VIBRATIONAL PROPERTIES OF IMPURE QUANTUM CRYSTALS

Thesis for the Degree of Ph. D. MICHIGAN STATE UNIVERSITY RICHARD D. NELSON 1972



This is to certify that the

thesis entitled

Vibrational Properties of Impure

Quantum Crystals presented by

Richard D. Nelson

has been accepted towards fulfillment of the requirements for

Ph.D. degree in Physics

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ABSTRACT

VIBRATIONAL PROPERTIES OF IMPURE QUANTUM CRYSTALS

Ву

Richard D. Nelson

Quantum crystals lack well localized atomic motion making classical treatment (Born-von Karman) inapplicable. Beginning with an equation of motion for the double-time thermal Green's function for atomic displacements, we derive a Dyson equation for the imperfect quantum crystal. The self-consistent force constants are found to be determined by both the bare two particle interactions and the particle dynamics. An isotopic substitutional defect will have vibrational properties which differ from those of the host atoms and will therefore induce force constant changes. Quantum crystals are the only systems where a mass defect induces a force constant defect. The equation of motion was solved in several approximations for the induced force constant changes. The results are applied to a calculation of defect induced spin-lattice relaxation time, displacement correlation functions, specific heat, and thermal conductivity.

To complete this work theorems concerning phonon lifetimes and static distortion fields are derived in the Appendices. In calculating phonon lifetimes using displacement propagators (descriptor of lattice displacement waves) it is necessary to ascertain the relationship between the phonon propagator and the displacement propagator. This relationship is found as well as the relationship between the associated T-matrices, which are a simple way of expressing phonon lifetimes. Several derivations of phonon lifetimes are given. Lattice distortion near a defect has an important effect on the phonon scattering rate and a simple general method for calculating it is found.

VIBRATIONAL PROPERTIES OF IMPURE

QUANTUM CRYSTALS

Ву

Richard D. Nelson

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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DEDICATION

I dedicate this thesis to my wife, Leigh, for her patience with my mumblings and this physics in the first two years of our marriage.

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Sincere thanks go to Professor William M. Hartmann whose guidance and friendship cannot escape a warm citation. I wish to thank my wife, Leigh, for her fortitude in helping prepare the rough draft of the original manuscript. To Dr. S. D. Mahanti, I owe appreciation for the physics he has taught me in the last two years. Finally I wish to express gratitude to the following members of my thesis committee for consenting to criticize this work and in several cases for their frequent encouragement:

> Dr. William M. Hartmann Dr. Gerald L. Pollack Dr. Wayne W. Repko Dr. Thomas A. Kaplan

> > * * * * *

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FIGURE 1. HELIUM-THREE PHASE DIAGRAM

CHAPTER I

INTRODUCTION

Historical Review

Quantum crystal theory is a transfiguration of classical lattice dynamics in an attempt to overcome the failures of the quasi-harmonic expansion of interparticle interactions and account for the quantum mechanical behavior of the atomic motion in some crystals. For historical perspective we begin with a cursory review of the infancy of lattice dynamics followed by a proleptic discussion of more recent developments.

In <u>Principia</u> (c. 1686) Newton began the study of lattices by using a one dimensional lattice of harmonic springs to calculate the velocity of sound in air. He considered only one dimension because the three dimensional problem was insoluble; partial differential equation methods had not yet been discovered. In 1753, John and Daniel Bernoulli¹ created the idea of proper vibrations. Lagrange² (1759) supplied mathematical connection between the continuous and the discrete vibration problems. These last two developments were both heavily criticized at the time

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because the principle of superposition was disputed until Fourier's proof in 1807. That the velocity of sound depended on wavelength was discovered by Baden-Powell³ (1841) and Cauchy (1830). They both understood that the velocity at long wavelengths was a constant but their velocities at short wavelengths did not agree with experiment. The concept of group velocity was yet to be discovered. Lord Kelvin^{4,5} understood the significance of phase velocity and a maximum lattice frequency in 1881.

