B_j(s)$ and indicate why these expressions are obvious.

Recall that our model consists of an infinite chain of particles, which contains a finite number R of isotopic impurities contained within a finite length L_0 of the chain. We label the positions of the impurities with the integers $n_1<n_2<\cdots<n_R$. The expressions for $B_j(s)$ on either side of the impurity bearing region are given by

$$\begin{aligned}
B_j(s)&=(a/L)^{1/2}|\Gamma(s)|^{-1}[\Gamma(s)e^{ijsa}+\Delta(s)e^{-ijsa}], && j\leq n_1\\
B_j(s)&=(a/L)^{1/2}|\Gamma(s)|^{-1}e^{ijsa}, && j\geq n_R\\
B_j(-s)&=(a/L)^{1/2}|\Gamma(s)|^{-1}e^{-ijsa}, && j\leq n_1\\
B_j(-s)&(a/L)^{1/2}|\Gamma(s)|^{-1}[\Gamma(s)e^{-ijsa}-\Delta^*(s)e^{ijsa}], && j\geq n_R
\end{aligned} \tag{34}$$

where $s\geq0$ and expressions for $\Gamma(s)$ and $\Delta(s)$ are given in Appendix A. It is also shown in Appendix A that

$$|\Gamma(s)|^2=1+|\Delta(s)|^2. \tag{35}$$

If we view this as a transmission line problem, the results given in Eqs. (34) are quite reasonable indeed. Equations (34) state simply that if we have a wave of complex amplitude $\Gamma(s)$ incident upon the scattering region from the left, then a wave of complex amplitude $\Delta(s)$ is reflected and a wave of amplitude unity is transmitted. Equation (35) is simply the relationship between reflection and transmission coefficients.

The solutions given by Eqs. (34) do not include the so-called localized modes for which s is complex. While the procedure outlined in Appendix A can be used to find the localized modes, we omit consideration of them here since they will not contribute to the thermal conductivity for this model. In this connection see the article by Woll.[10]

In Appendix B it is shown that

$$G^2(s,s) = -(4L_0/mL)^2|\Gamma(s)|^{-4}\sin^2 sa$$

and

$$G(s,-s)G(-s,s) = -\left(\frac{4L_0}{mL}\right)^2\frac{|\Delta(s)|^2}{|\Gamma(s)|^4}\sin^2 sa. \tag{36}$$

Using Eqs. (33), (35), and (36), and converting the integral over s to an integral over x, we obtain

$$K = \frac{k^2T}{2\pi\hbar}\int_0^{\Theta/T}\frac{L_0}{|\Gamma(s)|^2}\frac{x^2e^x}{(e^x-1)^2}dx \tag{37}$$

or

$$K = \frac{k^2T}{2\pi\hbar\zeta}\int_0^{\Theta/T} Re^{-\alpha(x)R}\frac{x^2e^x}{(e^x-1)^2}dx, \tag{38}$$

where $\zeta = R/L_0$ is the density of impurities taken over the impurity bearing portion of the chain,

$$\alpha(x) = (1/R)\ln|\Gamma(s)|^2, \tag{39}$$

and

$$\Theta = 2\hbar(\gamma/m)^{1/2}/k \tag{40}$$

is the Debye Θ for our system. The factor $e^{-\alpha(x)R}$ is exactly the square of the transmission amplitude which has been obtained by Rubin[14] using Monte Carlo techniques. Thus one is guaranteed that Eq. (38) may be evaluated using a computer even if analytic methods fail.

Equation (38), the Kubo expression for the thermal conductivity of our system, is the central result of this paper, and we now turn to a discussion of this equation. First, we observe that Eq. (38) yields a finite conductivity. This can be seen by noting from Eq. (35) that $|\Gamma(s)|$ is never less than unity. For comparison, the expression for the thermal conductivity, due only to one-dimensional isotopic scattering, given by the method leading to Eq. (4), is [10,11,20]

$$K = \frac{\hbar\omega_0^2}{2\pi\zeta\epsilon^2T}\int_0^{\Theta/T}\frac{e^x}{(e^x-1)^2}dx, \tag{41}$$

