ENERGY TRANSPORT IN THE HARMONIC LATTICE
WITH ISOTOPIC IMPURITIES

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Kenneth Richard Allen

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Chairman

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Date approved by Chairman: ______________

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SUMMARY

Energy transport in the crystal lattice has been under active investigation for over 50 years. Out of the early investigations in this field, a theory which is generally referred to as the phenomenological theory of thermal conductivity has evolved. While this theory has been fairly successful for describing in a qualitative way the behavior of the thermal conductivity of solids, it has generally been unsuccessful in its quantitative predictions.

In the phenomenological theory, it is assumed that a system which is disturbed from complete thermal equilibrium will return to complete thermal equilibrium exponentially. The dynamical equations of motion for the system are never used in order to determine the time evolvement of the system. In addition, this theory apparently suffers from some inconsistencies in its formulation. This is especially evident when the method is applied to some rather simple systems such as one whose only scattering mechanism is that due to isotopic impurities, in which case the thermal conductivity is found to diverge.

More recently a new approach, which utilizes the method of correlation functions, has been developed. This method shows considerable promise of avoiding many of the difficulties encountered by the phenomenological theory. However, almost all of the effort which has been expended along these lines has been directed toward placing the methods of the phenomenological theory on more rigorous grounds. Thus, there

has as yet been no detailed investigation of the thermal conductivity for some specific model using these methods.

It is the aim of this thesis to present a simple mechanical model of thermal conductivity which overcomes the difficulties of earlier theories. In particular it is hoped that this model will show how to avoid the logical inconsistencies of the phenomenological theory and can serve as an example system for which the method of correlation functions can be explicitly evaluated. It is also hoped that this model will indicate where other effects, such as anharmonic terms, must be introduced in order to obtain agreement with experiment.

The model consists of an infinite one-dimensional chain of particles which interact through harmonic forces of equal strength. In a finite section of this chain a finite number of the particles have been replaced at random by isotopes. The transformation equations to the phonon representation are solved by using a Green's function technique. These solutions are then used in conjunction with two different statistical methods in order to determine the energy per unit length as a function of position along the chain and the average thermal conductivity of the chain. The first statistical method is referred to here as the method of local equilibrium. It consists of assuming that the pure region to the left of the impurity bearing region of the chain has the same energy per unit length as a system which is at complete thermal equilibrium characterized by a temperature T_1, and that the pure region to the right of the impurity bearing region has the same energy per unit length as a system which is at complete thermal equilibrium characterized by a temperature T_2. This method is used to calculate both the energy per unit length as a function of position along the chain and the average thermal conductivity of the chain. The second statistical method is based upon the method of correlation functions and is used only to calculate the average thermal conductivity of the chain.

It is found by using the method of local equilibrium that the energy per unit length as a function of position along the chain decreases in a linear fashion from the high temperature pure region to the low temperature pure region. This holds true provided the average temperature of the chain is small and the total number of isotopic impurities in the chain is not too large. It is pointed out that, when these results break down, one would expect the contribution from anharmonic terms to be important.

On the other hand, when the method of local equilibrium is used to calculate the average thermal conductivity of the chain, it is found that the divergence encountered in the phenomenological theory remains. Thus the method does not lead to a finite thermal conductivity for our model.

Using the method of correlation functions to calculate the average thermal conductivity of the chain, however, one finds that the divergence does not occur. While the model is far too simple to give good quantitative agreement with experiment, its qualitative agreement is surprisingly good.

The results of this investigation indicate that it would be useful to extend this calculation to three dimensions and to include at least some of the contributions from anharmonic terms. By extending the calculation to three dimensions one might expect to obtain better quantitative agreement with experiment. By including anharmonic terms the system could be investigated at higher temperatures.

CHAPTER I

INTRODUCTION

In the first section of this chapter, a brief historical review of research on the conduction of heat in solids is given. In the second section, the phenomenological theory of thermal conductivity is outlined briefly. The final section is devoted to a discussion of the aims of this thesis and an outline of its remaining chapters.

Historical Introduction

For a little over 50 years attempts have been made to explain the behavior of the thermal conductivity of the crystal lattice. In 1914 Debye (1) successfully explained the 1/T temperature dependence of the thermal conductivity which had been observed earlier in experiments by Eucken (2) at temperatures above about 100° K. This behavior was attributed to the presence of anharmonic terms in the interatomic potential energy.

While Debye's theory was successful at high temperatures, it was not rigorous and was unsuccessful at low temperatures. In 1929 Peierls (3) gave a more satisfactory formulation of the thermal conductivity due to anharmonicities, and, using quantum methods, he was able to extend the theory to low temperatures. Peierls' theory predicted that at low temperatures (10°K to 50°K) the thermal conductivity should increase exponentially with decreasing temperature.

In low temperature experiments by de Haas and Biermasz (4), (5), (6), the thermal conductivities of quartz, diamond, and some alkali halides were observed to rise with decreasing temperature but not as rapidly as predicted by Peierls. This was first explained by Pomeranchuk (7) who pointed out that point defects, that is fluctuation in the mass distribution, could cause resistance to the flow of energy and thus prevent the thermal conductivity from rising exponentially. However, the resistance due to point defects did not appear to be adequate in the case of good crystals to explain this behavior until it was later realized (8), (9), that naturally occurring isotopes could contribute significantly to the point defect resistance.

At very low temperatures (below about 10°K) it was observed, in the experiments by De Haas and Biermasz, that the thermal conductivity decreased with decreasing temperature and that it depended upon the size of the crystal. This behavior was explained by Casimir (10) as being due to the diffuse scattering of lattice waves by the external boundaries of the crystal.

Klemens (11) extended the work of Peierls in order to account for all of the resistance causing mechanisms in one theory. In this work Klemens concluded that anharmonic processes which conserve quasi-momentum (normal processes) were unimportant except at low frequencies and, as had been pointed out earlier by Peirels, that the only anharmonic processes which actually cause thermal resistance are those which do not conserve quasi-momentum (umklapp processes). Attempts by Klemens to include the contributions from normal processes at low frequencies were found to be unsatisfactory in many cases. It was not until Callaway (12) successfully treated the low frequency contribution from normal processes that the theory assumed its present form.

This theory which was begun by Peierls, extended by Klemens, and cast into its present form by Callaway will henceforth be referred to as the phenomenological theory of thermal conductivity. Excellent reviews of this theory and discussions of techniques for calculating thermal conductivities from it can be found in articles by Klemens (13) and Carruthers (14).

While the phenomenological theory has been successful in explaining in a qualitative way the behavior of the thermal conductivity of solids, it has been generally unsuccessful in its quantitative predictions. In addition, there are several arguments in the derivation of the equations of the phenomenological theory which are not completely satisfactory.

Recently Hardy (15), (16), using the method of correlation functions originally developed by Kubo (17), has been successful in placing the methods of the phenomenological theory on a much more satisfactory basis. In addition, he and his co-workers (18), (19) have developed a perturbation expansion for the lattice thermal conductivity. These expressions, however, have not been evaluated using a specific model.

Some other investigations which utilize the statistical dynamical approach have been carried out by Teramoto and Kashiwamura (20), (21), (22) and Hemmer (23). Here the statistics are introduced only in the initial conditions, and the time evolvement of the system is determined purely by its dynamical equations of motion. These investigations, however, have not been carried far enough to yield definite conclusions about the thermal conductivities of the systems to which they are applied.

The Phenomenological Theory

In this section a brief outline of the phenomenological theory of thermal conductivity is given. The derivations of some of the expressions which follow are taken in part from the review article by Carruthers (24).

The basic problem is to calculate the heat current $\vec{J}$ which is given by

$$\vec{J} = \frac{1}{V} \sum_{s} N_s \hbar \omega_s v_s \qquad \text{(I-1)}$$

In this expression N_s is the number of phonons with wave number s, $\hbar\omega_s$ is the energy of a phonon with wave number s, $\vec{v}_s$ is the group velocity of a phonon with wave number s, and V is the volume of the crystal. This expression can be evaluated when N_s, the number of phonons with wave number s, is known.

In order to find N_s consider the flow of phonons with wave number s through the walls of an imaginary small volume. The number of phonons with a given wave number can change for two reasons. First, it can change because of collisions of phonons with each other and with impurities and, second, because of the transport of phonons due to the presence of a temperature gradient. The contribution from collisions is written as $(\partial N_s/\partial t)_c$ and it must be calculated from the scattering mechanisms involved. The contribution to $\partial N_s/\partial t$ due to a temperature gradient is given by $(-\vec{v}_s \cdot \nabla N_s)$. This expression may be written as $(-\vec{v}_s \cdot \nabla T \, dN_s/dt)$ with the understanding that N_s changes as a function of position only because T is a function of position. Since in the steady state the total rate of change of N_s must be zero, these two contributions yield the following Boltzmann transport equation for phonons:

$$\left(\frac{\partial N_s}{\partial t}\right)_c = \vec{v}_s \cdot \nabla T \left(\frac{dN_s}{dT}\right) \tag{I-2}$$

An exact solution to Equation (I-2) is usually very difficult to obtain. Nonetheless, one may approximate $(\partial N_s/\partial t)_c$ by assuming that any deviation from complete thermal equilibrium damps out exponentially in a time τ_s. In this case the expression for $(\partial N_s/\partial t)_c$ can be written as

$$\left(\frac{\partial N_s}{\partial t}\right)_c = \frac{N_s^o - N_s}{\tau_s} \tag{I-3}$$

where N_s^o is the number of phonons with wave number s at complete thermal equilibrium given by

$$N_s^o = \frac{1}{(e^x - 1)} \tag{I-4}$$

where $x = \hbar\omega_s/kT$ and k is the Boltzmann constant. Using Equations (I-2) and (I-3), one obtains for N_s the equation,

$$N_s = N_s^o - \tau_s \vec{v}_s \cdot \nabla T \left(\frac{dN_s}{dT}\right) \tag{I-5}$$

The relaxation time τ_s must be calculated according to the scattering processes involved. For the details of these calculations the reader is referred to the review article by Carruthers (14). For the purpose of this discussion, it will be sufficient to use the expression for the relaxation time which is given by Callaway (25) as

$$\tau_s = A\omega_s^4 + (B_1 + B_2)T^3\omega_s^2 + \frac{v_o}{L} \tag{I-6}$$

Here A and B_2 are constants independent of the temperature; B_1 is proportional to $e^{-\theta/aT}$ where θ is the Debye temperature and "a" is a constant; v_o is the speed of a phonon with wave number s = 0; and L is a length which depends upon the size of the crystal. The term which varies as ω_s^4 is the contribution from point defects; the terms which vary as ω_s^2 are the contributions from anharmonic terms; and the term which does not depend upon ω_s is due to diffuse boundary scattering.

Using Equation (I-4) and making the approximation $dN_s/dT = dN_s^o/dT$ which is valid for small deviations from equilibrium, the following expression for N_s is obtained:

$$N_s = \frac{1}{(e^x - 1)}\left[1 - \tau_s \frac{x\, e^x}{(e^x - 1)} \; \frac{\vec{v}_s \cdot \nabla T}{T}\right] \tag{I-7}$$

If this expression is used in Equation (I-1), then the expression for the heat current $\vec{J}$ becomes

$$\vec{J} = \frac{k}{V} \sum_s \frac{x^2 e^x}{(e^x - 1)^2} \tau_s \, \vec{v}_s \cdot \nabla T \, \vec{v}_s \tag{I-8}$$

Notice that there is no contribution from N_s^o since it is symmetric in s and $\vec{v}_s$ is antisymmetric in s.

By specializing to the isotropic case, Equation (I-8) can be written (26) as

$$\vec{J} = -\frac{k}{V} \sum_s \frac{x^2 e^x}{(e^x - 1)^2} \tau_s \, v_s^2 \cos\phi \; \nabla T \tag{I-9}$$

where ϕ is the angle between $\vec{v}_s$ and ∇T. Since the thermal conductivity K is defined by the equation

$$\vec{J} = -K \nabla T \tag{I-10}$$

it is easily seen that K is given by

$$K = \frac{k}{V} \sum_s \frac{x^2 e^x}{(e^x - 1)^2} \tau_s \, v_s^2 \cos^2\phi \tag{I-11}$$

Converting the sum over s to an integral and using the acoustic approximation $\omega(s) = v_o s$ where $v(s)$ is a constant equal to v_o, it is found that

$$K = \frac{3 k v_o^2}{(2\pi)^3} \int \frac{x^2 e^x}{(e^x - 1)^2} \tau(s) \cos^2\phi \, d^3s \qquad \text{(I-12)}$$

where the factor of 3 is due to the three polarization directions. This expression can be partially integrated to yield

$$K = \frac{k}{2\pi^2 v_o} \left(\frac{kT}{\hbar}\right)^3 \int_0^{\frac{\Theta}{T}} \frac{x^4}{(Dx^4 + Ex^2 + v_o/L)} \frac{e^x}{(e^x - 1)^2} \, dx \qquad \text{(I-13)}$$

where $D = A(kT/\hbar)^4$, $E = (B_1 + B_2)T^3 \, (kT/\hbar)^3$, and Equation (I-6) has been used for the relaxation time. The solutions to Equation (I-13) in the various temperature regions have been discussed thoroughly by Callaway (12) and will not be discussed here.

The expression for the relaxation time $\tau(s)$ which is given in Equation (I-6) and which was used in Equation (I-13) contains the term v_o/L which is the contribution from boundary scattering. While it will almost certainly be necessary to include the effects of boundary scattering in order to obtain a detailed agreement with experiment, they should not be crucial for a consistent formulation of the theory. Moreover, by making the crystal very thick the contribution from boundary scattering can be made negligibly small. The contribution from boundary scattering will therefore be dropped in the remainder of this discussion.

If the contributions from anharmonic terms are also omitted from Equation (I-13), then the expression

$$K = \frac{\hbar}{2\pi^2 v_0} \frac{1}{AT} \int_0^{x_0} \frac{e^x}{(e^x - 1)^2} \, dx \qquad \text{(I-14)}$$

is obtained. It can be seen that this expression diverges at the lower limit. This difficulty can be traced to Equation (I-7) where, if the contributions from boundary scattering and anharmonic terms are dropped, it is seen that the deviation from equilibrium becomes arbitrarily large as the frequency approaches zero. This of course is not permissible since it has been assumed that the deviation from equilibrium is small.

If the contribution from anharmonic terms is included, then the expression for the thermal conductivity no longer diverges. However, the deviation from equilibrium still becomes arbitrarily large as the frequency approaches zero. This is not a serious problem if the temperature is high enough since in that case these low frequencies contribute negligibly to the thermal conductivity. At low temperatures, however, the major contribution to the thermal conductivity comes entirely from these low frequencies, and therefore at low temperatures this large deviation from equilibrium represents a serious problem.

A careful examination of Equations (I-7) and (I-13), with the contribution from boundary scattering omitted, will show that these low frequency difficulties actually constitute a violation of the conservation of energy (see Chapter VI). This can be seen by noting that when N_s becomes negative the system is conducting more energy per unit time than there is available to be transported.

Purpose of Investigation

The phenomenological theory assumes that if a system is disturbed from complete thermal equilibrium it will return to equilibrium exponentially. The mechanical properties of the system are used only to calculate the relaxation time. At high temperatures it appears that the results of the phenomenological theory are qualitatively correct, and its failure to give good quantitative agreement with experiment is probably due to a lack of knowledge concerning the nature of anharmonic forces. However, at low temperatures it seems to encounter some fundamental difficulties, such as the divergence which is encountered when the system's only scattering mechanism is due to isotopic impurities.

The approach developed by Hardy is from a more mechanistic point of view than that of the phenomenological theory. However, the formalism developed by Hardy is somewhat difficult to work with, and no investigation of a particular model within this framework has been carried out.

All existing theory and experiment indicate that the low temperature thermal conductivity of insulators is determined by the isotopic scattering which occurs when the motion of the system is dominated by harmonic forces. Despite this well known fact, all previous efforts have failed to calculate a meaningful thermal conductivity for harmonic systems which contain impurities. It is the aim of this thesis to present a harmonic model of thermal conductivity which overcomes the difficulties of earlier theories. In particular it is hoped that this model will show how to avoid the logical inconsistencies of the phenomenological theory and can serve as an example system for which the method of correlation functions can be explicitly evaluated. It is also hoped that the investigation of this model will indicate where other effects, such as anharmonic terms, must be introduced in order to obtain agreement with experiment.

The model which has been chosen for this investigation consists of an infinite one-dimensional chain of particles. A short section of this otherwise pure chain contains a finite number of randomly placed isotopes. These isotopes have mass M while all other particles have mass m. All particles interact through nearest neighbor harmonic forces only.

The program for the investigation of this model is given in the following outline of the remaining chapters of this thesis. In Chapter II some preliminary formalism is discussed for the purpose of familiarizing the reader with the notation and to serve as a guide for the further formulation of the problem. In particular, the local energy and heat flux operators are defined and written in terms of the phonon representation.

In Chapter III a method for solving the equations of transformation to the phonon representation is discussed, and formal solutions to these equations are obtained. These formal solutions are not of much use in a general case because they are extremely complicated. However, for this model, due to the random positioning of the impurities and the fact that there are a finite number of them, a reliable approximation to these solutions can be obtained.

The basic statistics necessary for the calculation of the average values of the heat flux and the local energy of the system are introduced in Chapter IV. In Chapter V these statistical methods are used in conjunction with the solutions found in Chapter III to obtain explicit expressions for the average values of the local energy and the heat flux.

In Chapter VI the expressions obtained in Chapter V are discussed in detail. Finally, some conclusions about the results of this investigation are drawn and some recommendations for further investigations are made in Chapter VII.

In order that the conclusions of this thesis not be lost in the following welter of arithmetic, we review the final results to be obtained. The principal conclusion which can be drawn from this work is that a finite thermal conductivity can indeed be calculated for harmonic systems. Furthermore, exact solutions to the transformation equations for this system are obtained. By using these exact solutions it is possible to calculate expressions for the thermal properties of this harmonic system. Having obtained these expressions for the harmonic system it is then possible, by comparing them to experiment, to see clearly where other effects, such as the contributions from anharmonic terms, become important.

CHAPTER II

PRELIMINARY FORMALISM

This chapter is primarily devoted to the development of the formalism which is used throughout the remainder of this thesis. In the first section of this chapter the phonon representation is discussed in considerable detail for the purpose of familiarizing the reader with the notation and of illustrating procedures to be used in later chapters. In the second and third sections the Hamiltonian density operator and the heat flux operator are defined and cast into the phonon representation.

The development throughout is quantum mechanical and is done in the Heisenberg picture where the operators are time dependent and the state function is time independent. The formalism developed in this chapter for one dimension could easily be extended to three. The resulting formulas, however, are evaluated only for the one-dimensional system. We therefore confine our attention to one dimension from the onset.

The Phonon Representation

The mechanical system which is considered here consists of a one-dimensional chain of particles coupled by harmonic forces. That is, the expression for the potential energy of the system is of a quadratic form in the displacements of the particles from their equilibrium positions. The Hamiltonian for such a system is given by

$$H = \sum_{j} \frac{p_j^2}{2m_j} + \frac{1}{2}\sum_{j,k} \varphi_{j,k}\, u_j u_k \qquad \text{(II-1)}$$

where the sums over j and k are over all of the particles in the system, m_j is the mass of the j^{th} particle, and the $\phi_{j,k}$ are the usual harmonic force constants, which satisfy the relation

$$\varphi_{j,k} = \varphi_{k,j} \tag{II-2}$$

The u_j and p_j are quantum mechanical operators which correspond, respectively, to the displacement from the equilibrium of the j^{th} particle and the momentum of the j^{th} particle.

The system is quantized (28) by imposing upon the operators u_j and p_j the commutation relations

$$[u_j, p_k] = i\hbar\,\delta_{j,k} \quad , \quad [u_j, u_k] = [p_j, p_k] = 0 \tag{II-3}$$

where the square bracket stands for the quantum mechanical commutator of the operators which appear within and $\delta_{j,k}$ is the Kronecker delta.