The first mechanical and electrical filters were conceived as a result of response properties of discrete lattices. The first mechanical filter was built by Vincent⁶ in 1898 to test the ideas of Lord Kelvin. The first electrical filter was built in 1906 by Campbell.⁷ Born (1912) derived the existence of several branches of the sound dispersion curve due to several masses in a solid, and with von Karman⁸ related the microscopic and macroscopic properties of a solid. The shortcomings of the Einstein⁹ theory of specific heat were partially rectified by Debye¹⁰ when he related the spectrum of allowed frequencies to elastic properties. Of importance to the study of defects in solids are two theorems of Lord Rayleigh.¹¹ These are applicable to the case of a single defect which differs from the host atoms in mass and/or harmonic interactions.

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- Except for frequencies at a band edge the frequency of no mode is shifted by more than the distance to the next unperturbed frequency.
- Modes at band edges may split off and enter the interband forbidden gap.

Lord Rayleigh's¹² discovery in 1885 of elastic surface waves explained at that time the violent surface waves which follow the volume waves of earthquakes and has recently had a very important practical manifestation (acoustic surface wave devices) in microelectronics.¹³

Classical lattice dynamics as formulated by Born and von Karman considers a Hamiltonian with a kinetic energy and a pairwise potential which is expanded in a Taylor series in powers of atomic displacements. The symbol R will denote unit cell positions and u will denote atomic displacements from mean atomic positions.

$$H = \sum_{\ell} \frac{P_{\ell\alpha}^{2}}{2m_{\alpha}} + \frac{1}{2} \sum_{ij} V(R_{ij} + u_{ij})$$
(1)
$$= \sum_{\ell} \frac{P_{\ell\alpha}^{2}}{2m_{\alpha}} + \frac{1}{2} \sum_{ij} (V(R_{ij}) + \frac{\partial V(R_{ij})}{\partial u_{j\alpha}} u_{j\alpha} + \sum_{\alpha\beta} u_{i\alpha} \frac{\partial^{2} V}{\partial u_{i\alpha} \delta u_{j\beta}} u_{j\beta} + \cdots$$
(2)

 $R_{ij} = R_{i} - R_{j}$ $u_{ij} = u_{i} - u_{j}$

Latin indices label unit cells in the lattice and Greek indices refer to cartesian components and different atoms in the unit cell. Double subscripts on a Latin variable denote a vector between two unit cells. As is usual in small oscillation theory only the third term in the potential is kept. The first term in the potential is an arbitrary constant, the second term is zero for a lattice in equilibrium and the third term represents the lowest order term of importance. The coupling second rank tensor between the displacements in the term quadratic in displacements is known as a force constant (ϕ). With the Hamiltonian the equations of motion for the atomic displacements can be found from Newton's second law.

$$H = \sum_{\substack{\ell \\ \alpha}} \frac{P_{\ell \alpha}^{2}}{2m_{\alpha}} + \frac{1}{2} \sum_{\substack{i \\ \alpha\beta}} u_{i\alpha} \phi_{ij} u_{j\beta}$$
(3)

$$m\dot{u}_{\ell\alpha} = -\sum_{\ell'\beta} \phi_{\ell\ell'} u_{\ell'\beta}$$
(4)

Equation 4 is a set of coupled linear differential equations. The order of this set is the same as the number of unit cells in the crystal to be considered. The solution to the above equations is made possible by the translational symmetry of the lattice which implies that the equations of motion can be diagonalized by running waves.

$$u_{l\alpha} = \sum_{\substack{k \\ \sim}} u_{\alpha}(k) e^{i(k \cdot R_{l} - \omega t)}$$
(5)

Insertion of the above into the equations of motion, Fourier transforming the time variable, and summing on unit cells leaves a simple equation with dimensions equal to three times the number of atoms in the unit cell.

$$m_{\alpha}\omega^{2}u_{\alpha}(k) = \sum_{\beta} D_{\alpha\beta}(k) u_{\beta}(k)$$
(6)

$$D_{\alpha\beta}(\mathbf{k}) = \sum \phi_{\boldsymbol{\ell}\boldsymbol{\ell}} e^{-i\mathbf{k} \cdot (\boldsymbol{\ell} - \boldsymbol{\ell}')}$$

$$\ell_{\alpha\beta}$$
(7)