which diverges at its lower limit due to the pole in the integrand at $x=0$. The integrand of Eq. (38) diverges nowhere and hence K is always finite. This result is at such variance with previously accepted thought that we are obligated to explain it. In order to illuminate this difference, we observe that the Kubo theory[20] derives an expression for the heat current which may be written

$$J = -K(dT/dx) + \cdots, \tag{42}$$

where the dots represent terms proportional to higher powers of the gradient which are assumed to be negligibly small. It is important to realize that (dT/dx) which appears in Eq. (42) is that which is initially imposed on the system. It is assumed in the Kubo formalism that the value of (dT/dx), which exists in the sample after the steady state has been reached, is not significantly different from the initial value. For systems in which there is a reasonably strong scattering mechanism, this assumption is probably quite good. However, for a system in which there is no scattering mechanism (i.e., a pure chain), the phonon gas does not equilibrate. It is therefore not possible to uniquely define a local temperature or local temperature gradient within the central portion of the chain. Thus for systems in which there is no scattering mechanism, the K given by Eq. (38) is not the usual thermal conductivity.

Equation (38) can, however, still be used in conjunction with Eq. (42) to calculate the steady-state current for the pure system in terms of the initially imposed temperature difference between the two reservoirs. For a system which contains no impurities, the usual expressions for $B_j(s)$ are obtained from Eqs. (34) by setting $\Gamma(s)=1$ and $\Delta(s)=0$, and hence from Eq. (39), $\alpha(x)=0$. Since $\alpha(x)=0$, then by using Eqs. (38) and (42) one obtains

$$J = -\left[\frac{k^2T}{2\pi\hbar}\int_0^{\Theta/T}\frac{x^2e^x}{(e^x-1)^2}dx\right]\Delta T, \tag{43}$$

where $\Delta T = L_0(dT/dx)$ is the initial temperature difference impressed across the length of chain L_0. At low temperatures where the acoustic approximation is valid, Eq. (43) can be written

$$J = -\tfrac{1}{2}cv\Delta T, \tag{44}$$

where c is the heat capacity per unit length and v is the velocity of acoustic phonons. In the form given by Eq. (44) the expression for J is transparent. It states simply that in the absence of any scattering mechanism, the current must ultimately be limited by the amount of energy available for transport. Thus we see that even for the pure chain J is finite. This point has been stressed before by Erdos.[21]

At temperatures which are so small that only those phonons which suffer negligible impurity scattering are

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[20] K. R. Allen, thesis, Georgia Institute of Technology, 1966 (unpublished).

[21] Paul Erdos, Phys. Rev. **138**, A1200 (1965).

excited, Eq. (44) should be a reasonable approximation for chains which contain impurities. This situation is similar to boundary scattering in the three-dimensional crystal.[6]

One final remark about the pure chain result is in order. The classical limit of Eq. (43) can be obtained by allowing the temperature to approach infinity. If this is done, Eq. (43) becomes

$$J=\frac{-k^2\Theta}{2\pi\hbar}\Delta T=\frac{-k\omega_0}{2\pi}\Delta T. \tag{45}$$

Equation (45) is in agreement with a calculation independently performed by Visscher.[22]

For the impurity bearing chain one expects to be able to define a local temperature.[15] Thus for chains which contain impurities we shall discuss the energy transport in terms of the thermal conductivity given by Eq. (38). We shall do this even though in some cases K will be length-dependent and hence not a thermal conductivity in the usual sense. In fact we could have used Eq. (38) to discuss the pure chain, in which case K depends linearly upon the length L_0.

For the impurity bearing chain, an exact analytic calculation of $\alpha(x)$ given by Eq. (39) is prohibitive. In fact, it is difficult even to obtain reliable approximations to $\alpha(x)$. In principle one can expand $\alpha(x)$ in a power series in the concentration of impurities and thus calculate it to any desired order in ζ. We have so far obtained a controlled approximation for $\alpha(x)$ only to lowest order in ζ for a chain in which the impurities are randomly distributed. This result, while inadequate for a complete analysis of Eq. (38), is nevertheless interesting.