The transformation to the phonon representation is to be found by seeking that linear transformation of the u_j and p_j which reduces the Hamiltonian (II-1) to a sum over N mutually independent parts where N is the number of particles in the system. To this end, we begin by considering the real symmetric matrix D whose elements are given by

$$D_{j,k} = \frac{\varphi_{j,k}}{\sqrt{m_j m_k}} \tag{II-4}$$

Since D is real and symmetric it possesses a complete set of linearly independent eigenvectors which correspond to real non-negative eigenvalues. The set of equations from which these eigenvectors and their corresponding eigenvalues are determined is

$$\sum_{k} D_{j,k} B_{k}^{\alpha} = \omega_{\alpha}^{2} B_{j}^{\alpha} \tag{II-5}$$

where B_j^{α} is the j^{th} component of the α^{th} eigenvector and ω_{α}^{2} is the eigenvalue corresponding to it. Because of the symmetry of the matrix D, it is possible to find a set of eigenvectors which are real. However, in problems such as this one where degeneracies are involved, it is more advantageous to choose a complex set of eigenvectors where the complex conjugate $B_j^{\alpha *}$ of B_j^{α} satisfies the set of equations

$$\sum_{k} D_{j,k} B_{k}^{\alpha *} = \omega_{\alpha}^{2} B_{j}^{\alpha *} \tag{II-6}$$

Since D is symmetric it is always possible to orthonormalize its eigenvectors in such a way that

$$\sum_{j} B_{j}^{\alpha} B_{j}^{\alpha' *} = \delta_{\alpha,\alpha'} \tag{II-7}$$

And, when the eigenvectors are orthonormalized in this way, the fact that they form a complete set is contained in the closure relation which takes the form

$$\sum_{\alpha} B_j^{\alpha} B_k^{\alpha *} = \delta_{j,k} \tag{II-8}$$

Next, we introduce the non-hermitian operators a_α and $a_\alpha^\dagger$, where the $\dagger$ stands for hermitian conjugate, defined by the equations

$$a_\alpha = \frac{1}{\sqrt{2\hbar}} \sum_k B_k^{\alpha *} \left(\sqrt{m_k \omega_\alpha}\, u_k + i \frac{p_k}{\sqrt{m_k \omega_\alpha}} \right) \tag{II-9}$$

and

$$a_\alpha^\dagger = \frac{1}{\sqrt{2\hbar}} \sum_k B_k^{\alpha} \left(\sqrt{m_k \omega_\alpha}\, u_k - i \frac{p_k}{\sqrt{m_k \omega_\alpha}} \right)$$

These equations can be inverted with the aid of Equation (II-8) to yield the expressions for the u_j's and p_j's in terms of the new operators a_α and $a_\alpha^\dagger$. These expressions are

$$u_j = \sum_{\alpha} \sqrt{\frac{\hbar}{2 m_j \omega_\alpha}} \left(B_j^{\alpha} a_\alpha + B_j^{\alpha *} a_\alpha^\dagger \right) \tag{II-10}$$

and

$$p_j = -i \sum_{\alpha} \sqrt{\frac{\hbar m_j \omega_\alpha}{2}} \left(B_j^{\alpha} a_\alpha - B_j^{\alpha *} a_\alpha^\dagger \right)$$

Before the expression for the Hamiltonian in terms of the a_α and $a_\alpha^\dagger$ can be calculated the commutation relations between these new operators must be known. These relations are easily found by using Equations (II-3), (II-7), and (II-9) to be

$$[a_\alpha, a^+_{\alpha'}] = \delta_{\alpha,\alpha'} \quad , \quad [a_\alpha, a_{\alpha'}] = [a^+_\alpha, a^+_\alpha] = 0 \qquad \text{(II-11)}$$

If Equations (II-10) are now substituted into Equation (II-1) and use is made of Equations (II-5), (II-6), (II-7), and (II-11), then the expression for the Hamiltonian becomes

$$H = \sum_\alpha \hbar\omega_\alpha \left(a^+_\alpha a_\alpha + 1/2 \right) \qquad \text{(II-12)}$$

Thus the Hamiltonian is now in the desired form, namely a sum over N mutually independent simple harmonic oscillator Hamiltonians, and all of the formalism which has been developed elsewhere (29) for the simple harmonic oscillator is directly applicable here. If the notation $| \ell >$ is used to represent an eigenstate of the Hamiltonian such that

$$a^+_\alpha a_\alpha |\ell\rangle = n^\ell_\alpha |\ell\rangle \qquad \text{(II-13)}$$

then

$$H|\ell\rangle = \sum_\alpha \hbar\omega_\alpha (n^\ell_\alpha + 1/2) |\ell\rangle \qquad \text{(II-14)}$$

As is well known, the eigenvalues n_α^ℓ of the number operator $a_\alpha^\dagger a_\alpha$ take on all non-negative integer values, and they are interpreted as the number of phonons of energy $\hbar\omega_\alpha$ present in the system when it is in the eigenstate $|\ell>$.

It is also a well known property of the operators a_α and $a_\alpha^\dagger$, which are referred to as destruction and creation operators, respectively, that

$$a_\alpha |\ell\rangle = \sqrt{n_\alpha^\ell}\ |\ell, -1_\alpha\rangle \qquad \text{(II-15)}$$

and

$$a_\alpha^\dagger\ |\ell\rangle = \sqrt{n_\alpha^\ell + 1}\ |\ell, + 1_\alpha\rangle$$

In these expressions the notation $|\ell, -1\alpha>$ stands for the eigenstate of the system with one less phonon of energy $\hbar\omega_\alpha$ than in the state $|\ell>$ and the notation $|\ell_1 + 1\alpha>$ for the state with one more phonon of energy $\hbar\omega_\alpha$ than the state $|\ell>$.

Because the number operator is an hermitian operator, eigenstates of the system which correspond to different eigenvalues are automatically orthogonal and, as will be the case here, are usually normalized such that

$$\langle\ell|m\rangle = \delta_{\ell,m} \qquad \text{(II-16)}$$

When the number of particles in the system becomes arbitrarily large, it is convenient to replace the index α by a continuous variable and convert sums over α into integrals. In order to do this, let the particles be numbered such that the integer k which labels the k^{th} particle lies in the interval

$$-\frac{(N-1)}{2} \leq k \leq \frac{(N-1)}{2}$$

where the number of particles N is to be made arbitrarily large. Now let the variable s_α be defined such that

$$S_\alpha = \frac{2\pi}{Na}\alpha \tag{II-17}$$

where "a" is the lattice spacing and α is in the interval

$$-\frac{(N-1)}{2} \leq \alpha \leq \frac{(N-1)}{2}$$

Then, a sum which is of the form

$$\sum_{\alpha=-\frac{(N-1)}{2}}^{\frac{(N-1)}{2}} f_\alpha$$

can be written as

$$\sum_{\alpha=-\frac{(N-1)}{2}}^{\frac{(N-1)}{2}} f_\alpha = \frac{Na}{2\pi} \sum_{\alpha=-\frac{(N-1)}{2}}^{\frac{(N-1)}{2}} f(s_\alpha)\,\Delta s_\alpha \qquad \text{(II-18)}$$

where f(s) is a function of the continuous variable s such that

$$f_\alpha = f(s_\alpha)$$

Thus, as N becomes arbitrarily large

$$\sum_{\alpha=-\frac{(N-1)}{2}}^{\frac{(N-1)}{2}} f_\alpha = \frac{Na}{2\pi} \int_{-\pi/a}^{\pi/a} f(s)\,ds \qquad \text{(II-19)}$$

This conversion of a sum to an integral can be done rigorously by using the Euler-McLauren summation formula.

It is also necessary to know the behavior of the Kronecker delta $\delta_{\alpha,\alpha'}$ as N becomes arbitrarily large. This can be found by expressing $\delta_{\alpha,\alpha'}$ as a Fourier series. The Fourier expansion of $\delta_{\alpha,\alpha'}$ is

$$\delta_{\alpha,\alpha'} = \frac{1}{N} \sum_{j=-\frac{(N-1)}{2}}^{\frac{(N-1)}{2}} e^{ij\frac{2\pi}{Na}(\alpha-\alpha')a}$$

which, as N becomes arbitrarily large, can be written as

$$\delta_{\alpha,\alpha'} \Rightarrow \frac{2\pi}{Na}\,\delta(s-s') \qquad \text{(II-20)}$$

where $\delta(s-s')$ is the Dirac delta function.

Making use of Equations (II-19) and (II-20) the following expressions are obtained for arbitrarily large N:

$$H = \sum_{j} \frac{p_j^2}{2m_j} + \frac{1}{2}\sum_{j,k} \varphi_{j,k} u_j u_k \qquad \text{(II-21)}$$

$$\sum_{k} D_{j,k} B_k(s) = \omega^2(s)\, B_j(s) \qquad \text{(II-22)}$$

$$\sum_{k} B_k(s) B_k^*(s') = \frac{2\pi}{Na}\, \delta(s-s') \qquad \text{(II-23)}$$

$$\frac{Na}{2\pi}\int_{-\pi/a}^{\pi/a} B_j(s) B_k^*(s)\, ds = \delta_{j,k} \qquad \text{(II-24)}$$

$$u_k = \frac{Na}{2\pi}\int_{-\pi/a}^{\pi/a} \sqrt{\frac{\hbar}{2m_k\omega(s)}}\left[B_k(s)a(s) + B_k^*(s)a^{+}(s)\right] ds \qquad \text{(II-25)}$$

$$p_k = -i\,\frac{Na}{2\pi}\int_{-\pi/a}^{\pi/a} \sqrt{\frac{\hbar m_k \omega(s)}{2}}\left[B_k(s)a(s) - B_k^*(s)a^{+}(s)\right] ds \qquad \text{(II-26)}$$

$$[a(s), a^{+}(s')] = \frac{2\pi}{Na}\delta(s-s'),\ [a(s), a(s')] = [a^{+}(s), a^{+}(s')] = 0 \qquad \text{(II-27)}$$

and

$$H = \frac{Na}{2\pi}\int_{-\pi/a}^{\pi/a} \hbar\omega(s)\left(a^{+}(s)a(s) + \tfrac{1}{2}\right) ds \qquad \text{(II-28)}$$

In Equations (II-21) through (II-28) it is important to remember that N is to be made arbitrarily large; thus if a quantity which is calculated by using these expressions is to be meaningful it must ultimately be independent of N.

The Hamiltonian Density

The Hamiltonian operator which is defined in Equation (II-1) refers to the total energy of the system. For the treatment of the transport properties of a system, it is the Hamiltonian density rather than the total Hamiltonian which is important. Here, the Hamiltonian density will be defined (30) as

$$H(r) = \tfrac{1}{2} \sum_j \left\{ H_j \, \delta(r_j - r) + H.C. \right\} \tag{II-29}$$

where

$$H_j = \frac{p_j^2}{2m_j} + \frac{1}{2} \sum_k q_{j,k} \, u_j u_k \tag{II-30}$$

The variable "r" which appears in Equation (II-29) is a continuous parameter which labels the position along the chain and is not an operator. The quantity r_j is the position operator of the j^{th} particle which is given by

$$r_j = ja + u_j \tag{II-31}$$

if the 0^{th} particle has its equilibrium position at the origin. The notation H.C. stands for hermitian conjugate and Equation (II-29) is symmetrized because H_j and $\delta(r_j-r)$ do not commute. Here $\delta(r_j-r)$ is the coarse-grained delta function (31), (32), and it can be represented by

$$\delta(r_j-r) = \frac{1}{Na}\sum_p e^{i\frac{2\pi}{Na}p(r_j-r)} \tag{II-32}$$

In this expression "p" is an integer whose range is

$$-\frac{Na}{\ell} \leq p \leq \frac{Na}{\ell}$$

where ℓ is a distance which on a macroscopic scale is very small but which is still large enough to include a large number of particles. Notice that the size of ℓ determines the sharpness of the delta function. The delta function essentially includes all of the particles within an interval ℓ which is centered on the point r and excludes all of the particles which lie outside of this interval. If $\delta(r_j-r)$ in Equation (II-29) were the Dirac delta function, the Hamiltonian density would be discontinuous, yielding the zero operator for $r \neq r_j$ and the energy operator of the j^{th} particle for $r = r_j$. The coarse-grained delta function is used in order to obtain a smoothly varying energy density.

By making use of Equations (II-29) and (II-32) it can be shown that

$$\int_{-\frac{Na}{2}}^{\frac{Na}{2}} H(r)\, dr = H \tag{II-33}$$

The Heat Flux Operator

The expression for the heat flux operator $\mathcal{J}(r)$ can be obtained by requiring that it satisfy the equation of continuity for the Hamiltonian density which is given (33) by

$$\frac{\partial H(r)}{\partial t} = - \frac{\partial}{\partial r} \mathcal{J}(r) \tag{II-34}$$

This expression when integrated over the entire system yields a statement of the conservation of energy. That is, it states that the time rate of increase of the energy of the system is equal to the negative of the rate at which energy is flowing out of the system. After a somewhat lengthy calculation which is given in Appendix A, the heat flux operator is found to be

$$\mathcal{J}(r) = \frac{1}{2} \sum_{j} \Big\{ H_j\, \delta(r_j - r) \frac{p_j}{2m_j} + \frac{p_j}{2m_j} \delta(r_j - r) \tag{II-35}$$

$$+ \sum_{k} (i\hbar)^{-1} \left[\frac{p_j^2}{2m_j}, V_k \right] \times$$

$$\delta(r_j - r) \quad + \quad H.C. \Big\}$$

where

$$V_k = \tfrac{1}{2}\sum_m \varphi_{k,m} u_k u_m \qquad \text{(II-36)}$$

In order to determine the thermal conductivity of the system one needs an expression for the average heat flux J which is given by

$$J = \frac{1}{L}\int_{-L/2}^{L/2} J(r)\,dr \qquad \text{(II-37)}$$

where L is the length of chain over which the average is to be taken. If the integral in Equation (II-37) is performed, then the expression

$$J = \frac{1}{2L}\sum_{j=-\frac{L}{2a}}^{\frac{L}{2a}} \Big\{ H_j \frac{p_j}{2m_j} + \qquad \text{(II-38)}$$

$$\sum_k (i\hbar)^{-1}\Big[\frac{p_j^2}{2m_j}, V_k\Big](r_j - r_k) + \text{H.C.}\Big\}$$

is obtained. By making use of the commutation relations for the position and momentum operators r_j and p_j and Equation (II-36), this can be written as

$$J = \frac{1}{2L}\sum_{j=-\frac{L}{2a}}^{\frac{L}{2a}} \Big\{ H_j \frac{p_j}{2m_j} + \sum_k \varphi_{k,j} u_k \frac{p_j}{m_j} \times \qquad \text{(II-39)}$$

$$\big[(k-j)a + (u_k - u_j)\big] + \text{H.C.}\Big\}$$

The terms in Equation (II-39) which involve the product of three operators are present because energy is transferred between the actual positions of the particles and not between their equilibrium lattice sites. If the oscillations are restricted to be of small amplitude, as is the case with solids at low temperature, then these terms are completely negligible and a good approximation to the heat flux operator is given (34) by

$$J = \frac{1}{2L} \sum_{j=-\frac{L}{2a}}^{\frac{L}{2a}} \sum_{k} \left\{ (k-j) a \, \phi_{k,j} \, u_k u_j \frac{p_j}{m_j} + \text{H.C.} \right\} \tag{II-40}$$

In the case of nearest neighbor interactions of equal strength $\phi_{k,j}$ is given by

$$\phi_{k,j} = -\gamma \left(\delta_{k,j-1} - 2\delta_{k,j} + \delta_{k,j+1} \right) \tag{II-41}$$

where γ is the strength of the harmonic interaction. Using the above expression for $\phi_{k,j}$ in Equation (II-40), the average heat flux operator becomes

$$J = \frac{\gamma a}{L} \sum_{j=-\frac{L}{2a}}^{\frac{L}{2a}} \left(u_{j-1} - u_{j+1} \right) \frac{p_j}{m_j} \tag{II-42}$$

Equation (II-42) is equivalent to the expression obtained by Brillouin (35) who used a less rigorous method.

Using Equations (II-10) for u_j and p_j, the expression for the average heat flux operator, when expressed in the phonon representation, is

$$J = -i\,\frac{\hbar\gamma a}{2L} \sum_{j=-\frac{L}{2a}}^{\frac{L}{2a}} \sum_{\alpha,\alpha'} \sqrt{\frac{\omega_{\alpha'}}{\omega_\alpha}} \times \tag{II-43}$$

$$\left[\left(\frac{B^{\alpha}_{j-1}}{\sqrt{m_{j-1}}} - \frac{B^{\alpha}_{j+1}}{\sqrt{m_{j+1}}}\right) a_\alpha + \left(\frac{B^{\alpha *}_{j-1}}{\sqrt{m_{j-1}}} - \frac{B^{\alpha *}_{j+1}}{\sqrt{m_{j+1}}}\right) a^{\dagger}_{\alpha}\right] \times$$

$$\left[\frac{B^{\alpha'}_{j}}{\sqrt{m_j}}\, a_{\alpha'} - \frac{B^{\alpha' *}_{j}}{\sqrt{m_j}}\, a^{\dagger}_{\alpha'}\right]$$

If the number of particles in the system is allowed to become very large, Equation (II-43) may be written

$$J = -i\,\frac{\hbar\gamma a}{2L} \left(\frac{Na}{2\pi}\right)^2 \sum_{j=-\frac{L}{2a}}^{\frac{L}{2a}} \iint_{-\pi/a}^{\pi/a} \sqrt{\frac{\omega(s')}{\omega(s)}} \times \tag{II-44}$$

$$\left[\left(\frac{B_{j-1}(s)}{\sqrt{m_{j-1}}} - \frac{B_{j+1}(s)}{\sqrt{m_{j+1}}}\right) a(s) + \left(\frac{B^{*}_{j-1}(s)}{\sqrt{m_{j-1}}} - \frac{B^{*}_{j+1}(s)}{\sqrt{m_{j+1}}}\right) a^{\dagger}(s)\right] \times$$

$$\left[\frac{B_j(s')}{\sqrt{m_j}}\, a(s') - \frac{B^{*}_{j}(s')}{\sqrt{m_j}}\, a^{\dagger}(s')\right] ds\, ds'$$

In Equation (II-44) L is an arbitrary length. In the remainder of this thesis L is always chosen to be the length of the impurity bearing region of the chain.

CHAPTER III

THE TRANSFORMATION TO THE PHONON REPRESENTATION

In order to obtain explicit expressions for the various operators in the phonon representation one needs explicit expressions for the $B_j(s)$ which appear in Equations (II-22). In this chapter exact solutions to Equations (II-22) for an infinite chain of particles which contains a finite number of isotopic impurities are obtained. These exact solutions are very complicated for an arbitrary distribution of impurities. However, for the model considered here, due to the random positions of the impurities, a reliable approximation to the exact solutions can be obtained.

The procedure which is developed here is an extension of a development given by Marodudin (36). Recall that the model which is under consideration consists of an infinite chain of identical particles of mass m which interact through nearest neighbor Hooke's law type forces of equal strength. In a short section of the chain a finite number of the particles have been replaced at random by isotopes of mass M.

In order to obtain explicit expressions for the $B_j(s)$, one must solve the equation

$$\omega^2(s) B_j(s) = \sum_k \frac{\varphi_{j,k}}{\sqrt{m_j m_k}} B_k(s) \qquad \text{(III-1)}$$

The solution to this equation can be obtained by rewriting it in a form which can be treated by Green's function methods. If the new variable $C_j(s)$ is defined such that

$$B_j(s) = \sqrt{m_j}\; C_j(s) \tag{III-2}$$

then Equation (III-1) becomes

$$m_j \omega^2(s)\, C_j(s) = \sum_k \Phi_{j,k}\, C_k(s) \tag{III-3}$$

We now introduce the parameter

$$\epsilon_j = \left(1 - \frac{m_j}{m}\right) = \epsilon \sum_{r=1}^{R} \delta_{j,\ell_r} \tag{III-4}$$

where the ℓ_r, with $r = 1,2,\cdots,R$, are the positions of the isotopic impurities ordered from left to right with increasing values of r. R is the total number of impurities introduced into the chain and

$$\epsilon = \left(1 - \frac{M}{m}\right) \tag{III-5}$$

Using Equation (III-4), Equation (III-3) can be written as

$$\sum_k \left(m\omega^2(s)\delta_{j,k} - \Phi_{j,k}\right) C_k(s) = \epsilon_j m\omega^2(s)\, C_j(s) \tag{III-6}$$

It is convenient to introduce a more compact notation by letting

$$L_{j,k}(s) = m\omega^2(s)\delta_{j,k} - \varphi_{j,k} \qquad \text{(III-7)}$$

Equation (III-6) then becomes

$$\sum_k L_{j,k}(s)C_k(s) = \epsilon_j m\omega^2(s)\, C_j(s) \qquad \text{(III-8)}$$

This equation will now be solved by the use of Green's function methods.