D is known as the dynamical matrix. The sum in equation 7 is independent of l prime because of translational symmetry. Equation 6 is solved by equating the determinant of coefficients to zero. The dynamical matrix has eigenvectors σ which obey orthonomality and closure relations.

$$\left| D_{\alpha\beta} \left(\begin{array}{c} k \\ \end{array} \right) - m \omega^2 \delta_{\alpha\beta} \right| = 0$$
(8)

$$\sum_{\beta} \sum_{\alpha\beta} (k) \sigma_{\alpha}^{j} (k) = m \omega_{jk}^{2} \sigma_{\alpha}^{j} (k)$$
(9)

$$\Sigma \sigma_{\alpha}^{\star j}(\underline{k}) \sigma_{\alpha}^{j}(\underline{k}) = \delta_{jj}$$
(10a)

$$\sum_{j} \sigma_{\alpha}^{\star j} (k) \sigma_{\beta}^{j} (k) = \delta_{\alpha\beta}$$
(10b)

In order to effect a transformation of the Hamiltonian to quantum mechanical form, a set of normal coordinates will be found and conjugate variables will be found using Lagrange's equations.

Although the kinetic and potential energy in the harmonic Hamiltonian do not commute it is still possible to find a transformation which simultaneously diagonalizes both provided the kinetic energy is a positive definite form and the potential energy is an arbitrary quadratic form in the same number of variables.¹⁶ Moreover if both terms are in addition symmetric the eigenvalues of

$$\left|\phi - m\omega^{2}\right| = 0 \tag{11}$$

are all positive.¹⁷

The principle axis transformation is given by expanding the displacements in terms of plane waves

$$u_{\ell\alpha} = \frac{1}{\sqrt{NM_{\alpha}}} \sum_{\substack{k j \\ k j}} Q_{\underline{k}j} \sigma_{\alpha}^{j} (\underline{k}) e^{i\underline{k}\cdot\underline{R}} \ell$$
(12)

Wave vectors are labeled by k and branch indices by j.

If it were not for the mass term in the expansion the principle axis transformation would be unitary. In terms of the normal coordinates Q_{kj} the Hamiltonian becomes

$$H = \frac{1}{2} \Sigma \left(\dot{Q}_{kj}^{\star} \, \dot{Q}_{kj} + \omega_{kj}^{2} \, Q_{kj}^{\star} \, Q_{kj} \right)$$
$$= \frac{1}{2} \Sigma \left(P_{kj}^{\star} \, P_{kj} + \omega_{jk}^{2} \, Q_{kj}^{\star} \, Q_{kj} \right)$$
(13)

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using Lagrange's equation to find the conjugate momentum to the normal mode coordinate Q.

The Hamiltonian is now quantized by requiring the conjugate P and Q to satisfy commutation relations.

$$\begin{bmatrix} Q_{kj}, P_{k'j'} \end{bmatrix} = i \not k \delta_{jj'} \delta_{k,k'+G}$$
(14)

G is an arbitrary reciprocal lattice vector.

In order to obtain the second quantized form the coordinates Q are expanded directly in annihilation and creation operators.¹⁸

$$Q_{kj} = \sqrt{\frac{k}{2\omega_{jk}}} \left[a_{kj} + a_{-kj}^{\dagger}\right]$$
(15)

$$P_{kj} = -i \sqrt{\frac{\varkappa_{kj}}{2}} \left[a_{kj} - a^{\dagger}_{-kj}\right]$$
(16)

The results of using the annihilation and creation operators are listed below. Details may be found in quantum mechanics books such as the texts by Dirac or Messiah.

$$H = \sum_{\substack{k j \\ k j}} \varkappa_{\omega_{kj}} (a_{kj}^{\dagger} a_{kj} + \frac{1}{2}) = \sum_{\substack{k j \\ k j}} \varkappa_{\omega_{kj}} (N_{kj} + \frac{1}{2})$$
(17)

$$\begin{bmatrix} a_{kj}, a_{kj}^{\dagger} \end{bmatrix} = \delta_{jj}, \delta_{k}, k' + G$$
(18)

$$|n_{1}n_{2}n_{3}...n_{k}...\rangle = \frac{[(a_{1}^{\dagger})^{n_{1}} (a_{2}^{\dagger})^{n_{2}} ... (a_{k}^{\dagger})^{n_{k}} ...]}{[\sqrt{n_{1}^{\dagger}} \sqrt{n_{2}^{\dagger}} \sqrt{n_{k}^{\dagger}} ...]} |0 \ 0 ... 0 ... \rangle$$