To lowest order in the concentration of impurities, $\alpha(x)$ is given by[20]

$$\alpha(x)=\ln\left[1+\frac{\epsilon^2x^2}{(\Theta/T)^2-x^2}\right], \tag{46}$$

where

$$\epsilon=(1-M/m). \tag{47}$$

It is only when the impurity scattering is very weak (i.e., small values of x) that Eq. (46) is a reasonable approximation to $\alpha(x)$; and hence we can write

$$\alpha(x)=T^2\epsilon^2x^2/\Theta^2. \tag{48}$$

Using Eq. (48) in Eq. (38) we obtain

$$K=\frac{k^2T}{2\pi\hbar\zeta}\int_0^{\Theta/T}Re^{-T^2\epsilon^2Rx^2/\Theta^2}\frac{x^2e^x}{(e^x-1)^2}dx. \tag{49}$$

In order for Eq. (49) to be a reasonable approximation to the thermal conductivity, the condition

$$T^2\epsilon^2R/\Theta^2\ll 1 \tag{50}$$

must hold. When Eq. (50) is satisfied, Eq. (49) can be written

$$K=\frac{k^2TR}{2\pi\hbar\zeta}\int_0^{\Theta/T}\left[1-\frac{R\epsilon^2T}{\Theta^2}x^2\right]\frac{x^2e^x}{(e^x-1)^2}dx. \tag{51}$$

Since it is only for small values of T that Eq. (50) can be satisfied, the upper limit of the integral in Eq. (51) can be set equal to infinity, which yields

$$K=\frac{k^2\pi R}{6\hbar\zeta}T\left[1-\frac{4\pi^2R\epsilon^2}{5\Theta^2}T^2\right]. \tag{52}$$

The first term in Eq. (52) is simply the pure chain result. The second term is a small correction due to impurity scattering which diminishes K from the pure chain result somewhat. While this approximation to the impurity scattering has decreased the thermal conductivity slightly from the pure chain result, since $R/\zeta=L_0$, K is still length-dependent. Hence in this approximation we have not obtained a thermal conductivity in the normal sense.

We should remark at this point that Woll[10] has also used the Kubo formalism to calculate the thermal conductivity of an isotopically disordered chain correct to lowest order in the concentration of impurities. There is a slight but important difference between the model which Woll has used and our model. In our model the impurities are confined to a finite section of the chain and hence there are a finite number of them. In Woll's model the impurities are randomly distributed throughout the entire chain and there are an infinite number of them.

By examining Eq. (38) it is easily seen that

$$Re^{-\alpha(x)R}=R/e^{\alpha(x)R}=R/[1+\alpha(x)R+\cdots]. \tag{53}$$

As R tends to infinity it is clear that the term unity in the denominator of Eq. (53) is negligible. Thus as R tends to infinity,

$$Re^{-\alpha(x)R}=1/[\alpha(x)+\cdots]. \tag{54}$$

If we now use Eq. (48) for $\alpha(x)$, and retain only the leading term in the denominator of Eq. (54), the thermal conductivity becomes

$$K=\frac{k^2\Theta^2}{2\pi\hbar\epsilon^2\zeta T}\int_0^{\Theta/T}\frac{e^x}{(e^x-1)^2}dx. \tag{55}$$

Equation (55) is the same divergent result which has been obtained by Woll. It is also the same expression given in Eq. (41).

Equation (55) is not correct for at least two reasons. First, for very large values of R, $\alpha(x)$ is not correctly given by Eq. (48). Second, the terms which were neglected in the denominator of Eq. (54) are most important. It is clear that in order to proceed with the analysis of the Kubo thermal conductivity, for chains which contain a large number of impurities and at all but the very lowest temperatures, we must obtain more reliable approximations to $\alpha(x)$.

So far, we have not been able to obtain an analytic approximation to $\alpha(x)$ for cases in which the temperature T and the total number of impurities R are too large to satisfy Eq. (50). However, Rubin[14] has calcu-

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[22] W. M. Visscher (private communication).

lated $\alpha(x)$ numerically for a number of isotopically disordered chains, and his results allow us at least to speculate on the form of K for the larger values of T and R.