Let the Green's function $G_{j,k}(s)$ be defined such that

$$\sum_n L_{j,n}(s)G_{n,k}(s) = \delta_{j,k} \qquad \text{(III-9)}$$

It can be shown by direct substitution in Equation (III-9) that

$$G_{j,k}(s) = \frac{e^{i|(j-k)sa|}}{2\gamma i \,\mathrm{SIN}|sa|} \qquad \text{(III-10)}$$

where

$$\omega^2(s) = \omega_0^2 \,\mathrm{SIN}^2\left(\frac{sa}{2}\right) \qquad \text{(III-11)}$$

and

$$\omega_0 = \sqrt{\frac{4\gamma}{m}}$$

satisfies Equation (III-9).

Let us now introduce a new variable $W_n(s)$ via the equation

$$C_k(s) = e^{iksa} + \sum_n G_{k,n}(s)\, W_n(s) \qquad \text{(III-12)}$$

If Equation (III-12) is substituted into Equation (III-8), one obtains for the $W_n(s)$

$$W_n(s) = \epsilon_n m\omega^2(s)\, e^{insa} + \qquad \text{(III-13)}$$

$$\epsilon_n m\omega^2(s) \sum_k G_{n,k}(s)\, W_k(s)$$

where use has been made of Equations (III-9) and (III-10). Notice, since ϵ_n is zero unless n is the position of an impurity, that $W_n(s)$ is also zero unless n is the position of an impurity. Therefore Equation (III-13) can be written as

$$\sum_{k=1}^{R} \left(\delta_{\ell_n,\ell_k} - \epsilon m\omega^2(s)\, G_{\ell_n,\ell_k}(s)\right) W_{\ell_k} = \qquad \text{(III-14)}$$

$$\epsilon m\omega^2(s)\, e^{i\ell_n sa}$$

where k,n = 1,2,$\cdots$,R and

$$W_n(s) = 0$$

if n is not equal to the position of an impurity.

Equation (III-14) can be written in a more convenient form by using the explicit expression for the Green's function $G_{j,k}(s)$ given in Equation (III-10). Using Equation (III-10) and adding

$$\sum_{k=1}^{R} \frac{\epsilon m \omega^2(s)}{2\gamma i \, \mathrm{SIN}|sa|} e^{i(l_n-l_k)sa} W_{l_k}(s) \tag{III-15}$$

to both sides of Equation (III-14), one obtains

$$\sum_{k=n}^{R} \left[\delta_{l_n,l_k} + p(s)\,\mathrm{SIN}(l_n-l_k)sa\right] W_{l_k}(s) = \epsilon m \omega^2(s) f(s) e^{i l_n sa} \tag{III-16}$$

for s $\geq$ 0 ; and

$$\sum_{k=1}^{n} \left[\delta_{l_n,l_k} + p(s)\,\mathrm{SIN}(l_n-l_k)sa\right] W_{l_k}(s) = \epsilon m \omega^2(s) f(s) e^{i l_n sa} \tag{III-17}$$

for s $\leq$ 0, where

$$P(s) = \frac{\epsilon m \omega^2(s)}{\gamma \sin|sa|} \qquad \text{(III-18)}$$

and

$$f(s) = \left[1 + \left(\frac{1}{2\gamma i \sin|sa|}\right)\sum_{k=1}^{R} e^{-i l_k sa} W_{l_k}(s)\right] \qquad \text{(III-19)}$$

It is never necessary to evaluate f(s).

Equations (III-16) and (III-17) represent R equations in R unknowns which in principle at least can always be solved. In general finding the solutions for the R unknowns represents an extremely difficult problem. However, for a large but finite number of impurities randomly distributed throughout a finite section of the chain, an excellent approximation to their solutions can be obtained.

Equations (III-16) and (III-17) can be put into a form which is suitable for this approximation by noticing that the matrix whose elements are given by

$$M_{l_j,l_n}(s) = \delta_{l_j,l_n} - P(s)\sin(l_j - l_n)sa + \qquad \text{(III-20)}$$

$$P^2(s)\sum_{m=j+1}^{n-1} \sin(l_j - l_n)sa \, \sin(l_m - l_n)sa -$$

$$p^3(s)\sum_{k=j+1}^{m-1}\cdots\sum_{m=j+1}^{n-1} \mathrm{SIN}(\ell_j-\ell_k)sa\ \mathrm{SIN}(\ell_k-\ell_m)sa\ \mathrm{SIN}(\ell_m-\ell_n)sa\ +$$

$$\bullet\ \bullet\ \bullet\ +$$

$$(-p(s))\sum_{k=j+1}^{m-1}\cdots\sum_{q=j+1}^{n-1} \mathrm{SIN}(\ell_j-\ell_k)sa\ \bullet\ \bullet\ \bullet\ \mathrm{SIN}(\ell_q-\ell_n)sa\ +$$

$$\bullet\ \bullet\ \bullet$$

for $j \le n$ and

$$M_{\ell_j,\ell_n}(S) = 0$$

for $j > n$ is the inverse to the matrix of the coefficients of the $W_{\ell_k}(s)$ in Equation (III-16). Likewise the matrix whose elements are given by

$$M_{\ell_j,\ell_n}(S) = \delta_{\ell_j,\ell_n} - p(s)\,\mathrm{SIN}(\ell_j-\ell_n)sa\ + \tag{III-21}$$

$$p^2(s)\sum_{m=n+1}^{j-1} \mathrm{SIN}(\ell_j-\ell_n)sa\ \mathrm{SIN}(\ell_m-\ell_n)sa\ -$$

$$p^3(s)\sum_{k=n+1}^{j-1}\sum_{m=n+1}^{j-1} \mathrm{SIN}(\ell_j-\ell_k)sa\ \mathrm{SIN}(\ell_k-\ell_m)sa\ \mathrm{SIN}(\ell_m-\ell_n)sa\ +$$

$$\cdots +$$

$$(-p(s))^{r}\sum_{k=m+1}^{j-1}\cdots\sum_{q=n+1}^{j-1} \sin(l_j - l_k)sa \cdots \sin(l_q - l_n)sa +$$

$$\cdots$$

for $j \geq n$ and

$$M_{l_j, l_n} = 0$$

for $j < n$ is the inverse to the matrix of the coefficients of the $W_{l_x}(s)$ in Equation (III-17). Notice that Equations (III-20) and (III-21) represent, respectively, the cases in which s is greater than or equal to zero and s is less than or equal to zero. By using the appropriate expression for $M_{l_j, l_n}(s)$ the expression for $W_{l_j}(s)$ becomes

$$W_{l_j}(s) = \epsilon m \omega^2(s) f(s) \sum_{n=1}^{R} M_{l_j, l_n} e^{i l_n sa} \qquad \text{(III-22)}$$

If this expression is substituted into Equation (III-12), the following expression for $C_k(s)$ is obtained:

$$C_k(s) = e^{iksa} + \frac{p(s)}{2i} f(s) \times \qquad \text{(III-23)}$$

$$\sum_{j=1}^{R}\sum_{n=1}^{R} e^{i(k-\ell_j)sa} M_{\ell_j,\ell_n}(s)\, e^{i\ell_n sa}$$

It is convenient to rewrite Equation (III-23) for the cases in which s is less than or equal to zero and s is greater than or equal to zero. If s is less than or equal to zero the expression for $C_k(s)$ can be written as

$$C_k(s) = \Big[1 + \frac{P(s)}{2i} f(s) \sum_{j=M+1}^{R}\sum_{n=1}^{R} e^{-i\ell_j sa} \times \tag{III-24}$$

$$M_{\ell_j,\ell_n}(s)\, e^{i\ell_n sa}\Big] e^{iksa} +$$

$$\Big[\frac{P(s)}{2i} f(s) \sum_{j=1}^{M}\sum_{n=1}^{R} e^{i\ell_j sa} \times$$

$$M_{\ell_j,\ell_n}(s)\, e^{i\ell_n sa}\Big] e^{-iksa}$$

where $\ell_M \leq k \leq \ell_{M+1}$. By noticing that when $M = 0$, that is in the region to the left of the first impurity,

$$C_k(s) = f(s)\, e^{iksa}$$

the expression for $C_k(s)$ can be written as

$$C_k(s) = f(s)\Big[1 - \frac{\rho(s)}{2i}\sum_{j=1}^{M}\sum_{n=1}^{R} e^{-il_j sa} \times \qquad \text{(III-25)}$$

$$M_{l_j,l_n}(s)\, e^{il_n sa}\Big] e^{iksa} +$$

$$\Big[\frac{\rho(s)}{2i}\sum_{j=1}^{M}\sum_{n=1}^{R} e^{il_j sa} \times$$

$$M_{l_j,l_n}(s)\, e^{il_n sa}\Big] e^{-iksa}$$

where $\ell_M \le k \le \ell_{M+1}$. If s is greater than or equal to zero the expression for $C_k(s)$ is found in an analogous way to be

$$C_k(s) = f(s)\Big[1 - \frac{\rho(s)}{2i}\sum_{j=M+1}^{R}\sum_{n=1}^{R} e^{-il_j sa} \times \qquad \text{(III-26)}$$

$$M_{l_j,l_n}(s)\, e^{il_n sa}\Big] e^{iksa} +$$

$$\Big[\frac{\rho(s)}{2i}\sum_{j=M+1}^{R}\sum_{n=1}^{R} e^{il_j sa} \times$$

$$M_{l_j,l_n}(s)\, e^{il_n sa}\Big] e^{-iksa}$$

where $\ell_M \le k \le \ell_{M+1}$

The expressions for $C_k(s)$ which are given by Equations (III-25) and (III-26) are exact. They are, however, very complicated and not very useful in their present form. For this model, due to the random positions of the impurities, approximations to Equations (III-25) and (III-26) can be obtained. The approximations are carried out in Appendix B with the result:

$$C_k(s) = f(s)\left\{\left(1+i\frac{P(s)}{2}\right)^M e^{iksa} - \left(i\frac{P(s)}{2}\right)\sum_{g=1}^{M}\left(1+i\frac{P(s)}{2}\right)^{g-1} e^{i2k_g sa}\, e^{-iksa}\right\} \tag{III-27}$$

if $s \leq 0$; and

$$C_k(s) = f(s)\left\{\left(1+i\frac{P(s)}{2}\right)^{R-M} e^{iksa} - \left(i\frac{P(s)}{2}\right)\sum_{g=M+1}^{R}\left(1+i\frac{P(s)}{2}\right)^{g-1} e^{i2k_g sa}\, e^{-iksa}\right\} \tag{III-28}$$

if $s \geq 0$.

CHAPTER IV

STATISTICS

In Chapters II and III the mechanical problem was formulated and solved. Once a state function for the system has been specified, all of the physical properties of the system can be calculated. Here, rather than assigning to the system some definite state function, the state of the system will be specified statistically by means of a density matrix. Formally, at least, the statistical problem is clear. If one wishes the statistical average of some quantum mechanical operator, such as the average heat flux operator, then one has merely to take the trace of that operator times an appropriate density matrix. Thus the central problem is to determine just what the appropriate density matrix is.

In this chapter two methods for the determination of the density matrix are introduced. In the first method it is assumed that the infinite regions at either side of the impurity bearing region are at equilibrium characterized by different temperatures. This will be referred to as the method of local equilibrium. The second is the method of correlation functions. This method, in its present form, is not well suited to a calculation of the local energy, and it is therefore used only to calculate the thermal conductivity.

The Method of Local Equilibrium

In this approach it is assumed that the infinite pure region to the left of impurity bearing region has the same energy per unit length as a system which is at complete thermal equilibrium characterized by a temperature T_1. Likewise, the infinite pure region to the right of the impurity bearing region has the same energy per unit length as a system which is at complete thermal equilibrium characterized by a temperature T_2. When T_1 is greater than T_2, energy will flow from the pure region at the left to the pure region at the right. When T_1 is equal to T_2 the system is at complete thermal equilibrium, and there is no net transfer of energy.

In order to proceed with this calculation it is necessary to find an expression for the energy of a small region of the chain. The size of this region should be such that it is small compared to the total length of the impurity bearing region of the chain but large enough to contain many particles. If the size of this region is chosen to be large compared to the "graining" of the coarse-grained delta function, that is the distance ℓ in Equation (II-32), then the required expression for the local energy is found, by integrating the Hamiltonian density, Equation (II-29), over this region, to be

$$\overline{H(r)} = \sum_{[N]} H_j \tag{IV-1}$$

where the notation $\sum\limits_{[N]}$ stands for the sum over the particles which are in the region of interest.

Equation (IV-1) may be written in terms of the phonon representation by using Equation (II-30) for H_j and Equations (II-25) and (II-26) for u_j and p_j with the result

$$\overline{H(r)} = \left(\frac{Na}{2\pi}\right)^2 \sum_{[N]} \iint_{-\pi/a}^{\pi/a} \frac{\hbar}{4} \left\{ \left[\sqrt{\omega(s)\,\omega(s')} + \frac{\omega^2(s)}{\sqrt{\omega(s)\,\omega(s')}} \right] \times \right. \tag{IV-2}$$

$$\left[B_j(s) B_j^*(s') a(s) a^\dagger(s') + B_j^*(s) B_j(s') a^\dagger(s) a(s') \right] +$$

$$\left[\frac{\omega^2(s)}{\sqrt{\omega(s)\,\omega(s')}} - \sqrt{\omega(s)\,\omega(s')} \right] \times$$

$$\left. \left[B_j(s) B_j(s') a(s) a(s') + B_j^*(s) B_j^*(s') a^\dagger(s)\, a^\dagger(s') \right] \right\} ds\, ds'$$

By introducing the density matrix ρ the statistical average of $\overline{H(x)}$ which will be denoted by $[\overline{H(x)}]$, is

$$\left[\overline{H(r)}\right] = \left(\frac{Na}{2\pi}\right)^2 \sum_{[N]} \iint_{-\pi/a}^{\pi/a} \frac{\hbar}{4} \sum_{\ell} \left\{ \left[\sqrt{\omega(s)\omega(s')} + \frac{\omega^2(s)}{\sqrt{\omega(s)\omega(s')}} \right] \times \right. \tag{IV-3}$$

$$\left[B_j(s) B_j^*(s') \langle \ell | a(s) a^\dagger(s') | \ell \rangle + B_j^*(s) B_j(s') \langle \ell | a^\dagger(s) a(s') | \ell \rangle \right] +$$

$$\left[\frac{\omega^2(s)}{\sqrt{\omega(s)\omega(s')}} - \sqrt{\omega(s)\omega(s')} \right] \times$$

$$\left. \left[B_j(s) B_j(s') \langle \ell | a(s) a^\dagger(s') | \ell \rangle + B_j^*(s) B_j(s') \langle \ell | a^\dagger(s)\, a(s') | \ell \rangle \right] \right\} ds\, ds'$$

If the density matrix ρ represents a stationary state and an assumption of random phases is introduced, then the density matrix is diagonal (38). That is,

$$\rho|\ell\rangle = \rho_\ell\,|\ell\rangle$$

where ρ_ℓ is the eigenvalue of ρ corresponding to the state $|\ \ell >$. As a consequence, Equation (IV-3) takes the simple form

$$\left[\overline{H(r)}\right] = \left(\frac{Na}{2\pi}\right)^2 \sum_{[N]} \iint_{-\pi/a}^{\pi/a} \frac{\hbar}{H} \sum_{\ell} \left\{ \left[\sqrt{\omega(s)\omega(s')} + \frac{\omega^2(s)}{\sqrt{\omega(s)\omega(s')}} \right] \times \right. \tag{IV-4}$$

$$\left[B_j(s) B_j^*(s') \langle \ell | a(s) a^\dagger(s') | \ell \rangle + \right.$$

$$\left. \left. B_j^*(s) B_j(s') \langle \ell | a^\dagger(s) a(s') | \ell \rangle \right] \right\} ds\, ds'$$

where in obtaining this expression the fact that terms of the form $< \ell|a(s)\ a(s')|\ell >$ and $< \ell|a^\dagger(s)\ a^\dagger(s')|\ell >$ are zero has been used. Then by using Equations (II-15), (II-16), and (II-20) Equation (IV-4) can be written as

$$\left[\overline{H(r)}\right] = \left(\frac{Na}{2\pi}\right) \sum_{[N]} \int_{-\pi/a}^{\pi/a} \hbar\omega(s) B_j(s) B_j^*(s') \times \tag{IV-5}$$

$$\left[\sum_{\ell} n^\ell(s) + \frac{1}{2} \right] ds$$

and since $\omega(s)$ is symmetric in s this can be written as

$$\left[\overline{H(r)}\right] = \left(\frac{Na}{2\pi}\right)\sum_{[N]}\int_0^{\pi/a}\hbar\omega(s)\left\{B_j(s)B_j^*(s)\left[n(s)+\frac{1}{2}\right]+\right. \tag{IV-6}$$

$$\left. B_j(-s)B_j^*(-s)\left[n(s)+\frac{1}{2}\right]\right\} ds$$

The term $\sum_{\ell} n^{\ell}(s)\,\rho_{\ell}$ which appears in Equation (IV-5) is simply the average number of phonons with wave number s and has been written as n(s) in Equation (IV-6). The 1/2 which appears in these equations is the contribution from zero point oscillations.

The two regions upon which restrictions are to be placed are the infinite pure region to the left of the impurity bearing region and the infinite pure region to the right of the impurity bearing region. The sum over the left-hand region will be denoted by $\sum_{[N_1]}$, and the sum over the right-hand region will be denoted by $\sum_{[N_2]}$. The energy per unit length in the region $[N_1]$ is that of a system at equilibrium characterized by a temperature T_1, and the energy per unit length in region $[N_2]$ is that of a system at equilibrium characterized by a temperature T_2.

The energy per unit length, E(T), of a system at equilibrium characterized by a temperature T is given by

$$E(T) = \frac{1}{\pi}\int_0^{\pi/a}\frac{\hbar\omega(s)}{(e^x-1)}\,ds \tag{IV-7}$$

where the contribution from zero point oscillations has been dropped. By equating Equation (IV-7) evaluated at T_1 and T_2 to Equation (IV-6) divided by (Na/2) without the contribution from zero point oscillations, the following expressions are obtained:

$$\int_0^{\pi/a} \hbar\omega(s)\left\{\sum_{[N_1]} B_j(s)B_j^*(s)\, n(s) + \sum_{[N_1]} B_j(-s)B_j^*(-s)\, n(-s)\right\} ds = \int_0^{\pi/a} \frac{\hbar\omega(s)}{(e^{x_1}-1)}\, ds \tag{IV-8 a}$$

and

$$\int_0^{\pi/a} \hbar\omega(s)\left\{\sum_{[N_2]} B_j(s)B_j^*(s)\, n(s) + \sum_{[N_2]} B_j(-s)B_j^*(-s)\, n(-s)\right\} ds = \int_0^{\pi/a} \frac{\hbar\omega(s)}{(e^{x_2}-1)}\, ds \tag{IV-8 b}$$

These equations can be solved simultaneously to yield

$$n(s) = \frac{1}{A(s)}\left[\sum_{[N_2]} \frac{B_j(-s)B_j^*(-s)}{(e^{x_1}-1)} - \sum_{[N_1]} \frac{B_j(-s)B_j^*(-s)}{(e^{x_2}-1)}\right] \tag{IV-9 a}$$

and

$$n(-s) = \frac{1}{A(s)}\left[\sum_{[N_1]} \frac{B_j(s)B_j^*(s)}{(e^{x_2}-1)} - \sum_{[N_2]} \frac{B_j(s)B_j(s)}{(e^{x_1}-1)}\right] \tag{IV-9 b}$$

where

$$A(s) = \sum_{[N_1]} B_j(s) B_j^*(s) \sum_{[N_2]} B_j(-s) B_j^*(-s) -$$

$$\sum_{[N_2]} B_j(s) B_j^*(s) \sum_{[N_1]} B_j(-s) B_j^*(-s)$$

Approximate expressions for the sums which appear in these equations are given in Appendix B.

By using Equation (IV-9) for n(s) and n(-s), the statistical average of the local energy and the heat flux operators can now be calculated.

In the local equilibrium method it was assumed that the energy distribution in the reservoirs in the steady state was known. The resulting calculation leads to negative n(s), a nonsense result. We therefore turn to a calculation in which the final steady state distribution in the reservoirs need not be assumed.

The Method of Correlation Functions

In this section a brief discussion of the method of correlation functions is given. This discussion is primarily concerned with the mathematical development of the theory, and for a more detailed discussion the reader is referred elsewhere (17), (39), (40), (41), (42), (43).

In this approach the system is divided into a large number of small elements of macroscopic size which do not interact with each other. Initially each of these elements is at equilibrium characterized by a local temperature T(r) which depends upon its position in the sample. The size of these elements is small enough to allow T(r) to be considered a continuous function of r. The variation in the local temperature is taken to be the same as in the final steady state of the system. At the time t = 0 these small elements are allowed to interact with each other and through this interaction bring about a change in the density matrix. In the initial state of the system the temperature as a function of position is the same as one would expect in the steady state, but no energy is flowing. After releasing the constraints, energy begins to flow. After a time, long with respect to single particle oscillations, but short compared to the time required for complete thermal equilibrium, the system reaches a steady state. The temperature as a function of position has not changed, but the energy distribution in each reservoir is no longer precisely that of a system at complete thermal equilibrium.