(19)

The ket on the LHS of the last equation above represents a many phonon state with occupation numbers n_1 , n_2 , n_k , etc. and the ket on the RHS represents the many particle vacuum state.

While Lord Rayleigh¹¹ considered the problem of a single defect differing from the host particle in mass and/or harmonic interactions (point defect) the beginnings of the current analytic structure of the defect problem were contributed by Lifshitz¹⁹ in Russia and slightly later in time by Montroll^{20,21} at the University of Maryland. The method in the papers of Montroll and Lifshitz was a Green's function method for the classical equation of motion (equation 4).

$$\sum_{\beta \ell'} (m\omega^2 \delta_{\alpha\beta} \delta_{\ell'\ell} + \phi_{\ell\ell'}) G_{\ell'\ell''} = \delta_{\alpha\gamma} \delta_{\ell\ell'}$$
(20)

This Green's function is labeled G and the same symbol will be used throughout this thesis. If the atomic displacements are expanded in terms of normal mode coordinates as in equation 13, then an equation for the normal mode coordinates of the defect lattice can be found. The normal mode coordinates of the defect lattice can be used to determine the eigenfrequencies and the mean squared atomic displacements of the defect lattice. In the following set of equations chi represents the eigenvectors of the force constant matrix. Perfect crystal normal mode coordinates are labeled (k,j) and defect crystal normal modes by (f).

$$u_{l\alpha} = \sum_{\substack{kj \\ kj}} Q_{kj} \chi_{l\alpha}(kj) \qquad \text{perfect crystal} (21)$$

$$\chi_{l\alpha}(kj) = \sqrt{\frac{1}{Nm_{\alpha}}} \sigma_{\alpha}^{j}(k) e^{ik \cdot R} l$$

$$u_{l\alpha} = \sum_{f} Q_{f} \chi_{l\alpha}(f) \qquad \text{defect crystal} \quad (22)$$

$$\chi_{\ell\alpha}(f) = \sum_{\substack{\ell' \ell'' \\ \beta\gamma}} G_{\ell\ell} C_{\ell' \ell''} \chi_{\ell''\gamma}(f)$$
(23)

$$C_{\ell\ell} = -\Delta M_{\alpha}(\ell) \quad \omega^{2} \quad \delta_{\alpha\beta} \delta_{\ell\ell} + \Delta \Phi_{\ell\ell} \qquad (24)$$

det
$$|1-GC| = 0$$
 (25)

Equation 23 is the general result for the eigenvector of a differential or matrix operator having Green's function G and possessed by a perturbation C. Equation 25 follows directly from equation 23 and determines the new eigenvectors and eigenvalues.

As representative of the type of calculations performed with this classical (Newtonian equations) Green's function method we reference the work of Dawber and Elliott^{22,23} where the vibrational and optical properties of an impure crystal are studied. The difficulties with the classical Green's functions were threefold. The equations lacked a guantum mechanical foundation. The calculation of the eigenvectors was a serious numerical difficulty. And finally, there was lacking a physical interpretation of the Green's function. The first and second difficulties were resolved in the case of a harmonic Hamiltonian by Elliott and Taylor²⁴ in 1963. They use a retarded Green's function of the type described by Zubarev.²⁵

$$G_{ll}(t) = -\frac{2\pi i}{\cancel{M}} \Theta(t) < [u_{l\beta}(t), u_{l\beta}(0)] > =$$

$$\frac{2\pi}{\cancel{M}} < \langle u_{l\alpha}(t) | u_{l\beta}(0) > \rangle \qquad (26)$$

$$\langle Q \rangle = tr(e^{-\beta H}Q)/(tr e^{-\beta H})$$
, $\beta = M/kT$ (27)