We are reduced to speculation, since Rubin's results are not highly accurate at small values of x, which are of paramont importance in calculating K. This is due to the fact that there are significant fluctuations in the numerical values of $\alpha(x)$ from one random distribution of impurities to another for small values of x. This is not surprising, since in the numerical calculations the total number of impurities is limited to relatively small values ($\simeq 10^4$). Since at small values of x the scattering due to a single impurity is weak, this small number of impurities is evidently not large enough to insure that these random fluctuations in $\alpha(x)$ will be small. We hope to improve this accuracy in the near future; for the present, however, we note that Rubin's results are at least consistent with $\alpha(x)$ given by

$$\alpha(x)=b\epsilon^2(T/\Theta)x, \tag{56}$$

for

$$x\lesssim 0.3\Theta/T. \tag{57}$$

While for values of x larger than those allowed by Eq. (57) $\alpha(x)$ deviates significantly from the linear function given by Eq. (56), these larger values of x will not contribute significantly to the thermal conductivity for our model and hence may be neglected. The constant of proportionality b may be determined from the numerical calculations, and we find

$$b=0.10. \tag{58}$$

By inserting Eq. (56) into Eq. (38) we obtain

$$K=\frac{k^2T}{2\pi\hbar\zeta}\int_0^{\Theta/T} R\exp\left[-b\epsilon^2\left(\frac{T}{\Theta}\right)Rx\right]\frac{x^2e^x}{(e^x-1)^2}dx. \tag{59}$$

For values of T and R which satisfy the relation

$$b\epsilon^2(T/\Theta)R\gg 1, \tag{60}$$

the factor $x^2e^x/(e^x-1)^2$ in Eq. (59) may be replaced by unity. The integral in Eq. (59) can then be performed and yields

$$K=k^2\Theta/2\pi b\hbar\zeta\epsilon^2. \tag{61}$$

We notice immediately that K given by Eq. (61) is independent of L_0. Hence, we have obtained a thermal conductivity in the usual sense. Furthermore, it has the same dependence upon ζ and ϵ as that obtained by other theories,[10,11,20] and which seems to agree with experiment.[7] Finally, we observe that K is independent of the temperature. This temperature independence is characteristic of cases in which the total scattering by impurities is large, and hence the only significant contribution to K comes from small values of x. This may be understood from Eq. (38), where one observes that the temperature factor of the integrand $[x^2e^x/(e^x-1)^2]$ tends to unity when x is small.

Since our model is one-dimensional and does not contain any anharmonic contributions, the extent to which Eq. (61) is relevant to experiment is uncertain. It is nevertheless interesting to calculate a value predicted by Eq. (61) for typical values of the parameters. For this purpose we assume that a three-dimensional crystal may be approximated by a set of parallel one-dimensional chains having a cross-sectional diameter given by the lattice spacing. We find that

$$K_{3\text{-}D}=K/a^2=k^2\Theta/2\pi ba^2\hbar\zeta\epsilon^2. \tag{62}$$

Some typical values for the parameters are $b=0.10$, $\Theta=300°\mathrm{K}$, $\epsilon=0.10$, $a=4\times10^{-8}$ cm, and $\zeta=8.5\times10^6$ cm^{-1} (5% impurities). Using these values, Eq. (62) yields

$$K_{3\text{-}D}=43.2\ \mathrm{W/cm\,K^0}, \tag{63}$$

which is certainly in order-of-magnitude agreement with experiment.

III. CONCLUSIONS

In this paper we have attempted a first-principles calculation of the thermal conductivity due to isotopic scattering using a model for which one may obtain formally exact solutions to the equations of motion. Our intent has been to illuminate and perhaps resolve some of the problems in the theory of energy transport in solids. Our calculations are relevant to experiment only in so far as one may trust the assumption that energy in a solid is transported along independent one-dimensional chains.

We have obtained a finite conductivity for pure isotopic scattering by using the Kubo theory, which allows for a smooth transition from energy transport as heat (current proportional to gradient) to energy transport as sound (current proportional to the temperature difference). Moreover, we have suggested that previous theory encounters difficulty precisely because it insists that all energy flow be proportional to the gradient. While we are unable to evaluate the formal Kubo expression for K exactly, we have reduced it to a form amenable to Monte Carlo calculations of the type performed by Rubin.[14]

Recently there have been two attempts[23,24] to calculate the thermal conductivity due to isotopic scattering, using a computer to solve the equations of motion. Since it is difficult to compare our calculations directly with experiment, some type of computer validation would be valuable. However, the calculations of Jackson *et al.* and Payton *et al.* are for systems of microscopic size (100–1000 atoms) upon which a relatively large gradient has been imposed. The resulting large amplitudes of motion force Jackson to include the cubic terms in the current Eq. (22), and the high average

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[23] E. A. Jackson, J. R. Pasta, and J. F. Waters, J. Comput. Phys. (to be published).