The time dependent density matrix can be written as

$$\rho(t) = \rho(0) + \int_0^t \frac{\partial}{\partial t'} \rho(t')\, dt' \qquad \text{(IV-10)}$$

where $\rho(0)$ is the density matrix which describes the initial local equilibrium state of the system and is given by

$$\rho(0) = Z^{-1} \exp\left\{-\int \frac{H(r)}{kT(r)}\, dr\right\} \qquad \text{(IV-11)}$$

where Z is the partition function. In the Heisenberg Picture, the time dependence of ρ is given by

$$\rho(t') = e^{-i\left(t'\frac{H}{\hbar}\right)} \rho(0)\; e^{i\left(t'\frac{H}{\hbar}\right)} \tag{IV-12}$$

and by using this expression it follows that

$$\frac{\partial}{\partial t'} \rho(t') = (i\hbar)^{-1}\left[H, \rho(t')\right] = (i\hbar)^{-1} e^{-i\left(t'\frac{H}{\hbar}\right)} \left[H, \rho(0)\right] e^{i\left(t'\frac{H}{\hbar}\right)} \tag{IV-13}$$

If the new operator R is defined such that

$$R = \int \frac{T}{T(r)} H(r)\, dr - H \tag{IV-14}$$

then ρ(0) can be written as

$$\rho(0) = Z^{-1} \exp\left\{-\frac{1}{kT}(H + R)\right\} \tag{IV-15}$$

where T is the average temperature of the system. By making use of Equation (IV-15) and the identity (45)

$$\left[B, e^{-\beta A}\right] = \int_0^\beta d\lambda\; e^{-\lambda A}\left[A, B\right] e^{\lambda A}\; e^{-\beta A} \tag{IV-16}$$

Equation (IV-13) can be written

$$\frac{\partial}{\partial t'}\rho(t') = e^{-i\left(t'\frac{H}{\hbar}\right)} \int_0^{\frac{1}{kT}} d\lambda \, e^{-\lambda(H+R)} \times \qquad \text{(IV-17)}$$

$$\dot{R}\, e^{\lambda(H+R)} \rho_{(0)} \, e^{i\left(t'\frac{H}{\hbar}\right)}$$

where

$$\dot{R} = (i\hbar)^{-1}\,[R,H]$$

By examining Equation (IV-15) it is easy to see that $\dot{R}$ is a measure of the deviation of the system from complete thermal equilibrium. If only systems whose deviation from complete thermal equilibrium is small are considered, then it is permissible to expand the integrand of Equation (IV-17) in a power series in $\dot{R}$ and retain only the lowest order terms in R. By making use of the identity (46)

$$e^{-\beta(A+B)} = \left\{ 1 - \int_0^{\beta} d\lambda \, e^{-\lambda A} B \, e^{\lambda A} + \right. \qquad \text{(IV-18)}$$

$$\int_0^{\beta} d\lambda_1 \int_{\lambda_1}^{\beta} d\lambda_2 \, e^{-\lambda_1 A} B \times$$

$$\left. e^{(\lambda_1-\lambda_2)A} B \, e^{\lambda_2 A} + \cdots \right\} e^{-\beta A}$$

the required expansion is

$$\frac{\partial}{\partial t'} \rho(t') = \int_0^{\frac{1}{kT}} d\lambda \, e^{-\lambda H} e^{-i(t' \frac{H}{\hbar})} \dot{R} \times e^{i(t' \frac{H}{\hbar})} e^{\lambda H} \rho_0 \tag{IV-19}$$

where

$$\rho_0 = Z_0^{-1} e^{-\frac{H}{kT}} \tag{IV-20}$$

is the density matrix for the system at complete thermal equilibrium. By using Equation (IV-19) in Equation (IV-10) the expression for the density matrix $\rho(t)$ becomes

$$\rho(t) = \rho(0) + \int_0^t dt' \int_0^{\frac{1}{kT}} d\lambda \, e^{-\lambda H} \times e^{-i(t' \frac{H}{\hbar})} \dot{R} e^{i(t' \frac{H}{\hbar})} e^{\lambda H} \rho_0 \tag{IV-21}$$

For notational convenience this will be written as

$$\rho(t) = \rho(0) + \rho'(t)$$

where

$$\rho'(t) = \int_0^t dt' \int_0^{\frac{1}{kT}} d\lambda \quad e^{-\lambda H} \times \tag{IV-22}$$

$$e^{-i(t'\frac{H}{\hbar})} \; \mathring{R} \; e^{i(t'\frac{H}{\hbar})} \; e^{\lambda H} \rho_0$$

From Equation (IV-14) it is easily seen that

$$\dot{R} = \int \frac{T}{T(r)} \; \mathring{H}(r) \, dr \tag{IV-23}$$

and by using the definition of the heat flux operator which is given in Equation (II-34) this expression can be written as

$$\mathring{R} = - \int \frac{T}{T(r)} \frac{\partial}{\partial r} \mathcal{J}(r) \, dr \tag{IV-24}$$

This expression can be integrated by parts to yield

$$\dot{R} = - \int \mathcal{J}(r) \frac{T}{T^2(r)} \; \frac{\partial T(r)}{\partial r} \, dr \tag{IV-25}$$

Recall that in the derivation of Equation (IV-19) it was required that the deviation of the system from equilibrium be small. A careful examination of the expansion used to obtain Equation (IV-19) will show that it would be inconsistent to express $\mathring{R}$ to higher order in T(r) than that given by

$$\dot{R} = -\frac{1}{T}\int \mathcal{J}(r)\,\frac{\partial T(r)}{\partial r}\,dr \tag{IV-26}$$

By using this expression for $\dot{R}$ Equation (IV-22) becomes

$$\rho'(t) = -\frac{1}{T}\int_0^t dt'\int_0^{\frac{1}{kT}} d\lambda\, e^{-\lambda H}\, e^{-i(t'\frac{H}{\hbar})} \times \tag{IV-27}$$

$$\int \mathcal{J}(r)\,\frac{\partial T(r)}{\partial r}\,dr\; e^{i(t'\frac{H}{\hbar})}\, e^{\lambda H}\rho_0$$

The steady state statistical average of the average heat flux operator J is found by taking the trace of J times the density matrix ρ(t), where for an infinite system ρ(t) is evaluated at t equal to infinity. Mori has shown (47) that

$$Tr\left\{J\rho(0)\right\} = 0$$

which is certainly a plausible result. The statistical average of the average heat flux operator is therefore given by

$$[J] = Tr\left\{J\rho'(t=\infty)\right\} = -\frac{1}{T}\int_0^\infty dt'\int_0^{\frac{1}{kT}} d\lambda \times \tag{IV-28}$$

$$Tr\left\{J\, e^{-\lambda H}\, e^{-i(t'\frac{H}{\hbar})}\int \mathcal{J}(r)\,\frac{\partial T(r)}{\partial r}\,dr \times\right.$$

$$\left. e^{i(t'\frac{H}{\hbar})}\, e^{\lambda H}\rho_0\right\}$$

The system under consideration here was prepared at t = 0 such that T(r) was constant in the pure regions at either side of the impurity bearing region and decreased linearly from the left to the right side of that region. Equation (IV-28) can therefore be written as

$$[J] = -\frac{L}{T}\sum_{\ell n}\left\{\int_0^\infty e^{-it'(E_n-E_\ell)/\hbar}\,dt' \times \int_0^{\frac{1}{kT}} e^{-\lambda(E_n-E_\ell)}\,d\lambda \,\langle \ell|J|n\rangle \times \langle n|J|\ell\rangle Z_0^{-1} e^{-\frac{E_\ell}{kT}}\right\}\frac{\partial T}{\partial r} \tag{IV-29}$$

where L is the length of the impurity bearing region of the chain. The thermal conductivity of the system is thus given by

$$K = -\frac{L}{T}\sum_{\ell n}\left\{\int_0^\infty e^{-it'(E_n-E_\ell)/\hbar}\,dt' \times \int_0^{\frac{1}{kT}} e^{-\lambda(E_n-E_\ell)}\,d\lambda \,\langle \ell|J|n\rangle \times \langle n|J|\ell\rangle Z_0^{-1} e^{-\frac{E_\ell}{kT}}\right\} \tag{IV-30}$$

Since K must be a real number

$$K = \frac{1}{2}\left(K + K^*\right)$$

and therefore

$$K = -\frac{L}{2T} \sum_{l,n} \left\{ \int_{-\infty}^{\infty} e^{-it'(E_n - E_l)/\hbar}\, dt' \times \right. \tag{IV-31}$$

$$\int_0^{\frac{1}{kT}} e^{-\lambda(E_n - E_l)}\, d\lambda \, \langle l|J|n\rangle \times$$

$$\left. \langle n|J|l\rangle Z_0^{-1} e^{-\frac{E_l}{kT}} \right\}$$

The integral over t' is simply 2π times a delta function, and by using this fact and performing the integral over t' the expression for K becomes

$$K = \frac{\pi L}{kT^2} \sum_{l,n} \left\{ \delta\left(\frac{E_n - E_l}{\hbar}\right) \langle l|J|n\rangle \times \right. \tag{IV-32}$$

$$\left. \langle n|J|l\rangle Z_0^{-1} e^{-\frac{E_l}{kT}} \right\}$$

This expression can now be used in conjunction with the explicit expression for the operator J which is given in Chapter II.

Equation (IV-32) for the thermal conductivity was deduced from Equation (IV-29) for [J]. Equation (IV-29) is the first term in a series expansion for [J] in powers of $\dot{R}$. By examining Equation (IV-25) for $\dot{R}$, it can be seen that this series expansion in powers of $\dot{R}$ can be converted into a series expansion in powers of $\partial T/\partial r$. Equation (IV-29) represents the only term in that expansion which is directly proportional to $\partial T/\partial r$. If the thermal conductivity is defined as the coefficient of $\partial T/\partial r$, then Equation (IV-32) represents an exact expression for the thermal conductivity.

This new definition of the thermal conductivity differs from other definitions only when higher order contributions to the heat flux are significant. However, for systems in which higher order contributions to the heat flux are important, [J] is not directly proportional to $\partial T/\partial r$, and systems of this type are not usually analyzed in terms of a thermal conductivity.

CHAPTER V

RESULTS

In this chapter the methods which were developed in the preceding chapters are used in order to calculate expressions for the local energy, that is energy per unit length, as a function of position along the chain and the thermal conductivity of the chain. The local energy is calculated by using the method of local equilibrium, and the thermal conductivity is calculated by using both the method of local equilibrium and the method of correlation functions.

Local Energy

The local energy per unit length $E(r,T)$ at position r can be calculated from Equation (IV-6) by using the expressions which are given in Equations (IV-9) for $n(s)$ and $n(-s)$. This calculation is carried out in Appendix C with the result

$$E(r,T) = \frac{1}{\pi}\int_0^{\pi/a} \frac{\hbar\omega(s)}{2(e^{x_1}-1)(e^{x_2}-1)} \times \tag{V-1}$$

$$\left\{ \left[(e^{x_1}-1)+(e^{x_2}-1)\right] \frac{\cosh[\alpha(s)\zeta r]}{\cosh[\alpha(s)\zeta L/2]} - \right.$$

$$\left. (e^{x_2}-e^{x_1}) \frac{\sinh[\alpha(s)\zeta r]}{\sinh[\alpha(s)\zeta L/2]} \right\} ds$$

where ζ is the density of impurities, r is the position along the chain, and

$$\alpha(s) = \ln\left(1 + \frac{p^2(s)}{4}\right) \tag{V-2}$$

The case of interest here is that in which the difference in temperature $\delta T = T_2 - T_1$ between the two end regions of the chain is small. If Equation (V-1) is expanded in a power series about the average temperature $T = (T_1 + T_2)/2$ and only terms of first order in δT are retained, then the expression for the local energy becomes

$$E(r,T) = \frac{1}{\pi}\int_0^{\pi/a} \frac{\hbar\omega(s)}{(e^x - 1)} \times \tag{V-3}$$

$$\left\{ \frac{\cosh[\alpha(s)\zeta r]}{\cosh[\alpha(s)\zeta L/2]} + \right.$$

$$\left. \frac{x\, e^x}{(e^x - 1)} \frac{\delta T}{2T} \frac{\sinh[\alpha(s)\zeta r]}{\sinh[\alpha(s)\zeta L/2]} \right\} ds$$

At very low temperatures, because of the factor $1/(e^x-1)$, the only significant contribution to the local energy will come from small values of the frequency in which case $\alpha(s)$ is small and Equation (V-3) can be written

$$E(r,T) = \frac{1}{\pi}\int_0^{\pi/a} \frac{\hbar\,\omega(s)}{(e^x - 1)} \times \tag{V-4}$$

$$\left\{1 + \frac{x\,e^x}{(e^x-1)}\,\frac{\delta T}{T}\,\frac{r}{L}\right\} ds$$

A complete discussion of these results is given in the next chapter. However, let it be pointed out here that Equation (V-4) represents a linear change in the local energy as a function of position which is in complete agreement with experiment for small temperature differences.

Thermal Conductivity

In this section the thermal conductivity is calculated both by means of the method of local equilibrium and by means of the method of correlation functions.

Method of Local Equilibrium

The statistical average of the average heat flux operator is found by taking the trace of J times the density matrix ρ. If it is kept in mind that terms of the form $<\ell|a(s)\ a(s')|\ell>$ and $<\ell|a^\dagger(s)\ a^\dagger(s')|\ell>$ are zero, then, by using Equation (II-44) for J and the fact that ρ is diagonal, it follows that

$$[J] = -i\,\frac{\hbar\gamma a}{2L}\left(\frac{Na}{2\pi}\right)^2 \iint_{-\pi/a}^{\pi/a} \sqrt{\frac{\omega(s')}{\omega(s)}} \times \tag{V-5}$$

$$\sum_{j=-L/2a}^{L/2a} \left\{ \left(\frac{B^*_{j-1}(s)}{\sqrt{m_{j-1}}} - \frac{B^*_{j+1}(s)}{\sqrt{m_{j+1}}} \right) \frac{B_j(s')}{\sqrt{m_j}} \times \right.$$

$$\sum_{\ell} \langle \ell | a^+(s) a(s') | \ell \rangle \rho_\ell - \left(\frac{B_{j-1}(s)}{\sqrt{m_{j-1}}} - \frac{B_{j+1}(s)}{\sqrt{m_{j+1}}} \right) \times$$

$$\left. \frac{B^*_j(s')}{\sqrt{m_j}} \sum_{\ell} \langle \ell | a(s) a^+(s') | \ell \rangle \rho_\ell \right\} ds\, ds'$$

By using the properties of a(s) and $a^{\dagger}(s)$ as destruction and creation operators, it can be shown that this expression reduces to

$$[J] = -i \frac{\hbar \gamma a}{2L} \left(\frac{Na}{2\pi} \right) \int_{-\pi/a}^{\pi/a} \sum_{j=-L/2a}^{L/2a} \left\{ \left[\left(\frac{B^*_{j-1}(s)}{\sqrt{m_{j-1}}} - \frac{B^*_{j+1}(s)}{\sqrt{m_{j+1}}} \right) \frac{B_j(s)}{\sqrt{m_j}} - \right. \right. \tag{V-6}$$

$$\left. \left(\frac{B_{j-1}(s)}{\sqrt{m_{j-1}}} - \frac{B_{j+1}(s)}{\sqrt{m_{j+1}}} \right) \frac{B^*_j(s)}{\sqrt{m_j}} \right] n(s) -$$

$$\left. \left(\frac{B_{j-1}(s)}{\sqrt{m_{j-1}}} - \frac{B_{j+1}(s)}{\sqrt{m_{j+1}}} \right) \frac{B^*_j(s)}{\sqrt{m_j}} \right\} ds$$

where the last term in this expression can be shown to be zero by using Equation (II-24).

In Appendix B it is shown that

$$G(s,s) = \sum_{j=-L/2a}^{L/2a} \left\{ \left(\frac{B^*_{j-1}(s)}{\sqrt{m_{j-1}}} - \frac{B^*_{j+1}(s)}{\sqrt{m_{j+1}}} \right) \frac{B_j(s)}{\sqrt{m_j}} - \left(\frac{B_{j-1}(s)}{\sqrt{m_{j-1}}} - \frac{B_{j+1}(s)}{\sqrt{m_{j+1}}} \right) \frac{B^*_j(s)}{\sqrt{m_j}} \right\} = \frac{i\,8L}{Nam} \frac{\sin(sa)}{\left[\left(1+\frac{\rho^2(s)}{4}\right)^R + 1\right]}$$

and by using this result from Appendix B in Equation (V-6), the expression for [J] becomes

$$[J] = \frac{2\hbar\gamma a}{\pi m} \int_0^{\pi/a} \frac{\sin(sa)}{\left[\left(1+\frac{\rho^2(s)}{4}\right)^R + 1\right]} \left[n(s) - n(-s)\right] ds \qquad \text{(V-7)}$$

By using Equations (IV-9) for n(s) and n(-s) and the approximations which are given in Appendix B, Equation (V-7) can be written as

$$[J] = -\frac{k\omega_0 aL}{\pi} \int_0^{\pi/a} \frac{\cos\left(\frac{sa}{2}\right)}{\left[\left(1+\frac{\rho^2(s)}{4}\right)^R - 1\right]} \frac{x^2 e^x}{(e^x-1)^2}\, ds\, \frac{\partial T}{\partial r} \qquad \text{(V-8)}$$

where it has been assumed that δT is small compared to T. In Equation (V-8) $\partial T/\partial r = \delta T/L$.

Notice that at sufficiently low temperatures the major contribution to [J] comes from small values of s, in which case the thermal conductivity can be written as

$$K = \frac{8Tk^2}{\pi \varsigma \hbar} \int_0^{\frac{\Theta}{T}} \frac{1}{p^2(s)} \frac{x^2 e^x}{(e^x-1)^2} dx \qquad \text{(V-10)}$$

where θ is the Debye θ and is given by $\theta = \hbar\omega_o/k$. From Equation (III-18) the expression for p(s) is

$$p(s) = \frac{\epsilon m \omega^2(s)}{\gamma \sin|sa|}$$

which for small frequencies can be written as

$$p(s) = 2\epsilon\left(\frac{\omega(s)}{\omega_o}\right) \qquad \text{(V-11)}$$

By using this expression for p(s), the expression for the thermal conductivity becomes

$$K = \frac{2\hbar\omega_o^2}{\pi \varsigma \epsilon^2 T} \int_0^{x_o} \frac{e^x}{(e^x-1)^2} dx \qquad \text{(V-12)}$$

This expression for the thermal conductivity is identical to that which is obtained from the phenomenological theory (47) provided only isotopic impurities are considered, and, as is the case there, Equation (V-12) diverges at its lower limit. This problem and the reason for its existence is discussed in the next chapter. However, before proceeding to this discussion the thermal conductivity will be calculated by means of the method of correlation functions where it is found that this divergence problem does not exist.