Beta is the inverse temperature. Taking two time derivatives, equation 20 is rederived. The quantum mechanical foundation is buttressed by taking the time derivatives using Heisenberg's equation of motion. Needing the defect lattice eigenvectors (see equation 23) is circumvented by calculating the defect crystal Green's function by a Dyson equation

$$G = G^0 + G^0 CG$$
(28)

where matrix multiplication is implied. The calculation of mean squared displacements is simplified by a general relation between a retarded Green's function and its related correlation functions:²⁵

$$G(t-t') = -i\Theta(t-t') < [A(t),B(t')] >$$
 (29)

$$(A(t) B(t')) = \int_{\infty}^{\infty} J(\omega) e^{+\beta\omega} e^{-i\omega(t-t')} d\omega$$
 (30a)

$$\langle B(t') | A(t) \rangle = \int_{\infty}^{\infty} J(\omega) e^{-i\omega(t-t')} d\omega$$
 (30b)

$$J(\omega) = \liminf_{\epsilon \to 0} -i \frac{G(\omega + i\epsilon) - G(\omega - i\epsilon)}{e^{\beta \omega} \pm 1}$$
(31)

The minus sign is for bosons; plus is for fermions. Since we are concerned with phonons the minus sign will always be used.

The contribution of this thesis to the general framework of lattice dynamics is to derive a Green's function equation of motion for a lattice having general two body potential interactions (no harmonic approximation), to derive a set of useful formulas for lattice properties, and finally to probe the physical interpretation of the Green's function.

Quantum Crystals

Compared to the history of lattice dynamics, the active history of quantum crystals is still in its youth. The subject has been actively pursued now for about six years. In 1965 deWette and Nijboer²⁶ calculated the eigenfrequencies of solid helium and found them to be pure imaginary throughout the first Brillouin zone. Previous to this explosive catastrophe it had been known that certain crystals could not be accurately described by classical lattice dynamics but the deviations from classical behavior were considered innocuous. Quantum crystals are crystals where the zero point energy of the basis particles is comparable to the binding energy of the particle to a particular lattice site. This can be expressed using the uncertainty principle.

$$\frac{(\Delta p)^2}{2m} = \frac{3k^2}{8mD} \sim E_{\rm b}$$
(32)

The square root of D is a measure of the localization of the particle.

$$\sqrt{D} = 10^{-8}$$
 cm. atomic solids
= 10^{-13} cm. nuclear solids

As a consequence of large zero point energy the particles are not well spatially localized.

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One of the few evidences of a nucleon solid is the star quakes of neutron stars. These quakes or sudden changes in rotational velocity have been interpreted as the cracking of a rigid surface of the star.

The degree of nonclassical behavior of the atomic motion in a solid has been historically labelled by a parameter lambda. Lambda had its genesis in attempts to write reduced equations of state for solids which would allow all solids to be described by a single universal function.²⁷ In terms of the Schroedinger equation for a solid written in reduced variables, lambda is the coefficient of the atomic kinetic energy.²⁸ Because lambda is usually small the atomic kinetic energy is neglectable. Lambda is defined in terms of the atomic mass and interaction parameters.

$$\Lambda = \frac{\not M}{\sqrt{m\epsilon}\sigma} \qquad V(r) = \epsilon f(r/\sigma) \qquad (33)$$

Epsilon is the interaction strength (well depth) and sigma is the value of the interatomic distance for which the two particle potential is zero. For the rare gas solids a Leonard-Jones potential is often used.

$$V_{LJ} = -4\varepsilon \left[\left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r}\right)^{12} \right]$$

Note that lambda can be approximately interpreted as the ratio of de Broglie wavelength to diameter of a basis atom.