[24] D. N. Payton, III, M. Rich, and W. M. Visscher, Phys. Rev. **160**, 706 (1967).

temperature of the system forces Payton to consider localized modes. Our calculations, on the other hand, are for systems of macroscopic size, low average temperature, and small gradient. As a consequence there is no overlap between our theory and theirs. We have attempted computer verification by solving Eq. (A9), since this requires solving only R equations, one for each impurity atom, rather than one equation for every atom. Weighting the energy in each reservoir at a representative sampling of modes according to the Bose distribution, we are able to calculate a $K=-J/(dT/dx)$, which is in order-of-magnitude agreement with Eq. (38). However, this method requires that one introduce a low frequency cutoff, since the impurity scattering at low frequencies is insufficient to yield the low-frequency energy difference between the reservoirs. As a consequence, our computer studies of thermal conductivity are inconclusive.

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APPENDIX A

The central problem of this appendix is to find the solutions to Eq. (9). If we define the function $C_j(s)$ so that

$$B_j(s)=m_j^{1/2}C_j(s)\,, \tag{A1}$$

and recall that our model is one of nearest-neighbor harmonic forces with $\phi_{j,k}$ given by Eq. (11), then Eq. (9) reduces to

$$[2\gamma-m_j\omega^2(s)]C_j(s)=\gamma[C_{j+1}(s)+C_{j-1}(s)]\,. \tag{A2}$$

In Eq. (A2) we now require that all $m_j=m$ except for an integer number R of atoms which have a mass M and which lie somewhere in the interior of a region of length L_0. The atoms are labeled consecutively with the integer index j, increasing from left to right. The R atoms of mass M each bear an integer label $j=n_r$, where $n_1<n_2<\cdots<n_R$. We shall ultimately assume that the atoms of mass M are randomly positioned within L_0, but we do not need this assumption in formally solving Eq. (A2). Equation (A2) may then be written as

$$[2\gamma-m\omega^2(s)]C_j(s)=\gamma[C_{j+1}(s)+C_{j-1}(s)] \tag{A3a}$$

for $j\neq n_r$, and as

$$[2\gamma-M\omega^2(s)]C_j(s)=\gamma[C_{j+1}(s)+C_{j-1}(s)] \tag{A3b}$$

for $j=n_r$.

Equations (A3a) and (A3b) form a set of coupled, second-order difference equations whose solution may be obtained by straightforward, albeit tedious, methods. However, in attempting to solve equations of this type, it is customary to use one's physical intuition in order to guess a form for the solution which bypasses much of the algebraic labor. We first notice that Eqs. (A3a) and (A3b) are just the classical equations of motion for the running wave modes of our system. Thus, thinking classically, if energy at a single frequency passes to the right through the impurity bearing region of length L_0, we anticipate that a plane wave would emerge from the impurity region, propagating to the right without further attenuation. Moreover, we would expect each impurity atom to reflect energy back to the left. Hence we anticipate finding a certain number of standing waves, in the pure regions between impurities $n_r\leq j\leq n_{r+1}$, which decreases as r increases. With these intuitive arguments as prolog, we seek a solution to Eqs. (A3a) and (A3b) of the form

$$C_j(s)=f(s)\{e^{ijsa}+\sum_{l=r+1}^{R}A_l(s)\sin[(j-n_l)sa]\}\,, \tag{A4}$$

where j lies in the interval $n_r\leq j\leq n_{r+1}$ on the understanding that the labels n_0 and n_{R+1} denote minus and plus infinity, respectively, where $s\geq 0$ since the wave is traveling to the right, where $f(s)$ is the pure running wave amplitude, and where the $f(s)A_l(s)$ are standing wave amplitudes.