Method of Correlation Functions

Equation (IV-32) for the thermal conductivity is

$$K = \frac{\pi L}{kT^2} \sum_{\ell, n} \delta\left(\frac{E_n - E_\ell}{\hbar}\right) \langle \ell | J | n \rangle \langle n | J | \ell \rangle Z_0^{-1} e^{-\frac{E_\ell}{kT}}$$

By using Equation (II-44) for J and remembering that since the energy of the state $| \ell \rangle$ must be equal to the energy of the state $| n \rangle$ terms of the form $\langle \ell | a(s)\, a(s') | n \rangle$ and $\langle \ell | a^\dagger(s)\, a^\dagger(s') | n \rangle$ are zero, the following expression for the thermal conductivity is obtained:

$$K = \frac{\hbar^2 \gamma^2 a^2 \pi}{4 L k T^2} \left(\frac{Na}{2\pi}\right)^4 \sum_{j=-L/2a}^{L/2a} \sum_{k=-L/2a}^{L/2a} \iiiint_{-\pi/a}^{\pi/a} \sqrt{\frac{\omega(s')\omega(s'')}{\omega(s)\omega(s''')}} \times \tag{V-13}$$

$$\delta\left(\frac{E_n - E_\ell}{\hbar}\right) Z_0\, e^{-\frac{E_\ell}{kT}} \Bigg\{ \Bigg[\left(\frac{B^*_{j-1}(s)}{\sqrt{m_{j-1}}} - \frac{B^*_{j+1}(s)}{\sqrt{m_{j+1}}}\right) \frac{B_j(s')}{\sqrt{m_j}} \times$$

$$\langle \ell | a^\dagger(s)\, a(s') | n \rangle - \left(\frac{B_{j-1}(s)}{\sqrt{m_{j-1}}} - \frac{B_{j+1}(s)}{\sqrt{m_{j+1}}}\right) \frac{B^*_j(s')}{\sqrt{m_j}} \times$$

$$\langle \ell | a(s)\, a^\dagger(s') | n \rangle \Bigg] \Bigg[\left(\frac{B^*_{k-1}(s'')}{\sqrt{m_{k-1}}} - \frac{B^*_{k+1}(s'')}{\sqrt{m_{k+1}}}\right) \frac{B^*_k(s''')}{\sqrt{m_k}} \times$$

$$\langle n | a^\dagger(s'')\, a(s''') | \ell \rangle - \left(\frac{B_{k-1}(s'')}{\sqrt{m_{k-1}}} - \frac{B_{k+1}(s'')}{\sqrt{m_{k+1}}}\right) \frac{B^*_k(s'')}{\sqrt{m_k}} \times$$

$$\langle n|a(s'')\,a^{+}(s''')|\ell\rangle\Big]\Big\}\, ds\, ds'\, ds''\, ds'''$$

By introducing the function

$$G(s,s') = \sum_{j=-L/2a}^{L/2a}\Big[\Big(\frac{B^{*}_{j-1}(s)}{\sqrt{m_{j-1}}} - \frac{B^{*}_{j+1}(s)}{\sqrt{m_{j+1}}}\Big)\frac{B_j(s')}{\sqrt{m_j}} - \tag{V-14}$$

$$\Big(\frac{B_{j-1}(s')}{\sqrt{m_{j-1}}} - \frac{B_{j+1}(s')}{\sqrt{m_{j+1}}}\Big)\frac{B^{*}_j(s)}{\sqrt{m_j}}\Big]$$

and by using Equations (II-27), the expression for K can be written as

$$K = -\frac{\hbar^2\gamma^2 a^2\pi}{4LkT^2}\Big(\frac{Na}{2\pi}\Big)^4\sum_{\ell,n}\iiiint_{-\pi/a}^{\pi/a}\delta\Big(\frac{E_n-E_\ell}{\hbar}\Big)\,X \tag{V-15}$$

$$Z_o^{-1}\, e^{-\frac{E_\ell}{kT}}\, G(s,s')\,G(s'',s''')\langle\ell|a^{\dagger}(s)a(s')|n\rangle\, X$$

$$\langle n|a^{\dagger}(s'')a(s''')|\ell\rangle\, ds\, ds'\, ds''\, ds'''$$

The sum over the states $|\,n\,\rangle$ can be performed by noting that the matrix element $\langle\, n|a^{\dagger}(s')a(s''')|\ell\,\rangle$ is zero unless $\langle\, n| = \langle\, \ell, +1_{s''}, -1_{s'''}|$. When this sum over the states $|\,n\,\rangle$ is performed, K is given by

$$K = -\frac{\hbar^2\gamma^2 a^2 \pi}{4LkT^2}\left(\frac{Na}{2\pi}\right)^4 \sum_{\lambda} \iiiint_{-\pi/a}^{\pi/a} \delta(\omega(s'')-\omega(s''')) \times \tag{V-16}$$

$$G(s,s')G(s'',s''')\langle \ell | a^{\dagger}(s)a(s') | \ell, +1_{s''}, -1_{s'''}\rangle \times$$

$$\langle \ell, 1_{s''}, -1_{s'''} | a^{\dagger}(s'')a(s''') | \ell \rangle Z_0^{-1} e^{-\frac{E_\ell}{kT}} ds\, ds'\, ds''\, ds'''$$

The expression for G(s',s''')is found in Appendix B for s''' = s" and for s''' = -s". When s''' = s" it is seen to be an odd function of s". Since everything else in Equation (V-16) is an even function of s", there is no contribution to the thermal conductivity when s" = s'''. The thermal conductivity can therefore be written as

$$K = -\frac{\hbar^2\gamma^2 a^2 \pi}{4LkT^2}\left(\frac{Na}{2\pi}\right)^2 \iiiint_{-\pi/a}^{\pi/a} \frac{G(s,s')G(s'',s''')}{|v(s'')|} \times \tag{V-17}$$

$$\sum_{\ell} n^{\ell}(s''')[n^{\ell}(s'')+1] Z_0^{-1} e^{-\frac{E_\ell}{kT}} \delta(s-s''') \times$$

$$\delta(s'-s'')\,\delta(s''+s''')\, ds\, ds'\, ds''\, ds'''$$

where v(s) is the group velocity of phonons with wave number s. The integrals over the delta functions can now be performed to yield

$$K = -\frac{\hbar^2\gamma^2 a^2 \pi}{4LkT^2}\left(\frac{Na}{2\pi}\right)^2 \int_{-\pi/a}^{\pi/a} \frac{G(s,-s)G(-s,s)}{|v(s)|} \frac{e^x}{(e^x-1)^2} ds \tag{V-18}$$

where the sum over the states $| \ell >$ has also been performed to yield the equilibrium values for the number operators.

The product G(s, -s) G(-s, s) is shown in Appendix B to be

$$G(s,-s)\,G(-s,s) = -\left(\frac{8L}{mNa}\right)^2 \frac{\left[\left(1+\frac{\rho^2(s)}{4}\right)^R - 1\right]}{\left[\left(1+\frac{\rho^2(s)}{4}\right)^R + 1\right]^2} \, SIN^2(sa) \qquad \text{(V-19)}$$

and the use of this expression in Equation (V-18) yields

$$K = \frac{8k}{\pi\varsigma} \int_0^{\pi/a} \frac{R\left[\left(1+\frac{\rho^2(s)}{4}\right)^R - 1\right]}{\left[\left(1+\frac{\rho^2(s)}{4}\right)^R + 1\right]^2} \, \frac{x^2 e^x}{(e^x-1)^2} \, |v(s)| \, ds \qquad \text{(V-20)}$$

Equation (V-20) can be rearranged in the form

$$K = \frac{8k\omega_0 R}{\pi\varsigma\,\Theta/T} \int_0^{\frac{\Theta}{T}} \frac{(e^{\alpha(x)R} - 1)}{(e^{\alpha(x)R} + 1)^2} \, \frac{x^2 e^x}{(e^x - 1)^2} \, dx \qquad \text{(V-21)}$$

where

$$\alpha(x) = Ln\left\{1 + \epsilon^2 \frac{x^2}{[(\Theta/T)^2 + x^2]}\right\} \qquad \text{(V-22)}$$

Notice that the integral in Equation (V-21) does not diverge at its lower limit since the integrand no longer has a pole at x = 0.

If the thermal conductivity per unit frequency $K(\omega)$ is defined such that

$$K = \int_0^{\omega_0} K(\omega)\, d\omega \tag{V-23}$$

then from Equation (V-20) the method of correlation functions yields

$$K(\omega) = \frac{8kL}{\pi} \frac{(e^{\alpha(x)R} - 1)}{(e^{\alpha(x)R} + 1)^2} \frac{x^2 e^x}{(e^x - 1)^2} \tag{V-24}$$

By rearranging Equation (V-8), it can be seen that the method of local equilibrium yields

$$K(\omega) = \frac{2kL}{\pi} \frac{1}{(e^{\alpha(x)R} - 1)} \frac{x^2 e^x}{(e^x - 1)^2} \tag{V-25}$$

Equations (V-24) and (V-25) can now be used to compare the two statistical methods as a function of frequency.

At very low frequencies, the method of correlation functions yields a $K(\omega)$ which approaches zero as the frequency approaches zero, while the method of local equilibrium yields a $K(\omega)$ which becomes infinite as the frequency approaches zero. At very high frequencies, the method of correlation functions yields a $K(\omega)$ which is four times that yielded by the method of local equilibrium. The difference between the two statistical methods at very low frequencies is necessary if the method of correlation functions is to yield a thermal conductivity which is consistent with the conservation of energy. At first, one might expect the two statistical methods to be equivalent except at the very low frequencies where the method of local equilibrium is known to be incorrect. The fact that they are not equivalent even at the higher frequencies can apparently be traced to off-diagonal terms in the correlation function density matrix.

In the method of local equilibrium it was assumed that the steady state density matrix was diagonal, while in the method of correlation functions this assumption was not made. It is not necessary to require that the steady state density matrix be diagonal. It is only necessary that off-diagonal terms in the steady state density matrix be time independent. Since in this problem phonons with wave numbers s and -s have the same frequency, off-diagonal terms in the density matrix which connect phonons with wave numbers s and -s will be time independent. The correlation functions density matrix can contain off-diagonal terms of this type. A careful examination of Equation (II-44) for the heat flux operator will show that these off-diagonal terms can contribute significantly to the heat flux and, thus, to the thermal conductivity.

CHAPTER VI

DISCUSSION OF RESULTS

In the preceding chapter expressions for the local energy and the thermal conductivity were derived, but no discussion of them was given. In this chapter those results are discussed in detail.

Local Energy

The case of interest here is that in which the temperature difference δT between the two pure regions of the chain is small compared to the average temperature T of the chain. In this case the local energy is given by Equation (V-3) which is

$$E(r,T) = \int_0^{T/a} \frac{\hbar\,\omega(s)}{(e^x - 1)} \times \left\{ \frac{\cosh[\alpha(s)\xi r]}{\cosh[\alpha(s)\xi L/2]} + \frac{x e^x}{(e^x - 1)} \frac{\delta T}{2T} \frac{\sinh[\alpha(s)\xi r]}{\sinh[\alpha(s)\xi L/2]} \right\} ds \qquad \text{(VI-1)}$$

This result is more easily discussed if the local energy per unit wave number $E(r,T,s)$ is defined as

$$\mathcal{E}(r,T,s) = \frac{1}{\pi} \frac{\hbar\,\omega(s)}{(e^x - 1)} \left\{ \frac{\cosh[\alpha(s)\xi r]}{\cosh[\alpha(s)\xi L/2]} + \right. \qquad \text{(VI-2)}$$

$$\left. \frac{x\, e^{x}}{(e^{x}-1)} \frac{\delta T}{2T} \frac{\sinh[\alpha(s)\xi r]}{\sinh[\alpha(s)\xi L/2]} \right\}$$

since this expression can then be compared to the equivalent expression for a system which is locally at complete thermal equilibrium.

This suggested comparison is appropriate because experimentally it has been found that a system upon which a small temperature difference has been impressed appears to be locally at complete thermal equilibrium. This means that experimentally the energy per unit length per unit wave number is given by

$$E'(r,T,s) = \frac{1}{\pi} \frac{\hbar\,\omega(s)}{(e^{x(r)}-1)} \tag{VI-3}$$

where

$$x(r) = \frac{\hbar\,\omega(s)}{k\,T(r)} \tag{VI-4}$$

and T(r) is the temperature as a function of position which changes in a linear fashion from this high temperature region of the chain to the low temperature region of the chain. When the temperature difference between the ends of the chain is small compared to the average temperature of the chain Equation (VI-3) can be written as

$$E'(r,T,s) = \frac{1}{\pi} \frac{\hbar\,\omega(s)}{(e^{x}-1)} \left[1 + \frac{x\,e^{x}}{(e^{x}-1)} \frac{\delta T}{T} \frac{r}{L} \right] \tag{VI-5}$$

In Figure 1 $E(r,T,s)$ given by Equation (VI-2) is plotted as a function of position along the chain for several different frequencies. As a brief examination of this figure will show, when the frequency is small the energy changes in a linear fashion. However, as the frequency increases the energy in the central region of the chain is too low.

This deficiency of energy in the central region of the chain as (ω/ω_o) approaches unity is due to the exponential drop in the energy of a wave which is propagating through the impurity bearing region of the chain. That is, the impurity bearing region is such an effective barrier to energy flow at large frequencies that the system no longer yields a linear energy drop. This effect is insignificant at sufficiently low temperatures, since in that case the higher frequency terms make a negligible contribution to the local energy of the system. However, at higher temperatures the contribution from the higher frequency terms is no longer negligible, and thus the local energy will deviate significantly from experiment.

This deviation from experiment at the higher frequencies is not surprising since anharmonic terms have been neglected in this model. Recall that the transformation to the phonon representation was not in terms of plane wave phonons but rather in terms of the $B_j(s)$ which were solutions to Equation (III-2). The $B_j(s)$ can in turn be expanded in terms of plane waves. It is well known (48) that the phonon-phonon interaction for plane wave phonons (i.e. the contribution from anharmonic terms) is strong for the high frequencies and weak for the low frequencies.

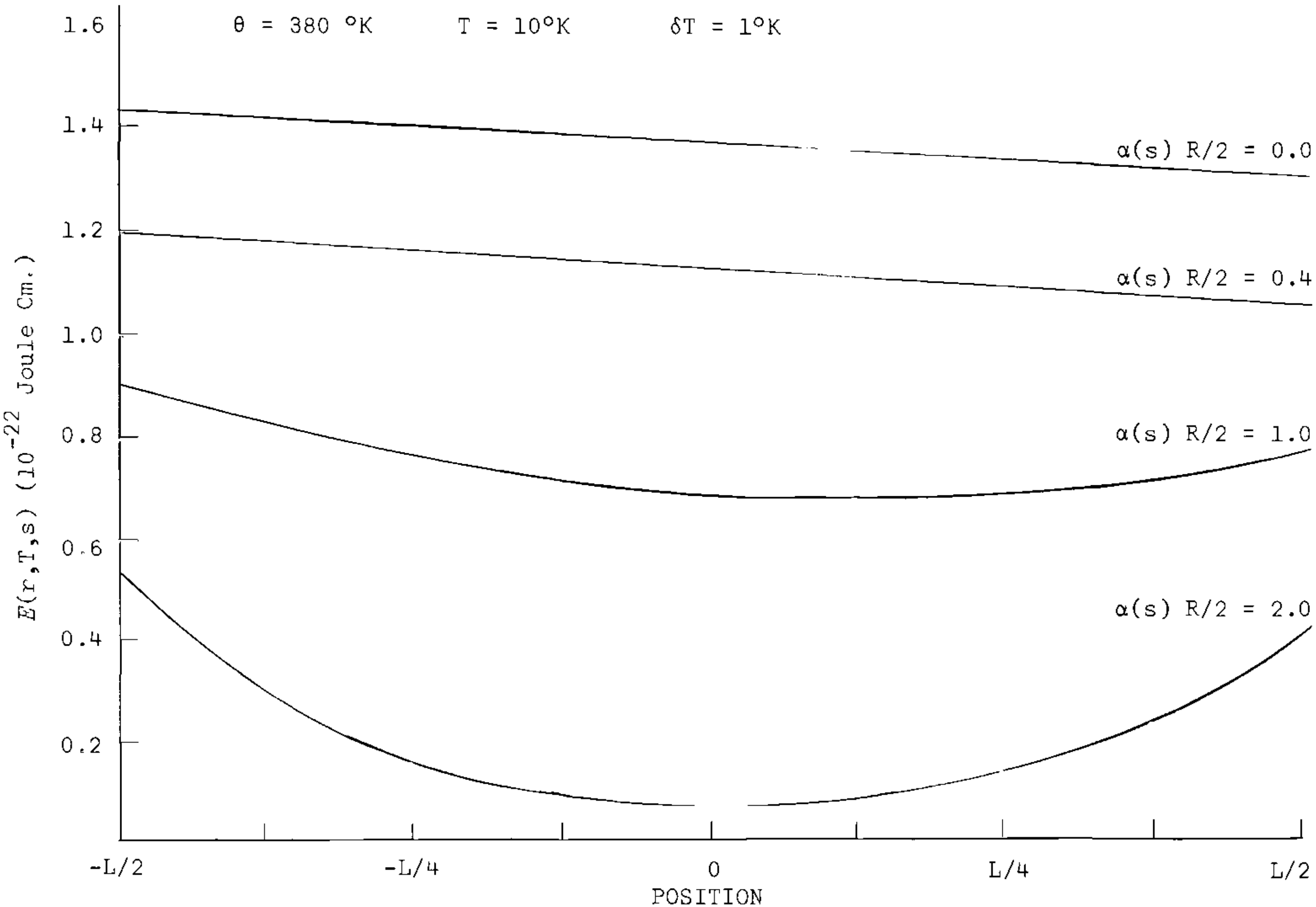

Figure 1. Local Energy as a Function of Position.

When the frequency associated with $B_j(s)$ is small and when the number of impurities is not too large, $B_j(s)$ does not differ by a great deal from a plane wave state of the same frequency. Therefore the plane wave expansion of $B_j(s)$ is dominated by plane waves of low frequency, and the effect of the phonon-phonon interaction would be expected to be small. However, if the frequency of the $B_j(s)$ is not small or if there is a very large number of impurities in the system, then $B_j(s)$ is very different from a plane wave of the same frequency, and its expansion in terms of plane waves contains a significant contribution from plane waves of high frequency. In this case one would expect the contribution from anharmonic terms to be large. Thus, in the region in which Equation (VI-2) exhibits a significant deviation from Equation (VI-5) one would expect the contribution from anharmonic terms to be important.

Equation (VI-2) is in good agreement with experiment so long as $\alpha(s)\,\zeta L/2 = \alpha(s)R/2$ is less than unity. If the temperature is sufficiently low, this condition can be satisfied for all values of the frequency which contribute significantly to the total local energy given by Equation (VI-1). The upper bound on the temperature depends upon the values of ε, R, and θ. A practical upper bound on ε is about 0.10 and a typical value for θ is about 400°K. By using these values for ε and θ, it can be shown that if R does not exceed about 10^5, then the upper bound on the temperature is not less than about 10°K.

Thermal Conductivity

In Chapter V expressions for the thermal conductivity were calculated both by means of the method of local equilibrium and by means of the method of correlation functions. In this section the results of those calculations are discussed.

The Method of Local Equilibrium

The expression for the thermal conductivity as calculated by the method of local equilibrium is given by Equation (V-12) as

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

As was mentioned in Chapter V this expression diverges at its lower limit. This is a problem which is well known in the phenomenological theory. There, this divergence is usually avoided (49) by introducing anharmonic terms into the potential energy.

It was pointed out in Chapter I that while the introduction of anharmonic terms prevents the divergence of the thermal conductivity, it does not eliminate the reason for this divergence and the resulting violation of the conservation of energy. In order to understand the reason for this divergence one first evaluates the expressions for n(s) and n(-s) which are given in Equations (IV-9) and finds

$$n(s) = \frac{1}{(e^x-1)}\left\{1 - \frac{x e^x}{(e^x-1)}\,\frac{\delta T}{T}\,\frac{\left[\left(1+\frac{\rho^2(s)}{4}\right)^R+1\right]}{\left[\left(1+\frac{\rho^2(s)}{4}\right)^R-1\right]}\right\} \qquad \text{(VI-6 a)}$$

and

$$n(s) = \frac{1}{(e^x-1)}\left\{1 + \frac{x\, e^x}{(e^x-1)}\,\frac{\delta T}{T}\,\frac{\left[\left(1+\frac{p^2(s)}{4}\right)^R+1\right]}{\left[\left(1+\frac{p^2(s)}{4}\right)^R-1\right]}\right\} \qquad \text{(VI-6 b)}$$

where the results of Appendix B have been used with the assumption that $\delta T/T$ is small. It is obvious from Equation (VI-6 b), that at very low frequencies n(-s) becomes negative if δT is negative (i.e. the left-hand side of the chain is at a higher temperature than the right-hand side). This is of course physically impossible since n(s) must be positive for all values of s. From Equation (V-7) it can be seen that if negative values of n(-s) are used in the expression for the heat flux a result will be obtained in which more energy per unit time is being conducted than there is available to be conducted. This is clearly a violation of the conservation of energy. It can also be seen from Equation (VI-6 b) that as s approaches zero the product $n(-s)(e^{x-1})$ approaches minus infinity. This results not only in a violation of the conservation of energy but also in a divergence of the thermal conductivity.

The introduction of anharmonic terms in the phenomenological theory will prevent the divergence of the thermal conductivity (14), but, as pointed out in Chapter I, it will not prevent n(-s) from taking on negative values with the resulting violation of the conservation of energy. The physical reason for the divergence and the negative n(-s) can be traced to the requirement that in the steady state the two pure regions have equilibrium energy distributions characterized by different temperatures. The resistance to the flow of energy offered by isotopic impurities, or by anharmonic terms for that matter, is insufficient to allow the difference in energy between the two end regions which is required by the two different equilibrium distributions. It is therefore clear that the steady state density matrix obtained by the method of local equilibrium is incorrect at low frequencies.