A measure of localization is implied. Some values of lambda are displayed in Table 1. For values of lambda less than one-half, classical dynamics has proved applicable with good results. In the case of neon quantum corrections amount to several percent.²⁹ Neon is then a quantum crystal or at least quasi-quantum. The value for a neutron solid was calculated by averaging the Hamada-Johnson singlet and triplet s=0 central potential for two nucleons. The values for the rare gas solids were taken from Cook.³⁰

To have an idea of what the potential seen by a helium atom is in the proximity of its lattice site, we have calculated this potential due to two shells of nearest neighbors interacting via a Leonard-Jones potential. The result is in Figure 2. The abscissa is the displacement from the lattice site in the (100) direction of a BCC lattice. The curvature at the origin indicates the cause of the imaginary eigenfrequencies of de Wette and Nijboer. Clearly the classical quasiharmonic expansion makes no sense here. The use of the harmonic expansion should also be questioned for several additional reasons.

- The root mean square displacement of the atoms can be as much as one-third of the interparticle distance. The harmonic expansion is essentially a power series in u/R. In quantum crystals this is not a small expansion parameter.
- A Taylor series for an inverse power series converges slowly.

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Solid	ε/k _B (Κ)	σ (Å)	۸*
Xe	221	4.10	.063
Kr	171	3.60	.102
° ₂	118	3.58	.198
A	120	3.41	.186
^N 2	95	3.70	.230
Ne	35.5	2.75	. 593
^H 2	37.0	2.93	1.73
⁴ He	10.2	2.56	2.68
³ He	10.2	2.56	3.08
NUCLEON	750 MeV	.5 f	.950

POTENTIAL PARAMETERS FOR SOLIDS

TABLE 1



FIGURE 2. HELIUM LATTICE POTENTIAL (BCC PHASE)

$$V(R+u) = \left(\frac{\sigma}{R+u}\right)^{m} = \sum_{n=0}^{\infty} V_{n} \left(\frac{u}{\sigma}\right)^{n}$$
$$\frac{V_{n+1}}{V_{n}} = -\frac{m+n}{n+1} \left(\frac{\sigma}{R}\right)$$
$$\lim \frac{V_{n+1}}{V_{n}} = -\frac{\sigma}{R}$$

Both of these difficulties are overcome by not making the Taylor expansion at all but by averaging the potential over the two particle distribution function. The average of the Taylor expansion keeping all even order derivatives will be shown to be equivalent to using a gaussian distribution function.

Nosanow³¹ has done a variational treatment of solid helium. He finds values of the solid energy which are too large (in fact greater than zero). However, his values of pressure and compressibility agree with experiment to within ten percent. More will be said about Nosanow's procedures when we calculate force constants.

There are now a number of reasons motivating the study of isotopic defects in solid helium.

Experimental motivation:

1. There is a large enhancement of the longitudinal spin-lattice relaxation time in ³He provided by only a small addition of ⁴He defects. The experiments of Gifford and Hatton³² find at T = .425 K and specific

volume = 20 cc/mole τ^{-1} = .004 + 10³x = .004 (1 + 2.5 X 10⁵x) sec⁻¹. Tau is the relaxation time constant and x the defect concentration.

- 2. Thermal conductivity remains unexplained by a mass defect theory. This topic is further complicated by lack of agreement between different experimentalists. A chart of experimental results is included in the discussion of thermal conductivity.
- 3. Mixtures of helium isotopes undergo phase separation below a critical temperature. Phase separation has been studied experimentally by Edwards, McWilliams, and Daunt^{33,34} and theoretically by Mullins.³⁵ Phase separation in solid helium mixtures may be of further interest because it is perhaps the only solid to undergo phase separation in laboratory times.

Theoretical motivation:

1. Phonons exist. The elementary excitations of a harmonic crystal with translational invariance are phonons. Solid helium lacks both of these criteria because of isotopic disorder and anharmonicity. However, phonons are still observed experimentally. Harmonicity is salvaged by use of an effective two particle interaction in the solid which is related to the free two particle potential. This was first demonstrated by Nosanow.³¹ In the case of defects the phonon lifetime can be related to the imaginary part of the phonon self energy.

- 2. A quantum crystal is the only system where an isotopic defect induces a force constant defect. The interparticle interactions will be determined by the particle dynamics. Changing the dynamics with a mass defect will change the interparticle interactions, to wit, the interparticle force constants.
- 3. In a classical crystal a mass defect changes the density of vibrational states and consequently the vibrational specific heat. In a quantum crystal the aforementioned force constant change will compensate for the mass change. The degree of this compensation is discussed later.