Substituting Eq. (A4) into Eq. (A3), we obtain the dispersion equation

$$\omega^2(s)=4(\gamma/m)\sin^2(\tfrac{1}{2}sa)\,. \tag{A5}$$

Notice that Eq. (A5) is the dispersion equation for the pure chain. This point will be discussed later.

Substituting Eq. (A4) into Eq. (A3), we obtain

$$\sum_{l=r}^{R}\{\delta_{r,l}+2p(s)\sin[(n_r-n_l)sa]\}A_l(s)=-p(s)e^{in_rsa}\,, \tag{A6}$$

where

$$p(s)=\epsilon\tan|\tfrac{1}{2}sa| \tag{A7}$$

and

$$\epsilon=1-(M/m)\,. \tag{A8}$$

By writing Eq. (A6) in the matrix form

$$\sum_{l=1}^{R}L_{k,l}(s)A_l(s)=-2p(s)e^{in_ksa}\,, \tag{A9}$$

where $L_{k,l}(s)$ is the triangular matrix

$$\begin{aligned}&L_{k,l}(s)=\delta_{k,l}+2p(s)\sin(n_k-n_l)sa\,, && k\leq l\\ &L_{k,l}(s)=0 && \text{otherwise}\,,\end{aligned} \tag{A10}$$

one obtains the formal solution

$$A_l(s)=-2p(s)\sum_{k=1}^{R}M_{l,k}(s)e^{in_ksa}\,, \tag{A11}$$

where $M_{l,k}(s)$ is the matrix inverse to $L_{l,k}(s)$.

Equation (A11) can now be used to write Eq. (A4) as

$$C_j(s)=f(s)[\Gamma_r(s)e^{ijsa}+\Delta_r(s)e^{-ijsa}]\,, \tag{A12}$$

where

$$\Gamma_r(s)=[1+ip(s)\sum_{l=r+1}^{R}\sum_{k=1}^{R}e^{-in_l sa}M_{l,k}(s)e^{in_k sa}] \quad \text{(A13)}$$

and

$$\Delta_r(s)=-ip(s)\sum_{l=r+1}^{R}\sum_{k=1}^{R}e^{in_l sa}M_{l,k}(s)e^{in_k sa}. \quad \text{(A14)}$$

Recall that $n_r \leq j \leq n_{r+1}$ and $s \geq 0$.

If $s \leq 0$, a similar argument shows that $C_j(s)$ is still given by Eq. (A12), where

$$\Gamma_r(s)=[1+ip(s)\sum_{l=1}^{r}\sum_{k=1}^{R}e^{-in_l sa}M_{l,k}(s)e^{in_k sa}], \quad \text{(A15)}$$

and

$$\Delta_r(s)=-ip(s)\sum_{l=1}^{r}\sum_{k=1}^{R}e^{in_l sa}M_{l,k}(s)e^{in_k sa}. \quad \text{(A16)}$$

It can also be shown that

$$M_{l,k}(s)=M_{k,l}(-s). \quad \text{(A17)}$$

We must now choose $f(s)$ so that the normalization condition, Eq. (10), is satisfied. For this purpose, as well as for the calculation of the thermal conductivity, we need the $B_j(s)$ only in the pure infinite regions at either side of the impurity bearing regions of the chain. By using Eq. (A1) and Eqs. (A12)–(A17), we can write

$$B_j(s)=m^{1/2}f(s)[\Gamma(s)e^{ijsa}+\Delta(s)e^{-ijsa}], \quad j \leq n_1 \quad \text{(A18a)}$$

$$B_j(s)=m^{1/2}f(s)e^{ijsa}, \quad j \geq n_R \quad \text{(A18b)}$$

$$B_j(-s)=m^{1/2}f(s)e^{-ijsa}, \quad j \leq n_1 \quad \text{(A18c)}$$

$$B_j(-s)=m^{1/2}f(s)[\Gamma(s)e^{-ijsa}-\Delta^*(s)e^{ijsa}], \quad j \geq n_R \quad \text{(A18d)}$$

where $s \geq 0$, and $\Gamma(s)$ and $\Delta(s)$, are obtained from Eqs. (A13) and (A14), with $r=R$.