While the use of the local equilibrium density matrix causes a divergence in the thermal conductivity it does not appreciably effect the local energy if $\delta T/T$ is small. This can be seen by noting that it is only when the second term in Equation (VI-6 b) is large that difficulties arise. For very small frequencies the second term in Equation (VI-6 b) can be approximated by $4\delta T/p^2(s)T = \delta T/\varepsilon^2 RT(\omega/\omega_o)^2$, and as long as this is small compared to unity, the local equilibrium calculation should be valid. Requiring that $\delta T/\varepsilon^2 R(\omega/\omega_o)^2 T$ be small compared to unity requires that $(\omega/\omega_o)^2$ be large compared to $\delta T/\varepsilon^2 RT$. This can be satisfied for almost the entire range of the frequency ω provided $\delta T/T$ is sufficiently small.

If in the small region over which $(\omega/\omega_o)^2$ is not large compared to $\delta T/\varepsilon^2 RT$, $E(r,T,s)$ does not become extremely large, then the contribution from this small frequency region to the total local energy will be small. But $E(r,T,s)$ cannot exceed its value at the high temperature end of the chain, and $E(r,T,s)$ is not extremely large at the high temperature end of the chain. Therefore, the contribution to the total local energy from these frequencies for which the local equilibrium method is incorrect, is negligibly small provided $\delta T/T$ is sufficiently small.

The Method of Correlation Functions

As was mentioned in Chapter V the problem of a divergent thermal conductivity does not arise when the method of correlation functions is used. This is easily seen by examination of Equation (V-21) which, when the temperature is low and when R is not too large, can be written as

$$K = \frac{8 k \omega_0 R^2}{\pi \varsigma \Theta/T} \int_0^{\frac{\Theta}{T}} \frac{\alpha(x)}{[2 + R\alpha(x)]^2} \frac{x^2 e^x}{(e^x - 1)^2} \, dx \qquad \text{(VI-7)}$$

In order to obtain this expression $e^{\alpha(x)R}$ has been expanded in a power series about $R\alpha(x) = 0$, and only the first order terms in $R\alpha(x)$ have been retained. By using the low frequency approximation $\alpha(x) = \varepsilon^2 (T/\theta)^2 x^2$, Equation (VI-7) can be written as

$$K = \frac{8 k \omega_0 \Theta}{\pi \varsigma \epsilon^2 T} \int_0^{\frac{\Theta}{T}} \frac{x^4}{(b^2 + 2bx^2 + x^4)} \frac{e^x}{(e^x - 1)^2} \, dx \qquad \text{(VI-8)}$$

where

$$b = \frac{2\Theta^2}{R\epsilon^2 T^2} \qquad \text{(VI-9)}$$

For large values of b, that is for small T, the value of the integral in Equation (VI-8) is given (50) by

$$\int_0^{\frac{\Theta}{T}} \frac{x^4}{(b^2 + 2bx^2 + x^4)} \frac{e^x}{(e^x - 1)^2} \, dx = \frac{4\pi^2}{15 b^2} \qquad \text{(VI-10)}$$

which results in the following expression for the thermal conductivity:

$$K = \frac{8 k^4 \pi^3 \xi \epsilon^2}{15 \hbar^3 \omega_0^2} L^2 T^3 \qquad \text{(VI-11)}$$

Notice that Equation (VI-11) for the thermal conductivity approaches zero as the temperature approaches zero. This property is to be expected from a system for which the ratio $\delta T/T$ can be chosen arbitrary.

This can be seen in the following way. For a one-dimensional Bose system at very low temperatures the energy per unit length is given by AT^2 where A is a constant of proportionality which is independent of the temperature. Even if all of the energy in a region of temperature T were transferred to another region of the chain and no energy were transferred in the opposite direction, the current could not exceed

$$J = A v_0 T^2 \qquad \text{(VI-12)}$$

where v_o is the maximum velocity that a phonon of this system can have. Now if the current is written as

$$J = -K \frac{\partial T}{\partial r} = -\frac{KT}{L} \frac{\delta T}{T}$$

where T is the temperature of the sample and L is its length, then

$$-\frac{KT}{L} \frac{\delta T}{T} \leq A v_0 T^2$$

and thus

$$K \leq - \frac{A v_0 L}{\delta T/T} T \tag{VI-13}$$

Since $\delta T/T$ can be chosen arbitrarily, let us choose it equal to a small but non-zero constant. When the ratio $\delta T/T$ is chosen in this way, it is obvious from Equation (VI-13) that as T approaches zero K must approach zero. In the method of correlation functions it was assumed that $\delta T/T$ was small but otherwise arbitrary. It is therefore to be expected that the method of correlation functions yield a value for the thermal conductivity which approaches zero as the temperature approaches zero.

Equation (VI-11) is valid at very low temperatures. However, one should be able to extend the temperature somewhat above the region of validity of Equation (VI-11) before anharmonic terms become important. For this reason a computer program has been written which performs the integration in Equation (V-21). Some typical results of this calculation are given in Figure 2. In these curves the thermal conductivity K divided by the Debye θ is plotted as a function of T/θ for several different values of the impurity density. The length of the sample is 1 mm and ε is 0.01.

A brief examination of any of these curves will show the low temperature behavior just discussed. It will also show that the thermal conductivity exhibits a tendency to become independent of temperature at the higher temperatures. The nature of this temperature independent

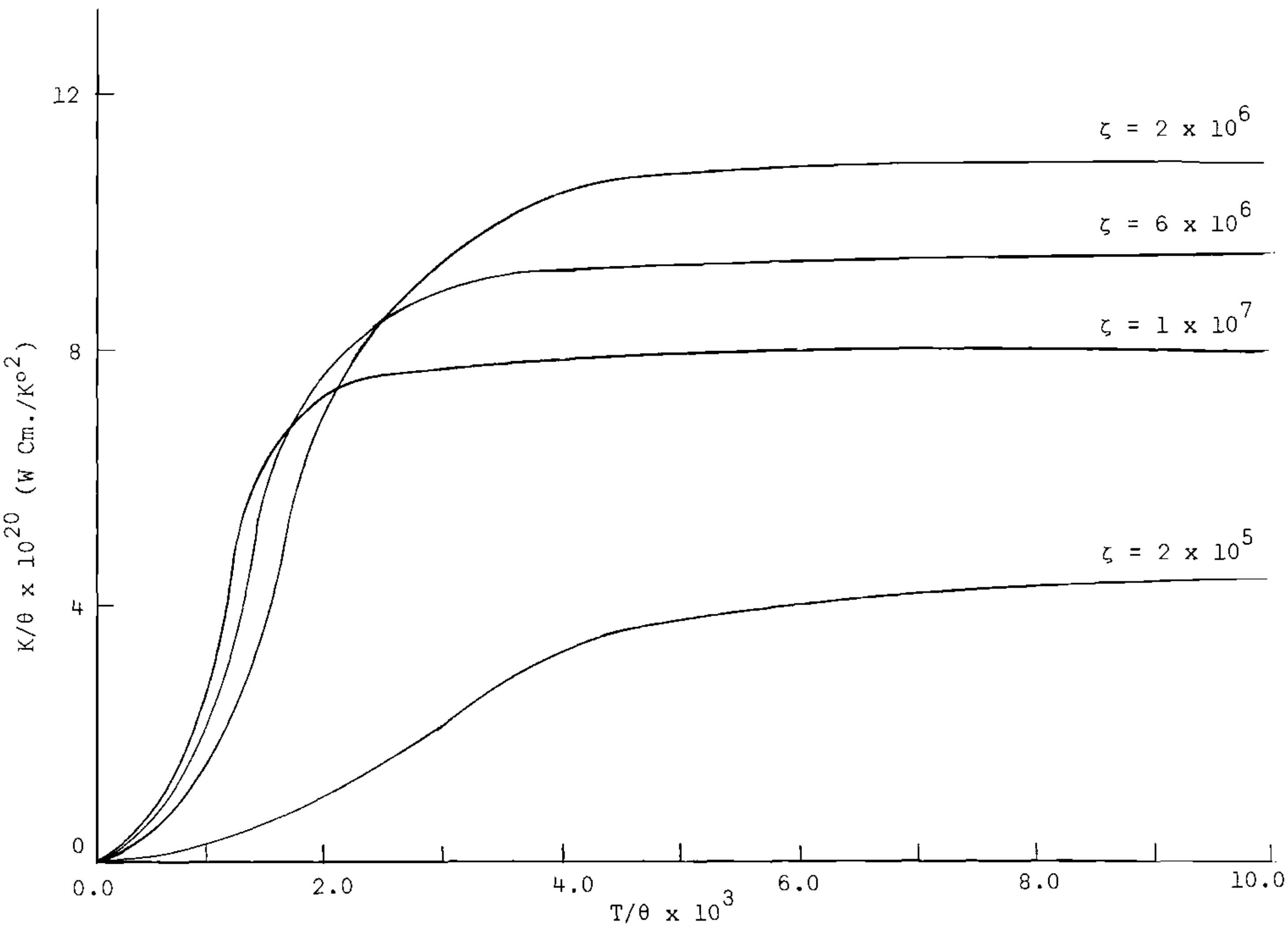

Figure 2. Calculated Thermal Conductivity as a Function of Temperature

behavior can be seen more easily by examining Equation (V-20). In this expression the entire temperature dependence is contained in the factor $x^2e^x/(e^x-1)^2$ which approaches unity at high temperatures thus leaving the thermal conductivity independent of temperature. The factor $x^2e^x/(e^x-1)^2$ comes from the statistics and essentially represents the deviation of the system from complete thermal equilibrium. The remaining part of Equation (V-20) represents the resistance offered by the system to the flow of energy at the given frequency and, in the case in which only harmonic contributions are considered, is independent of the temperature.

This is not expected to be the case when anharmonic terms are included since the strength of the anharmonic contribution increases as the amplitude of oscillation increases. Since the amplitude of oscillation increases as the temperature of the system increases one would expect the contribution to the thermal conductivity from anharmonic terms to increase as the temperature increases.

Another interesting feature of this model is the dependence of its thermal conductivity upon the density of impurities ζ. In Figure 3 the thermal conductivity K divided by the Debye θ is plotted as a function of ζ for several different values of θ/T. From these curves it can be seen that as the density of impurities approaches zero so does the thermal conductivity. Also, as the density of impurities becomes large the thermal conductivity again decreases.

The behavior of the thermal conductivity at low impurity densities can be explained in the following way. Recall from the discussion of the thermal conductivity based upon the method of local equilibrium

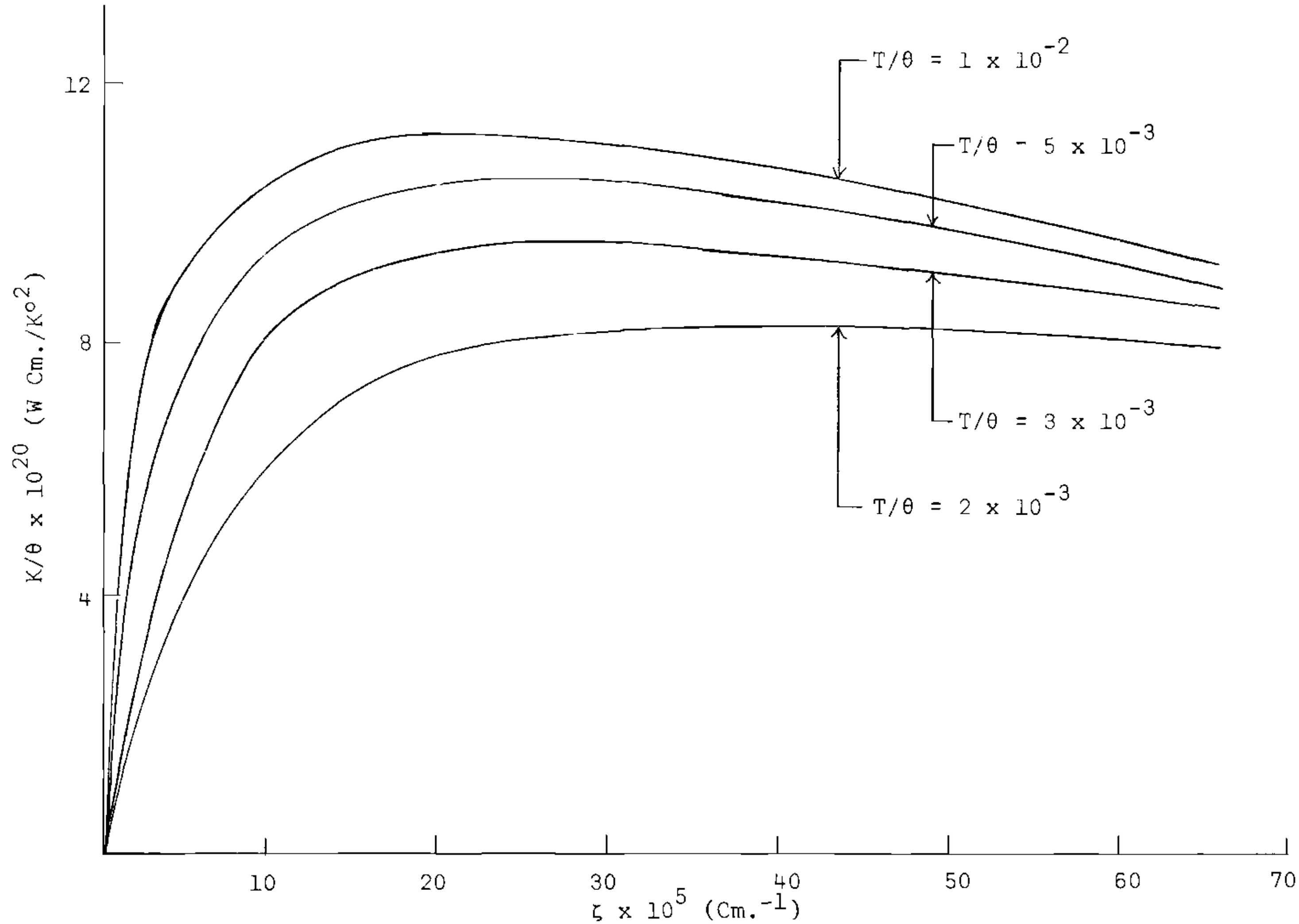

Figure 3. Calculated Thermal Conductivity as a Function of Impurity Density

that in order to conserve energy the very low frequency phonons must be limited in their participation in the transport of energy. At very low impurity densities it is only the high frequency phonons which are allowed to participate in any significant way in the transport of energy. Since at high frequencies the resistance to the flow of energy is large, the thermal conductivity is small. As the impurity density is increased the degree to which the lower frequency phonons can participate in the flow of energy increases very rapidly, and even though the resistance to the flow of energy at each given frequency is also increasing the increased participation of the lower frequency phonons overpowers this and the thermal conductivity rises. As the impurity density is increased still further a point is reached at which phonons of practically all frequencies are allowed to participate to their maximum degree, and any further increase in the impurity density will result in a decrease in the thermal conductivity.

There is one more feature of the thermal conductivity of this model which deserves some discussion. That is its dependence upon the total length of the sample. From Equation (VI-11) it can be seen that at very low temperatures the thermal conductivity depends upon the square of this length. This length dependence is to be expected at very low temperatures since there it is only the low frequency phonons which are present in the system, and the degree to which they are allowed to participate in the transport of energy is determined by the total number of impurities present which in turn is determined by the total length of the sample. As the temperature increases, examination of Equation (V-21) will show that this length dependence becomes weaker and that eventually the thermal conductivity increases as the square root of the length.

The failure of the thermal conductivity to become independent of length at the higher temperatures is evidently due to the omission of anharmonic terms from the potential energy. Recall that the method of correlation functions introduces restrictions upon the amount by which the low frequency phonons may participate in the transport of energy. As the total length of the sample becomes large, only the very low frequency phonons are significantly restricted. However, these restrictions never become negligible, as would be necessary for the thermal conductivity to become independent of length, since without them the contribution to the thermal conductivity from these low frequency phonons become infinite.

Calculations based upon the phenomenological theory indicate that when anharmonic terms are included the thermal conductivity no longer diverges. Even though the restrictions on the very low frequency phonons are still necessary in order to prevent a violation of the conservation of energy, if these restrictions are significant only at very low frequencies and if the contribution to the thermal conductivity from these low frequencies does not become infinite, then the effects of these restrictions can be made negligibly small for sufficiently large samples.

Comparison with Experiment

Comparison of the results of calculations based upon this model with experiment must be made with a certain amount of caution. At very low temperatures at least one important contribution to the thermal conductivity, that from diffuse boundary scattering, is known (51) to be a multi-dimensional effect. At higher temperatures the contribution from anharmonic terms is certainly important. Since this model is one dimensional and does not include anharmonic terms, definite conclusions about the comparison of these results with experiment cannot be drawn until the effects which these considerations may have upon this model are more fully understood. Nevertheless, it is interesting to note some striking similarities between these results and experiment.

The comparison of the local energy with experiment was made in the first section of this chapter, and, as was point out there, the agreement was quite good for samples which contain less than about 10^5 isotopic impurities and at temperatures which are less than about 10°K. For larger samples and at higher temperatures the deviation from experiment becomes significant. This is not surprising, however, since above these limits the contribution from anharmonic terms is expected to be large.

The thermal conductivity as calculated by the method of correlation functions exhibits some striking similarities with experiment. In Figure 4 an experimental curve of the thermal conductivity versus temperature for diamond (54) has been plotted along with the results of Equation (V-21) for a sample 1 mm in length. In the evaluation of Equation (V-21) the Debye θ was adjusted to give the best possible fit to the experimental data. The values of ε, a, and ζ were those appropriate for diamond (55) with the isotopic impurity being C^{13}. The Debye θ which was used in this calculation was larger by a factor of ten than

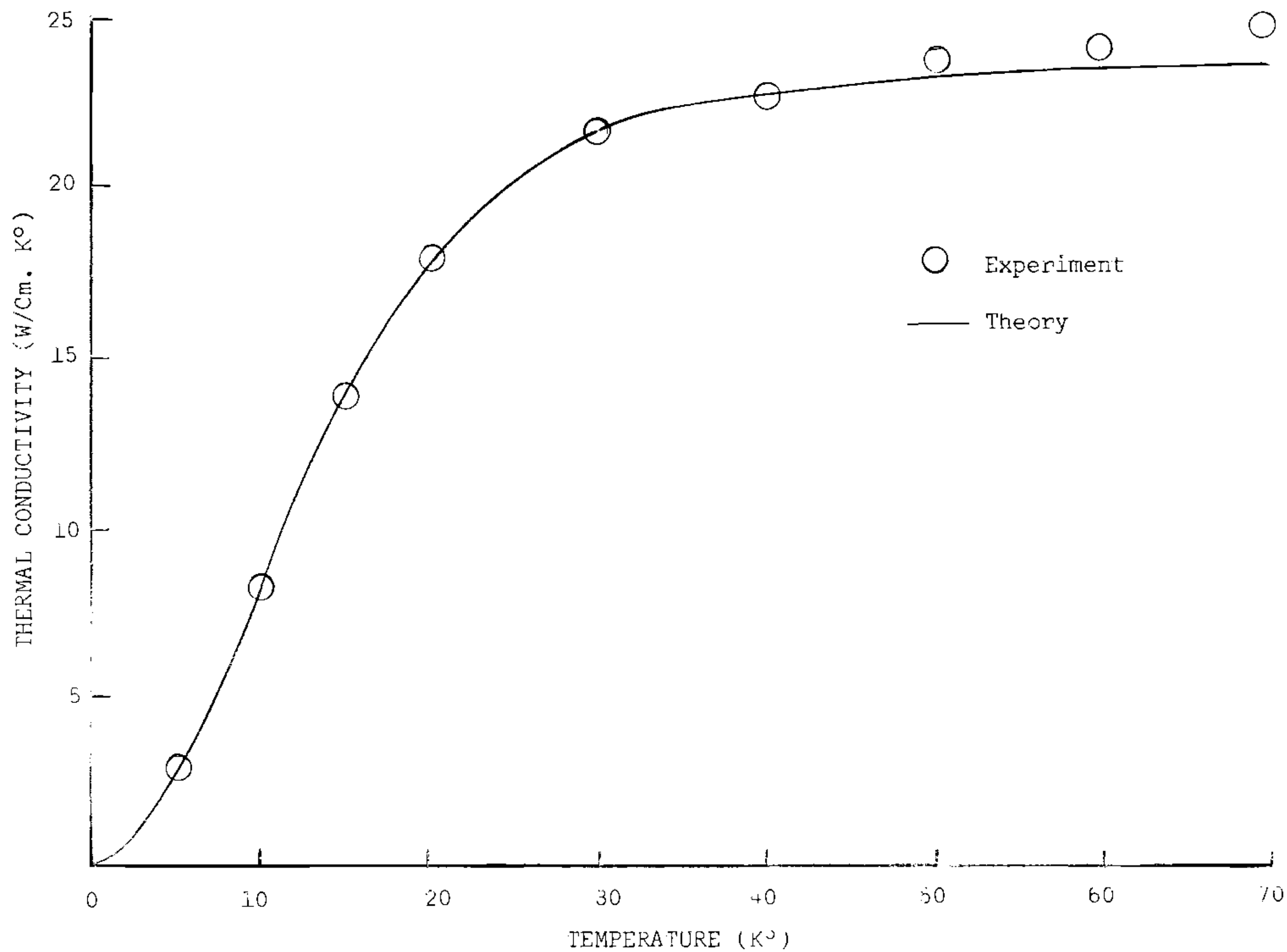

Figure 4. Comparison of Calculated and Experimental Thermal Conductivity for Diamond

the corresponding experimental value. In comparing Equation (V-21) to the experimental curves for diamond, we assume that diamond may be thought of as a collection of one-dimensional chains in parallel with a cross-sectional diameter given by the lattice spacing.