CHAPTER II

THEORETICAL DEVELOPMENT

Derivation of Equation of Motion

This thesis is an attempt to deduce the collective behavior of quantum crystals by a Green's function technique. As is well known,³⁶ the poles of the Green's function yield the excitation spectrum (viz. phonons) and the Green's function itself is a linear response function. It will be later shown that the density of states is proportional to the trace of the product of a mass matrix and the Green's function and also that the defect crystal Green's function contains the phonon scattering rates. From the density of states all of the thermodynamic properties may be readily calculated. The displacement double-time Green's function is defined as:

$$G_{ll}(t) = -\frac{2\pi i}{\not k} \Theta(t) < [u_{l\alpha}(t), u_{l\beta}(0)] > \equiv$$

$$< u_{l\alpha}(t) | u_{l\beta}(0) > > \qquad (34)$$

$$\Theta(t) = \begin{cases} 1 & t > 0 \\ 0 & t < 0 \end{cases}$$

$$[A,B] = AB-BA$$

$$\langle Q \rangle = tr (e^{-\beta H}Q) / (tr e^{-\beta H}) \qquad (35)$$

$$\beta = \not{M} / kT$$

Beta is the inverse temperature. The retarded Green's function has the previously mentioned properties (equation 29) which allows the calculation of displacement auto and cross correlations. We now specialize to the case of one particle per unit cell. The Hamiltonian to be used assumes pair-wise interactions and we shall remove into an operator form the particle dynamics by using Taylor's expansion.

$$H = \sum_{\ell \alpha} \frac{P_{\ell \alpha}^{2}}{2m_{\ell}} + \frac{1}{2} \sum_{ij} V(\mathbf{R}_{ij} + \mathbf{u}_{ij})$$
(36)

$$= \sum_{\ell\alpha} \frac{P_{\ell\alpha}^{2}}{2m_{\ell}} + \frac{1}{2} \sum_{ij} e^{u}_{ij} V(R_{ij})$$
(37)

The gradient operator is defined to operate on lattice coordinates only. Using Heisenberg's equation of motion we take two time derivatives of the Green's function.

$$G_{\underline{\ell}\underline{\ell}} = \frac{1}{\underline{i}\underline{M}} << [u_{\underline{\ell}\alpha}(t), H] \quad u_{\underline{\ell}} = (0) >>$$
(38)

$$= \langle \langle \frac{P_{\ell\alpha}(t)}{m_{\ell}} | u_{\ell'\beta}(0) \rangle \rangle$$
(39)

$$m_{\ell} \tilde{G}_{\ell \ell} = - \frac{2\pi i}{\not M} \delta(t) < [P_{\ell \alpha}(t), u_{\ell'\beta}(0)] > + \frac{1}{i \not M} < [P_{\ell \alpha}(t), H] | u_{\ell'\beta}(0) >>$$
(40)

$$\dot{\mathbf{P}}_{\boldsymbol{\ell}\alpha} = \frac{1}{\mathbf{i}\mathbf{k}} \frac{1}{2} \sum_{ij}^{c} [\mathbf{P}_{\boldsymbol{\ell}\alpha}, \mathbf{e}^{\mathbf{u}_{ij}\cdot\nabla_{ij}}] \mathbf{V}(\mathbf{R}_{ij})$$

$$= \frac{1}{2\mathbf{i}\mathbf{k}} \sum_{ij}^{c} \sum_{n=1}^{\infty} [\mathbf{P}_{\boldsymbol{\ell}\alpha}, \mathbf{u}_{ij}\cdot\nabla_{ij}] \frac{(\mathbf{u}_{ij}\cdot\nabla_{ij})^{n-1}}{(n-1)!} \mathbf{V}(\mathbf{R}_{ij})$$

$$= -\frac{1}{2} \sum_{ij}^{c} (\delta_{\boldsymbol{\ell}i} - \delta_{\boldsymbol{\ell}j}) \mathbf{e}^{\mathbf{u}_{ij}\cdot\nabla_{ij}} \nabla_{ij}^{\alpha} \mathbf{V}(\mathbf{R}_{ij})$$