Since the $B_j(s)$ satisfy Eq. (9), it is only when $\omega(s)=\omega(s')$ [or, from Eq. (A5), when $s=s'$ or $s=-s'$] that Eq. (10) is nonzero. We shall first choose $f(s)$ so that Eq. (10) is satisfied when $s=s'$, and then show that Eq. (10) is zero for $s=-s'$. We shall illustrate the calculation of $f(s)$ for the case in which $s \geq 0$.

For $j \leq 0$ we use Eq. (A18a) for $B_j(s)$, and for $j \geq 0$ we use Eq. (A18b) for $B_j(s)$. We thus approximate a finite number of the $B_j(s)$. As we will show, this approximation causes a negligible error. The left-hand side of Eq. (10) thus becomes

$$\sum_{j=-L/2a}^{L/2a}B_j(s)B_j^*(s)$$

$$=|f(s)|^2\frac{mL}{2a}[1+|\Gamma(s)|^2+|\Delta(s)|^2], \quad \text{(A19)}$$

where we have neglected terms of order $1/L$. In the limit $L \to \infty$ we can write

$$\left(\frac{2\pi}{L}\right)\delta(s-s')=\frac{a}{L}\sum_{j=-L/2a}^{L/2a}e^{ij(s-s')a}. \quad \text{(A20)}$$

Hence, Eq. (10) is satisfied if

$$|f(s)|^2\frac{mL}{2a}[1+|\Gamma(s)|^2+|\Delta(s)|^2]=1 \quad \text{(A21)}$$

or

$$f(s)=(2a/mL)^{1/2}[1+|\Gamma(s)|^2+|\Delta(s)|^2]^{-1/2}. \quad \text{(A22)}$$

It is clear that negligible error has been introduced by approximating certain of the $B_j(s)$. Equation (A19) is of order L and differs from the true value of $\sum_j B_j(s)B_j^*(s)$ only by a fixed finite number. Hence as $L \to \infty$, this finite correction is negligible.

The expression for $f(s)$ given by Eq. (A22) can be simplified somewhat. By using Eq. (9) it can be shown that if $s=s'$ or $s=-s'$, the combination in brackets in Eq. (26) is independent of j. By evaluating that combination when $s=s'$ in each of the two pure infinite regions of the chain, one obtains

$$1+|\Delta(s)|^2=|\Gamma(s)|^2. \quad \text{(A23)}$$

Equation (A22) thus becomes

$$f(s)=(a/mL)^{1/2}|\Gamma(s)|^{-1}. \quad \text{(A24)}$$

Finally we can write Eqs. (A18a)–(A18d) as

$$B_j(s)=(a/L)^{1/2}|\Gamma(s)|^{-1}[\Gamma(s)e^{ijsa}+\Delta(s)e^{-ijsa}], \quad j \leq n_1 \quad \text{(A25a)}$$

$$B_j(s)=(a/L)^{1/2}|\Gamma(s)|^{-1}e^{ijsa}, \quad j \geq n_R \quad \text{(A25b)}$$

$$B_j(-s)=(a/L)^{1/2}|\Gamma(s)|^{-1}e^{-ijsa}, \quad j \leq n_1 \quad \text{(A25c)}$$

$$B_j(-s)=(a/L)^{1/2}|\Gamma(s)|^{-1}[\Gamma(s)e^{-ijsa}-\Delta^*(s)e^{ijsa}], \quad j \geq n_R \quad \text{(A25d)}$$

where $s \geq 0$. By direct substitution of Eqs. (A25a)–(A25d), it follows that $\sum_j B_j(s)B_j^*(-s)=0$.

Before leaving this appendix, Eq. (A5) requires some further discussion. Normally, one would expect to have to solve a secular equation for the eigenfrequencies $\omega(s)$. Fortunately, for this model (i.e., a finite number of impurities in an infinite chain) it is not necessary to do so. Since the density of impurities taken over the entire infinite chain is zero, the dispersion relation is simply that for the pure chain. This can be shown by making use of a theorem due to Lord Rayleigh,[25] which has been stated by Maradudin[17] as: "If in a dynamical system composed of an array of masses coupled to each other by Hookeian springs a single mass is reduced by δM, all frequencies are unchanged or increased by no more than the distance to the next unperturbed fre-

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[25] Lord Rayleigh, *The Theory of Sound* (Dover Publications, Inc., New York, 1945), Vol. I, Chap. IV.

quency. An increase of a single mass by δM leaves the frequencies unchanged or reduces them by amounts no greater than the distance to the next unperturbed frequency."