In Figure 5 are shown some experimental curves for lithium fluoride and sapphire (54). Again it can be seen that the shapes of these experimental curves, up to their peaks, are very similar to those which were calculated from Equation (V-21) as shown in Figure 2. As was the case with diamond, the data for these materials can be fitted quite well by adjusting their Debye θ's and possibly their cross-sectional diameters.

The decrease in the experimental thermal conductivity at temperatures which are higher than that at which the peak conductivity occurs is due to anharmonic terms and cannot be expected to appear in this model.

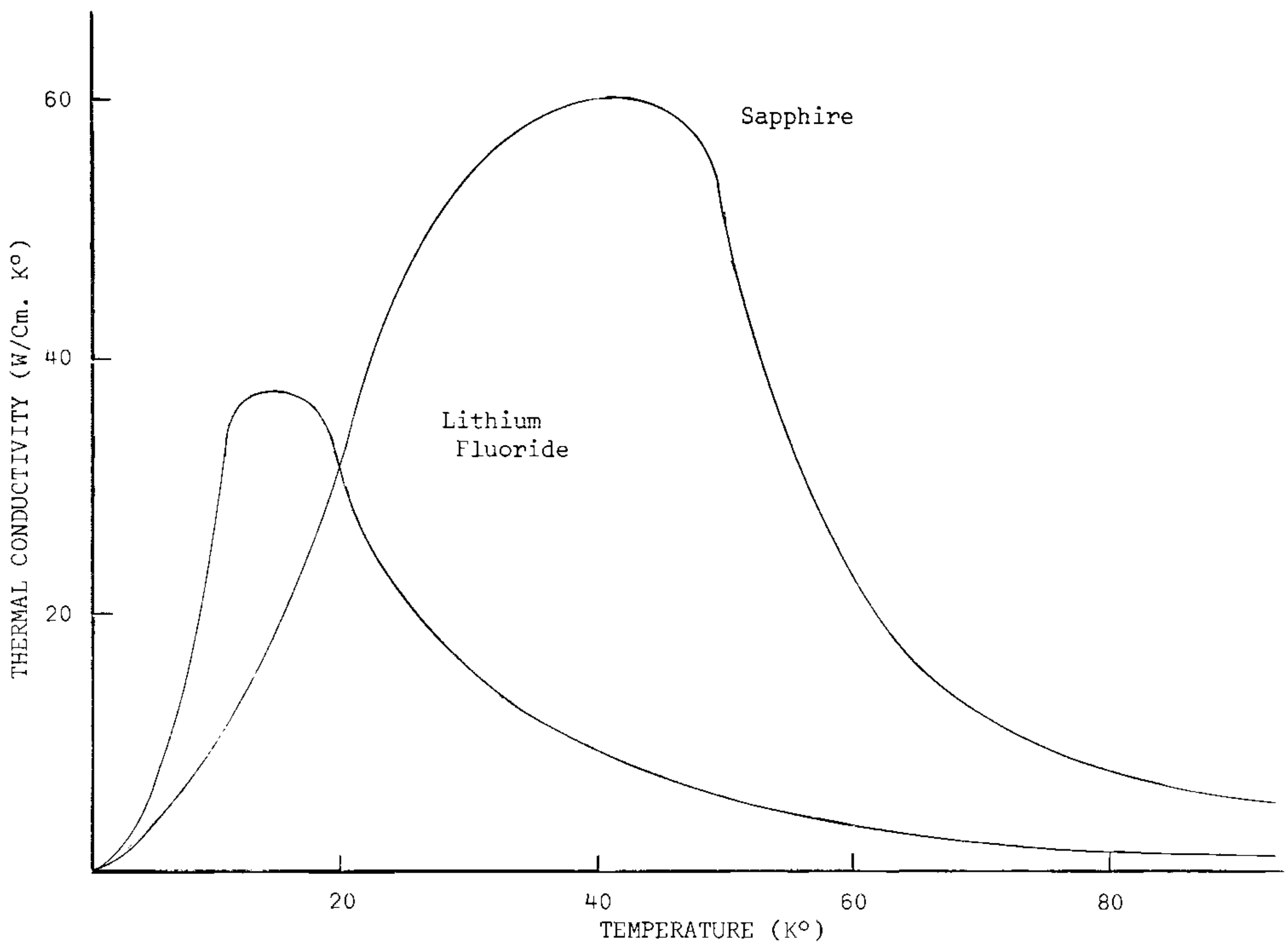

Figure 5. Experimental Thermal Conductivities of Sapphire and Lithium Fluoride

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

All existing theory and experiment indicate that the low temperature thermal conductivity of insulators is determined by the isotopic scattering which occurs when the motion of the system is dominated by harmonic forces. Despite this well known fact, all previous efforts have failed to calculate a meaningful thermal conductivity for harmonic systems which contain impurities. The principal conclusion which can be drawn from this work is that a meaningful thermal conductivity can indeed be calculated for harmonic systems. Furthermore, exact solutions to the equations of motion for this model have been obtained. By using these exact solutions it is possible to calculate expressions for the thermal properties of this harmonic system. Having obtained these expressions for the harmonic system it is then possible, by comparing them to experiment, to see clearly where other effects, such as anharmonic forces, become important.

It is also worthwhile to point out again that in the method of correlation functions a new definition of the thermal conductivity has been introduced. That is, in the method of correlation functions the thermal conductivity of the system is determined only from that portion of the heat current which is proportional to the temperature gradient. This new definition of the thermal conductivity avoids any consideration of infinite thermal conductivities which may arise in systems which cannot support a temperature gradient.

In the method of correlation function, it was assumed that terms in the density matrix which were of higher order than linear in the deviation from complete thermal equilibrium were small and could therefore be neglected. It would be very interesting to use the solutions to the equations of motion in order to calculate the contributions from these higher order terms and show that they are indeed small.

Since this model did not contain any contributions from anharmonic terms it was not possible to investigate the thermal conductivity at high temperatures or for samples which contain a very large number of isotopic impurities. It would be very interesting to include at least some anharmonic contributions within this framework in order to investigate the behavior of the thermal conductivity in these regions.

It would also be very useful to extend this model to three dimensions. If this were done, then the low temperature approach of the thermal conductivity to zero could be compared to the contribution from diffuse boundary scattering. It could well be that at low temperatures there is a measurable contribution from the restrictions which must be placed upon the very low frequency phonons.

APPENDIX A

CALCULATION OF $\mathcal{J}(r)$

The heat flux operator $\mathcal{J}(r)$ is defined in Equation (II-34) as

$$\frac{\partial H(r)}{\partial t} = -\frac{\partial}{\partial r}\mathcal{J}(r) \tag{A-1}$$

The Hamiltonian density H(r) is defined by Equation (II-29) as

$$H(r) = \frac{1}{2}\sum_{j}\left\{ H_j\,\delta(r_j - r) + \delta(r_j - r)\,H_j \right\} \tag{A-2}$$

where

$$H_j = \frac{p_j^2}{2m_j} + \frac{1}{2}\sum_{k}\varphi_{j,k}\,u_j\,u_k \tag{A-3}$$

The time derivitive of the Hamiltonian density is given by

$$\frac{\partial H(r)}{\partial t} = (i\hbar)^{-1}\left[H(r), H\right] \tag{A-4}$$

which, by using Equation (A-2) and the fact that

$$H = \sum_{k} H_k$$

can be written as

$$\frac{\partial H(r)}{\partial t} = (i\hbar)^{-1}\frac{1}{2}\sum_{j,k}\Big\{\big[H_j\delta(r_j-r), H_k\big] + \big[\delta(r_j-r)H_j, H_k\big]\Big\} \tag{A-5}$$

Using Equation (A-3) and the commutation relations for u_j and p_j which are given in Equations (II-3), one finds that Equation (A-5) can be written as

$$\frac{\partial H(r)}{\partial t} = \frac{1}{2}(i\hbar)^{-1}\sum_{j,k}\Big\{H_j\Big(\big[\delta(r_j-r), p_k\big]\frac{p_k}{2m_k} + \frac{p_k}{2m_k}\big[\delta(r_j-r), p_k\big] + \Big[\Big(\frac{p_j^2}{2m_j}+V_j\Big), \Big(\frac{p_k^2}{2m_k}+V_k\Big)\Big] \times \Big(\delta(r_j-r) - \delta(r_k-r)\Big)\Big\} + H.C. \tag{A-6}$$

where

$$V_k = \frac{1}{2}\sum_n \varphi_{j,n}u_j u_n \tag{A-7}$$

It follows from the commutation relations on u_j and p_j that

$$(i\hbar)^{-1}\left[\delta(r_j-r), P_k\right] = \frac{\partial}{\partial r_k}\delta(r_j-r) = \tag{A-8}$$

$$-\delta_{j,k}\frac{\partial}{\partial r}\delta(r_j-r)$$

It can also be shown by expanding $\delta(r_j-r)$ in a Taylor series and by retaining only the lowest order terms that

$$\delta(r_j-r)-\delta(r_k-r) = -(r_j-r_k)\frac{\partial}{\partial r}\delta(r_j-r) \tag{A-9}$$

Using these two expressions in Equation (A-6) it can be shown after a considerable amount of simplification that

$$\frac{\partial H(r)}{\partial t} = -\frac{\partial}{\partial r}\frac{1}{2}\sum_j\Big\{H_j\,\delta(r_j-r)\frac{P_j}{2m_j} + \tag{A-10}$$

$$H_j\frac{P_j}{2m_j}\,\delta(r_j-r) +$$

$$\sum_k (i\hbar)^{-1}\left[\frac{P_j^2}{2m_j}, V_k\right](r_j-r_k)\,\delta(r_j-r)\Big\} + H.C.$$

By comparing Equation (A-10) to Equation (A-1) it follows that

$$J(r) = \frac{1}{2}\sum_j\Big\{H_j\,\delta(r_j-r)\frac{P_j}{2m_j} + \tag{A-11}$$

$$H_j \frac{p_j}{2m_j} \delta(r_j - r) \quad +$$

$$\sum_k (i\hbar)^{-1} \left[\frac{p_j^2}{2m_j}, V_k\right] (r_j - r_k) \, \delta(r_j - r) \Big\} + H.C.$$

This expression for J(r) and its derivation is the one-dimensional case of a more general calculation performed by Hardy (52).

APPENDIX B

APPROXIMATION TO THE SOLUTIONS OF EQUATION (II-22) AND RELATED CALCULATIONS

The Approximation

From Equations (III-30) and (III-34) the expression for $C_n(s)$ is

$$C_n(s) = f(s)\Big\{ e^{insa} - \tag{B-1}$$

$$p(s) \sum_{g=1}^{M} \mathrm{SIN}\,(n-\ell_g)sa\; e^{i\ell_g sa} +$$

$$p^2(s) \sum_{g=2}^{M} \sum_{h=1}^{g-1} \mathrm{SIN}\,(n-\ell_g)sa\, \mathrm{SIN}\,(\ell_g-\ell_h)sa\; e^{i\ell_h sa} +$$

$$\bullet\;\bullet\;\bullet\; +$$

$$(-p(s))^m \sum_{g=m}^{M} \sum_{h=m-1}^{g-1} \cdots \sum_{k=1}^{j-1} \mathrm{SIN}(n-\ell_g)sa \;\times$$

$$\mathrm{SIN}(\ell_g-\ell_h)sa \cdots \mathrm{SIN}(\ell_j-\ell_k)sa\; e^{i\ell_k sa} +$$

$$\bullet\;\bullet\;\bullet\; +$$

$$(-p(s))^M \;\mathrm{SIN}(n-\ell_M)sa \cdots \mathrm{SIN}(\ell_2-\ell_1)sa\; e^{i\ell_1 sa}\Big\}$$

where $\ell_M \le n \le \ell_{M+1}$ and $s \le 0$. By writing the sine functions in their complex exponential form and performing the indicated multiplications this expression becomes

$$C_n(s) = f(s)\Big\{e^{insa} + \tag{B-2}$$

$$\left(i\frac{P(s)}{2}\right)\sum_{g=1}^{M}\left[e^{insa} - e^{-i(n-2\ell_g)sa}\right] +$$

$$\left(i\frac{P(s)}{2}\right)^2\sum_{g=2}^{M}\sum_{h=1}^{g-1}\left[e^{insa} - e^{-i(n-2\ell_g)sa} -\right.$$

$$\left. e^{i(n-2\ell_g+2\ell_h)sa} + e^{-i(n-2\ell_h)sa}\right] +$$

$$\bullet\bullet\bullet +$$

$$\left(i\frac{P(s)}{2}\right)^m\sum_{g=m}^{M}\cdots\sum_{k=1}^{j-1}\left[e^{insa} - e^{-i(n-2\ell_g)sa} + \cdots +\right.$$

$$\left.(-1)^{m-1}\, e^{i(-1)^m(n-2\ell_g+\cdots+(-1)^m 2\ell_k)sa} + \cdots +\right.$$

$$\left(i\frac{P(s)}{2}\right)^M\left[e^{insa} - e^{-i(n-2\ell_M)sa} + \cdots +\right.$$

$$\left.(-1)^{M-1}\, e^{i(-1)^M(n-2\ell_M+\cdots+(-1)^M 2\ell_1)sa}\right]\Big\}$$

It can be shown by induction that

$$\sum_{g=A+B}^{C} \sum_{h=A+B-1}^{g-1} \cdots \sum_{j=A+2}^{i-1} \sum_{k=A+1}^{j-1} 1 = \tag{B-3}$$

$$\binom{C-B}{A} = \frac{(C-B)!}{(C-B-A)!\,A!}$$

where A, B, and C are integers. By using Equations (B-2) and (B-3), the expression for $C_n(s)$ can be written as

$$C_n(s) = f(s)\Big\{\left(1+i\frac{p(s)}{2}\right)^M e^{insa} - \tag{B-4}$$

$$\left(i\frac{p(s)}{2}\right)\sum_{g=1}^{M}\left(1+i\frac{p(s)}{2}\right)^{g-1} e^{-i(n-2l_g)sa} +$$

$$\left(i\frac{p(s)}{2}\right)^2 \sum_{g=1}^{M}\sum_{h=1}^{g-1}\left(1+i\frac{p(s)}{2}\right)^{h-1} \times$$

$$\left[e^{-i(n-2l_h)sa} - e^{i(n-2l_g+2l_h)sa}\right] + \cdots\Big\}$$

It will now be shown that if p(s) is sufficiently small, the term which varies as $(ip(s)/2)^{m+1}$ is small compared to the preceding term which varies as $(ip(s)/2)^m$. This will be done by treating the case in which $m = 1$, since the extension to larger values of m is obvious.

The term in Equation (B-4) which varies as $(ip(s)/2)^2$ is given by

$$\left(i\frac{p(s)}{2}\right)^2 \sum_{g=1}^{M} \sum_{h=1}^{g-1} \left(1 + i\frac{p(s)}{2}\right)^{h-1} \times \tag{B-5}$$

$$\left[e^{-i(n-2\ell_h)sa} - e^{i(n-2\ell_g+2\ell_h)sa}\right]$$

while the term which varies as (ip(s)/2) is given by

$$\left(i\frac{p(s)}{2}\right) \sum_{g=1}^{M} \left(1+i\frac{p(s)}{2}\right)^{g-1} e^{-i(n-2\ell_g)sa} \tag{B-6}$$

An upper bound on Equation (B-5) can be obtained by setting h = g - 1 in the term $(1 + i\ p(s)/2)^{h-1}$, which yields

$$\left(i\frac{p(s)}{2}\right) \sum_{g=1}^{M} \left(i\frac{p(s)}{2}\right)\left(1+i\frac{p(s)}{2}\right)^{g-2} \times \tag{B-7}$$

$$\sum_{h=1}^{g-1} \left[e^{-i(n-2\ell_h)sa} - e^{i(n-2\ell_g+2\ell_h)sa}\right]$$

An upper bound on Equation (B-7) can be obtained by replacing $e^{-i(n-2\ell_h)sa}$ by $e^{-i(n-2\ell_g)sa}$ and $e^{i(n-2\ell_g+2\ell_h)sa}$ by $e^{i(n-2\ell_g)sa}$. With these replacements the upper bound on Equation (B-7) becomes

$$\left(i\frac{p(s)}{2}\right) \sum_{g=1}^{M} \left(1+i\frac{p(s)}{2}\right)^{g-1} \left[e^{-i(n-2\ell_g)sa} - \right. \tag{B-8}$$

$$e^{i(n-2\ell_g)sa}\Big]\ \frac{(g-1)\left(i\,\frac{p(s)}{2}\right)}{\left(1+i\,\frac{p(s)}{2}\right)}$$

The last term in Equation (B-8) does not exceed Mp(s)/2 and thus if M is not too large and p(s) is sufficiently small, the product Mp(s)/2 will be small compared to unity and Equation (B-8) will be small compared to Equation (B-6).

If, however, M is very large, then it is useful to rewrite Equations (B-6) and (B-7) in the following form:

$$\left(i\,\frac{p(s)}{2}\right)\sum_{g=1}^{Q}\left(1+i\,\frac{p(s)}{2}\right)^{g-1} e^{-i(n-2\ell_g)sa} + \qquad \text{(B-6a)}$$

$$\left(i\,\frac{p(s)}{2}\right)\sum_{g=Q+1}^{M}\left(1+i\,\frac{p(s)}{2}\right)^{g-1} e^{-i(n-2\ell_g)sa}$$

and

$$\left(i\,\frac{p(s)}{2}\right)\sum_{g=1}^{Q}\left(i\,\frac{p(s)}{2}\right)\left(1+i\,\frac{p(s)}{2}\right)^{g-2} \times \qquad \text{(B-7a)}$$

$$\sum_{h=1}^{g-1}\left[e^{-i(n-2\ell_h)sa} - e^{i(n-2\ell_g+2\lambda_h)sa}\right] +$$

$$\left(i\,\frac{p(s)}{2}\right)\sum_{g=Q+1}^{M}\left(i\,\frac{p(s)}{2}\right)\left(1+i\,\frac{p(s)}{2}\right)^{g-2} \times$$

$$\sum_{h=1}^{g-1}\left[e^{-i(n-2\ell_h)sa} - e^{i(n-2\ell_g+2\lambda_h)sa}\right]$$

where $1 << Q << M$. The first double sum in Equation (B-7a) can be shown to be small compared to the first sum in Equation (B-6a) in the same way that Equation (B-7) was shown to be small compared to Equation (B-6) for smaller values of M.

The second double sum in Equation (B-7a) can be shown to be small compared to the second sum in Equation (B-6a) in the following way. Since the impurities are randomly positioned, the ℓ_h represent a set of random integers and thus the sum over h in Equation (B-7a) can be treated as a two-dimensional random walk. It has been shown, in a paper by Chandrasekhar (53), that in a random walk of M steps of length ℓ the probability of moving a distance greater than $\sqrt{M}\,\ell$ is negligibly small for large M. By using this result of Chandrasekhar it can be shown that there is a negligible probability that the second double sum in Equation (B-7a) will exceed

$$\left(i\frac{P(s)}{2}\right)\sum_{g=Q+1}^{M}\left(1+i\frac{P(s)}{2}\right)^{g-1}\left[e^{-i(n-2\ell_g)sa}-e^{i(n-2\ell_g)sa}\right]\left[\frac{\sqrt{g-1}\,\left(i\frac{P(s)}{2}\right)}{\left(1+i\frac{P(s)}{2}\right)}\right] \tag{B-9}$$

If s is restricted such that

$$\frac{P(s)}{2} < \frac{\alpha}{\sqrt{R}} \tag{B-10}$$

where α is a small number to be chosen later, then

$$\left[\frac{\sqrt{g-1}\,\left(i\frac{P(s)}{2}\right)}{\left(1+i\frac{P(s)}{2}\right)}\right] < \frac{\sqrt{g-1}}{\sqrt{R}}\,\alpha < \alpha \tag{B-11}$$

Thus, when α is small compared to unity Equation (B-9) is small compared to the second sum in Equation (B-6a).

This procedure can be used to show that each term in Equation (B-4) is small compared to the term which precedes, if s satisfies the condition given by Equation (B-10). This condition on s can be satisfied for all values of s which make a significant contribution to the local energy or the heat flux, if the temperature is sufficiently low. The upper bound on the temperature is determined by the values of ε, R, θ, and α. If, for example, α is chosen to be 0.01, then each term in Equation (B-4) is no more than 2 per cent of the term which precedes it. If R does not exceed about 10^5, then for practical values of ε and θ the upper bound on the temperature is between 1°K and 50°K.

Since it is only the leading term in Equation (B-4) which is important, the expression for $C_n(s)$ can be written to a good approximation at low temperatures as

$$C_n(s) = f(s)\left(1 + i\frac{p(s)}{2}\right)^M e^{insa} \qquad \text{(B-12)}$$

where $\ell_M \leq n \leq \ell_{M+1}$ and $s \leq 0$. This approximation will usually be sufficient. However, there is at least one calculation to be done here where the contribution from what has been retained in Equation (B-12) is zero, and in that case the approximation must be carried to the next largest term which yields

$$C_n(s) = f(s)\left\{\left(1+i\frac{P(s)}{2}\right)^M e^{insa} - \right. \tag{B-13a}$$

$$\left.\left(i\frac{P(s)}{2}\right)\sum_{g=1}^{M}\left(1+i\frac{P(s)}{2}\right)^{g-1} e^{i2l_g sa}\, e^{-insa}\right\}$$

When $s \geq 0$ the same argument yields

$$C_n(s) = f(s)\left\{\left(1+i\frac{P(s)}{2}\right)^{R-M} e^{insa} - \right. \tag{B-13b}$$

$$\left.\left(i\frac{P(s)}{2}\right)\sum_{g=M+1}^{R}\left(1+i\frac{P(s)}{2}\right)^{g-1} e^{i2l_g sa}\, e^{-insa}\right\}$$

where $\ell_M \leq n \leq \ell_{M+1}$.

<u>Normalization of $B_n(s)$</u>

From Equation (III-3) and Equation (B-12) the expression for $B_n(s)$ when $s \leq 0$ and $\ell_M \leq n \leq \ell_{M+1}$ is given by

$$B_n(s) = \beta\sqrt{m_n}\; f(s)\left(1+i\frac{P(s)}{2}\right)^M e^{insa} \tag{B-14}$$

where we have introduced a normalization factor β which must be chosen such that

$$\sum_n B_n(s)B_n^*(s') = \frac{2\pi}{Na}\,\delta(s-s') = \tag{B-15}$$

$$\frac{1}{N}\sum_{n} e^{ik(s-s')a}$$

Since $B_n(s)$ must also satisfy the Equation

$$\sum_{n} D_{j,n} B_n(s) = \omega^2(s) B_j(s)$$

One can prove that the sum on the left of Equation (B-15) is non-zero only when $\omega(s) = \omega\,(s')$. Thus, for this model (i.e. a finite number of impurities in an infinite chain), the sum is non-zero only when $s = s'$ or $s = -s'$. In calculating the sum on the left side of Equation (B-15), we shall use the expression for $B_n(s)$ given in Equation (B-14) except for those n lying in the interval $\ell_1 \leq n \leq \ell_{R-1}$. For those $B_n(s)$ in this interval, we use Equation (B-14) with M and m_n set equal to R and m, respectively. We shall show in the following derivation that this replacement causes negligible error.

If Equation (B-15) is added to its complex conjugate it can be written as

$$\sum_{n} \left(B_n(s) B_n^*(s') + B_n^*(s) B_n(s') \right) = \frac{4\pi}{Na}\,\delta(s-s') \qquad \text{(B-16)}$$

By restricting both s and s' to be less than zero and using Equation (B-14) this expression can be written as

$$|\beta^2||f(s)|^2 m \Big\{ \sum_{n=-\frac{(N-1)}{2}}^{0} \Big[e^{in(s-s')a} + e^{-in(s-s')a} \Big] + \sum_{n=0}^{\frac{(N-1)}{2}} \Big[\left(1+i\frac{p(s)}{2}\right)^R \left(1-i\frac{p(s')}{2}\right)^R \times e^{in(s-s')a} + \left(1-i\frac{p(s)}{2}\right)^R \left(1+i\frac{p(s)}{2}\right)^R \times e^{-in(s-s')a} \Big] \Big\} = \frac{4\pi}{Na}\,\delta(s-s') \tag{B-17}$$

Since it is only when s is arbitrarily close to s' that this expression is non-zero, p(s) can be replaced by p(s') and Equation (B-17) becomes

$$|\beta|^2 |f(s)|^2 m \left\{ 1 + \left(1+\frac{p^2(s)}{4}\right)^R \right\} \times \sum_n e^{in(s-s')a} = \frac{4\pi}{Na}\,\delta(s-s') \tag{B-18}$$

We may now show that negligible error has been made in approximating certain of the $B_n(s)$. First, the sum on the left side of Equation (B-18) is zero for $s \neq s'$ just as it should be. For $s = s'$ the sum equals N. The left side of Equation (B-18) differs from the true value only by a fixed finite number. Hence as $N \to \infty$, this finite correction is negligible. From Equation (B-18), we have that

$$\beta = \frac{1}{f(s)}\sqrt{\frac{2}{Nm}}\left\{1 + \left(1 + \frac{p^2(s)}{4}\right)^R\right\}^{-1/2} \tag{B-19}$$

hence $B_n(s)$ is given by

$$B_n(s) = \sqrt{\frac{2m_n}{Nm}}\left\{1 + \left(1 + \frac{p^2(s)}{4}\right)^R\right\}^{-1/2}\left\{\left(1 + i\,\frac{p(s)}{4}\right)^M e^{insa} - \right. \tag{B-20}$$

$$\left.\left(i\,\frac{p(s)}{2}\right)\sum_{g=1}^{M}\left(1 + i\,\frac{p(s)}{2}\right)^{g-1} e^{i2\ell_g sa}\; e^{-insa}\right\}$$

where $\ell_M \le n \le \ell_{M+1}$ and $s \le 0$. The same calculation for $s \ge 0$ yields

$$B_n(s) = \sqrt{\frac{2m_n}{Nm}}\left\{1 + \left(1 + \frac{p^2(s)}{4}\right)^R\right\}^{-1/2}\left\{\left(1 + i\,\frac{p(s)}{2}\right)^{R-M} e^{insa} - \right. \tag{B-21}$$

$$\left.\left(i\,\frac{p(s)}{2}\right)\sum_{g=M+1}^{R}\left(1 + i\,\frac{p(s)}{2}\right)^{g-1} e^{i2\ell_g sa}\; e^{-insa}\right\}$$

where $\ell_M \le n \le \ell_{M+1}$. In most cases the last term can be dropped from Equations (B-20) and (B-21).

It is now easy to show by using Equations (B-20) and (B-21) that

$$\sum_{n=-\frac{(N-1)}{2}}^{\frac{(N-1)}{2}} B_n(s)\,B_n^*(-s) =$$

$$\sum_{n=-\frac{(N-1)}{2}}^{\frac{(N-1)}{2}} B_n(-s)B_n^*(s) = 0$$

when N is arbitrarily large. Thus, the normalization of the $B_n(s)$ such that they satisfy Equation (B-15) is complete.

<u>Calculation of G(s,s) and G(s,-s) G(-s,s)</u>

From Equation (V-14)

$$G(s,s) = \sum_{j=-\frac{1}{2}a}^{\frac{1}{2}a} \left\{ \left(\frac{B_{j-1}^*(s)}{\sqrt{m_{j-1}}} - \frac{B_{j+1}^*(s)}{\sqrt{m_{j+1}}} \right) \frac{B_j(s)}{\sqrt{m_j}} - \left(\frac{B_{j-1}(s)}{\sqrt{m_{j-1}}} - \frac{B_{j+1}(s)}{\sqrt{m_{j+1}}} \right) \frac{B_j^*(s)}{\sqrt{m_j}} \right\} \tag{B-22}$$

By using Equations (II-41) and (III-4) 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

$$G(s,s) = \frac{L}{ma} \left\{ \left(B_{j-1}^*(s) - B_{j+1}^*(s) \right) B_j(s) - \left(B_{j-1}(s) - B_{j+1}(s) \right) B_j^*(s) \right\} \tag{B-23}$$

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

The expression for G(s,s) when s ≤ 0 can be calculated most easily by choosing j in the pure region at the left of the impurity bearing region. From Equation (B-20) the expression for $B_j(s)$ in this region is given by

$$B_j(s) = \sqrt{\frac{2}{N}} \left\{ 1 + \left(1 + \frac{\rho^2(s)}{4}\right) R \right\}^{-1/2} e^{ijsa} \tag{B-24}$$

The use of this expression in Equation (B-23) yields

$$G(s,s) = \frac{i8L}{mNa} \left\{ 1 + \left(1 + \frac{\rho^2(s)}{4}\right) R \right\}^{-1} \mathrm{SIN}(sa) \tag{B-25}$$

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

$$G(s,s) = \frac{i8L}{mNa} \left\{ 1 + \left(1 + \frac{\rho^2(s)}{4}\right) R \right\}^{-1} \mathrm{SIN}(sa)$$

In the same way that Equation (B-23) was derived for G(s,s) it can be shown that

$$G(s,-s) = \frac{L}{ma} \Big\{ \left(B^*_{j-1}(s) - B^*_{j+1}(s) \right) B_j(-s) - \tag{B-26}$$

$$\left(B_{j-1}(-s) - B_{j+1}(-s) \right) B^*_j(s) \Big\}$$

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 the expressions for $B_j(s)$

and $B_j(-s)$ are

$$B_j(s) = \sqrt{\frac{2}{N}} \left\{ 1 + \left(1 + \frac{\rho^2(s)}{4}\right)^R \right\}^{-1/2} e^{ijsa} \qquad \text{(B-27)}$$

and

$$B_j(-s) = \sqrt{\frac{2}{N}} \left\{ 1 + \left(1 + \frac{\rho^2(s)}{4}\right)^R \right\}^{-1/2} \left\{ \left(1 + i\frac{\rho(s)}{2}\right)^R e^{-ijsa} - \right. \qquad \text{(B-28)}$$

$$\left. \left(i\frac{\rho(s)}{2}\right) \sum_{g=1}^{R} \left(1 + i\frac{\rho(s)}{2}\right)^{g-1} e^{-i2l_g sa} e^{ijsa} \right\}$$

where $s \geq 0$. The substitution of these expressions into Equation (B-26) yields

$$G(s,-s) = \frac{8L}{mNa} \left\{ 1 + \left(1 + \frac{\rho^2(s)}{4}\right)^R \right\}^{-1} \mathrm{SIN}\,(sa) \times \qquad \text{(B-29)}$$

$$\left(\frac{\rho(s)}{2}\right) \sum_{g=1}^{R} \left(1 + i\frac{\rho(s)}{2}\right)^{g-1} e^{-i2l_g sa}$$

It is the product G(s,-s) G(-s,s) rather than G(s,-s) itself which is of interest here. By noting from Equation (B-26) that

$$G(s,-s) = -G^*(-s,s)$$

it is easy to see that

$$G(s,-s)G(-s,s) = -\left(\frac{8L}{mNa}\right)^2 \left\{1+\left(1+\frac{\rho^2(s)}{4}\right)^R\right\}^{-2} \times \tag{B-30}$$

$$\sin^2(sa)\left(\frac{\rho^2(s)}{4}\right)\left\{\sum_{g=1}^{R}\left(1+\frac{\rho^2(s)}{4}\right)^{g-1}+\right.$$

$$\left.\sum_{\substack{g=1\\g\neq h}}^{R}\sum_{h=1}^{R}\left(1+i\frac{\rho(s)}{2}\right)^{g-1}\left(1-i\frac{\rho(s)}{2}\right)^{h-1}e^{-i2(\ell_g-\ell_h)sa}\right\}$$

The second sum in this expression is, on the average, zero for a random distribution of impurities, and thus the expression for G(s,-s) G(-s,s) can be written as

$$G(s,-s)G(-s,s) = -\left(\frac{8L}{mNa}\right)^2 \frac{\left[\left(1+\frac{\rho^2(s)}{4}\right)^R-1\right]}{\left[\left(1+\frac{\rho^2(s)}{4}\right)^R+1\right]}\sin^2(sa) \tag{B-31}$$

Notice that G(s,-s) G(-s,s) is symmetric about $s \leq 0$.

<u>Calculation of $\sum_{[N_1]} B_j(s)\, B_j^*(s)$ and $\sum_{[N_2]} B_j(s)\, B_j^*(s)$</u>

By using Equation (B-20) it is easy to see that

$$\sum_{[N_1]} B_j(s)\, B_j^*(s) = \sum_{j=-\frac{(N-1)}{2}}^{\ell_1} B_j(s) B_j^*(s) = \left\{1+\left(1+\frac{\rho^2(s)}{4}\right)^R\right\}^{-1} \tag{B-32}$$

where $s \leq 0$. By using Equation (B-21) and by dropping the sum over g, whose contribution is negligible in this case, it follows that

$$\sum_{j=-\frac{(N-1)}{2}}^{\ell_1} B_j(s)\,B_j^*(s) = \left\{1 + \left(1+\frac{\rho^2(s)}{4}\right)^R\right\}^{-1}\left(1+\frac{\rho^2(s)}{4}\right)^R \qquad \text{(B-33)}$$

where $s \geq 0$. In the same way it can be shown that

$$\sum_{j=\ell_R}^{\frac{(N-1)}{2}} B_j(s)\,B_j^*(s) = \left\{1 + \left(1+\frac{\rho^2(s)}{4}\right)^R\right\}^{-1}\left(1+\frac{\rho^2(s)}{4}\right)^R \qquad \text{(B-34)}$$

where $s \leq 0$, and

$$\sum_{j=\ell_R}^{\frac{(N-1)}{2}} B_j(s)\,B_j^*(s) = \left\{1 + \left(1+\frac{\rho^2(s)}{4}\right)^R\right\}^{-1} \qquad \text{(B-35)}$$

where $s \geq 0$. In Equations (B-32) through (B-35) it must be remembered that N is to be taken arbitrarily large.

APPENDIX C

CALCULATION OF E(r,T)

The local energy E(r,T) can be written, with the aid of Equation (IV-6), as

$$E(r,T) = \frac{1}{D}\left(\frac{Na}{2\pi}\right)\sum_{[N_r]}\int_0^{\pi/2} \hbar\omega(s) \times \tag{C-1}$$

$$\left\{ B_j(s) B_j^*(s)\, n(s) + B_j(-s) B_j^*(-s)\, n(-s) \right\} ds$$

where D is the length of the region of interest, $\sum_{[N_r]}$ represents the sum over the particles within the region of interest which is centered on r, and the contribution from the zero point oscillations has been dropped. By substituting from Equations (IV-9) and by using the expressions which are given in Appendix B for $B_j(s)$, Equation (C-1) can be written

$$E(r,T) = \frac{1}{D}\left(\frac{a}{\pi}\right)\sum_{[N_r]}\int_0^{\pi/a} \frac{\hbar\omega(s)}{\left[\left(1+\frac{\rho^2(s)}{4}\right)^{2R}-1\right]} \frac{m_j}{m} \times \tag{C-2}$$

$$\left\{ \left(1+\frac{\rho^2(s)}{4}\right)^{R-M} \left[\frac{\left(1+\frac{\rho^2(s)}{4}\right)^R}{(e^{x_1}-1)} - \frac{1}{(e^{x_2}-1)} \right] + \right.$$

$$\left(1+\frac{\rho^2(s)}{4}\right)^M\left[\frac{\left(1+\frac{\rho^2(s)}{4}\right)^R}{(e^{x_2}-1)}-\frac{1}{(e^{x_1}-1)}\right]\Bigg\}\,ds$$

If the sum $\sum_{[N_r]}$ is performed then this expression can be written as

$$E(r,T)=\frac{(1-\epsilon\,\varsigma a)}{\pi}\int_0^{\pi/a}\frac{\hbar\omega(s)\left(1+\frac{\rho^2(s)}{4}\right)^{\frac{\varsigma L}{2}}}{\left[1-\left(1+\frac{\rho^2(s)}{4}\right)^{2\varsigma L}\right]}\;\times \tag{C-3}$$

$$\Bigg\{\left(1+\frac{\rho^2(s)}{4}\right)^{\frac{\varsigma L}{2}-\varsigma r}\left[\frac{\left(1+\frac{\rho^2(s)}{4}\right)^{\frac{\varsigma L}{2}}}{(e^{x_1}-1)}-\frac{\left(1+\frac{\rho^2(s)}{4}\right)^{-\frac{\varsigma L}{2}}}{(e^{x_2}-1)}\right]+$$

$$\left(1+\frac{\rho^2(s)}{4}\right)^{\frac{\varsigma L}{2}+\varsigma r}\left[\frac{\left(1+\frac{\rho^2(s)}{4}\right)^{\frac{\varsigma L}{2}}}{(e^{x_2}-1)}-\frac{\left(1+\frac{\rho^2(s)}{4}\right)^{-\frac{\varsigma L}{2}}}{(e^{x_1}-1)}\right]\Bigg\}\,ds$$

where

$$R=\varsigma L$$

and

$$M=\frac{\varsigma L}{2}+\varsigma r$$

Here, r is in the interval $-L/2 \leq r \leq L/2$, where L is the length of the impurity bearing region of the chain. If $\alpha(s)$ is defined such that

$$\alpha(s)=\mathrm{Ln}\left(1+\frac{\rho^2(s)}{4}\right) \tag{C-4}$$

then

$$\left(1 + \frac{p^2(s)}{4}\right)^N = e^{\alpha(s) N} \tag{C-5}$$

and Equation (C-3) can be written as

$$E(r,T) = \frac{(1-\epsilon\zeta a)}{\pi} \int_0^{\pi/a} \frac{\hbar\, \omega(s)}{\mathrm{SINH}[\alpha(s)\zeta L]} \times \tag{C-6}$$

$$\left\{ \frac{\mathrm{SINH}[\alpha(s)(\frac{\zeta L}{2} - \zeta r)]}{(e^{x_1} - 1)} + \frac{\mathrm{SINH}[\alpha(s)(\frac{\zeta L}{2} + \zeta r)]}{(e^{x_2} - 1)} \right\} ds$$

which, after rearranging terms, can be written

$$E(r,T) = \frac{(1-\epsilon\zeta a)}{\pi} \int_0^{\pi/a} \frac{\hbar\, \omega(s)}{2(e^{x_1}-1)(e^{x_2}-1)} \times \tag{C-7}$$

$$\left\{ \left[(e^{x_1}-1) + (e^{x_2}-1)\right] \frac{\mathrm{COSH}[\alpha(s)\zeta r]}{\mathrm{COSH}[\alpha(s)\zeta L/2]} - \right.$$

$$\left. (e^{x_2} - e^{x_1}) \frac{\mathrm{SINH}[\alpha(s)\zeta r]}{\mathrm{SINH}[\alpha(s)\zeta L/2]} \right\} ds$$

In all practical cases, the term $\epsilon\zeta a$ is very small compared to one and can be dropped.

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*Abbreviations here follow the form of American Institute of Physics *Style Manual* (1959).

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VITA

Kenneth Richard Allen was born on December 11, 1939 in Cleveland, Ohio. He was graduated from Chamblee High School, Chamblee, Georgia, in 1957. He received a Bachelor of Science degree in Physics from the Georgia Institute of Technology in June, 1961. From 1961 until 1962 he was associated with United Aircraft Corporation in Hartford, Connecticut. He entered the graduate school of physics at the Georgia Institute of Technology in September, 1962.

Mr. Allen was employed as a graduate research assistant at the Georgia Institute of Technology from August, 1962 until September, 1963. He was employed as a graduate teaching assistant in the school of physics from September, 1963 until June, 1965. He received the degree Master of Science in Physics from the Georgia Institute of Technology in June, 1964. In June, 1965, he received a National Science Foundation Research Assistantship for research toward the Ph.D. degree in physics at the Georgia Institute of Technology.

Mr. Allen was married to the former Caroline McClellan of Atlanta, Georgia, on December 19, 1959. They have two children.