As $L \longrightarrow \infty$, the dispersion relation for the pure chain becomes continuous. Thus, by successive application of Rayleigh's theorem, it is seen that if $M > m$ the introduction of a finite number R of impurities into an infinite pure chain will not produce a finite shift in the frequencies. The same is true if $M < m$, except for a finite number R of frequencies which can shift to values greater than $2(\gamma/m)^{1/2}$. These out-of-band frequencies correspond to complex values of s, and are referred to as localized modes.

The procedure outlined here can be altered slightly to account for the localized modes. At low temperatures, however, they will not contribute to the thermal conductivity and we therefore neglect them.

APPENDIX B

From Eq. (26) we have

$$G(s,s)=\sum_{j=-L_0/2a}^{L_0/2a}\left\{\left[\frac{B_{j-1}^*(s)}{m_{j-1}^{1/2}}-\frac{B_{j+1}^*(s)}{m_{j+1}^{1/2}}\right]\frac{B_j(s)}{m_j^{1/2}}-\left[\frac{B_{j-1}(s)}{m_{j-1}^{1/2}}-\frac{B_{j+1}(s)}{m_{j+1}^{1/2}}\right]\frac{B_j^*(s)}{m_j^{1/2}}\right\}. \quad \text{(B1)}$$

As noted in Appendix A, it can be shown that the combination over which the sum is performed is independent of j. Thus, the expression for $G(s,s)$ can be written as

$$G(s,s)=(L_0/ma)\{[B_{j-1}^*(s)-B_{j+1}^*(s)]B_j(s)-[B_{j-1}(s)-B_{j+1}(s)]B_j^*(s)\}, \quad \text{(B2)}$$

where j corresponds to a particle in either of the two pure regions of the chain.

The expression for $G(s,s)$, where $s \geq 0$, can be calculated most easily by choosing j in the pure region at the right of the impurity bearing region. The use of Eq. (A25b) in Eq. (B2) yields

$$G(s,s)=i(4L_0/mL)\,|\Gamma(s)|^{-2}\sin sa, \quad \text{(B3)}$$

where $s \geq 0$. The same calculation for $s \leq 0$ with j chosen in the pure region to the left of the impurity bearing region also yields

$$G(s,s)=i(4L_0/mL)\,|\Gamma(s)|^{-2}\sin sa. \quad \text{(B4)}$$

Notice that Eqs. (B3) and (B4) are antisymmetric about $s=0$. From Eqs. (B3) and (B4) we find

$$G^2(s,s)=-(4L_0/mL)^2|\Gamma(s)|^{-4}\sin^2 sa \quad \text{(B5)}$$

for all values of s.

In the same way that Eq. (B2) was derived for $G(s,s)$, it can be shown that

$$G(s,-s)=(L_0/ma)\{[B_{j-1}^*(s)-B_{j+1}^*(s)]B_j(-s)-[B_{j-1}(-s)-B_{j+1}(-s)]B_j^*(s)\}, \quad \text{(B6)}$$

where j is in either of the two pure regions of the chain. If j is chosen in the pure region at the right, then by using Eqs. (A25b) and (A25d) for $B_j(s)$ and $B_j(-s)$ in Eq. (B6), we obtain

$$G(s,-s)=-i(4L_0/mL)\,|\Gamma(s)|^{-2}\Delta^*(s)\sin sa, \quad \text{(B7)}$$

where $s \geq 0$.

It is the product $G(s,-s)(G(-s,s)$ rather than $G(s,-s)$ itself which is of interest here. By noting from Eq. (B6) that $G(-s,s)=-G^*(s,-s)$, it is easy to see that

$$G(s,-s)G(-s,s)=-(4L_0/mL)^2|\Gamma(s)|^{-4}|\Delta(s)|^2\sin^2 sa, \quad \text{(B8)}$$

where $s \geq 0$.

Notice that $G(s,-s)G(-s,s)$ is symmetric about $s=0$, thus Eq. (B8) holds for $s \leq 0$ as well.