$$= -\sum_{j}^{c} \mathbf{e}^{\mathbf{u}_{\boldsymbol{\ell}j}\cdot\nabla_{\boldsymbol{\ell}j}} \nabla_{\boldsymbol{\ell}j}^{\alpha} \nabla(\mathbf{R}_{\boldsymbol{\ell}j}) \qquad (41)$$

$$m_{\ell} \ddot{G}_{\ell \ell}, (t) = -2\pi\delta(t) \delta_{\ell \ell}, \delta_{\alpha\beta} - \alpha\beta$$

$$\sum_{j}^{\nu} \langle e^{u_{\ell j}}(t) \cdot \nabla_{\ell j} | u_{\ell'\beta}(0) \rangle \langle \nabla_{\ell j} \nabla_{\ell j} \nabla_{\ell j} \nabla_{\ell j} \rangle$$

$$(42)$$

The RHS of the last equation contains a higher order Green's function. Shortly this will be reduced to a new quasi-harmonic series, but first some preliminary theorems are needed.

Commutator Theorems

The proofs can be found in Appendix A. A, B, and x will be general operators (which are distributive, associative, but not commutative) and we define:

$$A = A_0; A_1 = [x, A]; A_2 = [x, [x, A]]; A_{n+1} = [x, A_n]$$

$$\binom{n}{k} \equiv \frac{n!}{k! (n-k)!}$$

Theorem 1

$$A_{n} = \sum_{k=0}^{n} {n \choose k} (-1)^{k} x^{n-k} A x^{k}$$

Theorem 2

$$A \mathbf{x}^{n} = \sum_{k=0}^{n} {n \choose k} (-1)^{k} \mathbf{x}^{n-k} A_{k}$$

Theorem 3

$$[e^{\mathbf{x}}, \mathbf{A}] = -e^{\mathbf{x}} \sum_{p=1}^{\infty} \frac{(-1)^{p}}{p!} \mathbf{A}_{p}$$

Theorem 4 If [H,A] = 0, $H(t) = e^{ixt} He^{-ixt}$ then

$$[H(t),A] = -4H(t) \sum_{p=1}^{\infty} \frac{(it)^p}{p!} A_{2p}$$

Theorem 5 If $e^x e^y = e^z$ then

$$z = x + y + \sum_{p=1}^{\infty} a_p y_p + \sum_{p,q=1}^{\infty} a_{pq} (y_p)_q + p_{q=1}$$

 $\sum_{p,q,r=1}^{\infty} a_{pqr} ((y_p)_q)_r + \dots,$

where a and a ... are defined in Appendix A.

Theorem 6

If we define a symmetry ordering operator S such that

$$S(yx^{n}) = \sum_{\alpha=0}^{n} x^{\alpha}yx^{n-\alpha}$$

then

$$y_{p}x^{n} + xS(y_{p}x^{n-1}) = S(x^{n}y_{p})$$

Theorem 7

The difference in the ordering of the product of two operators is given by the symmetry ordering operator.

$$y_{p}x^{n} - x^{n}y_{p} = -S(y_{p+1}x^{n-1})$$

Theorem 8

$$e^{\mathbf{x}} \mathbf{y} = \frac{\partial}{\partial \mathbf{x}} e^{\mathbf{x} + \lambda \mathbf{z} \mid}_{\lambda=0}$$

where

$$z = y + a_1 y_1 + a_2 y_2 + \dots$$

= $\sum_{j=0}^{\infty} a_j y_j$.

The higher order Green's function in equation 42 can now be written as a series of lower order functions using Theorem 3.

$$\begin{bmatrix} e^{u_{\ell_j}(t) \cdot \nabla_{\ell_j}}, u_{\ell_j} \end{bmatrix} = -e^{u_{\ell_j}(t) \cdot \nabla_{\ell_j}} \sum_{p=1}^{\infty} \frac{(-1)^p}{p!} (u_{\ell_j})_p$$
(43)

$$(\underbrace{\mathbf{u}}_{\ell},)_{1} = [\underbrace{\mathbf{u}}_{\ell} \underbrace{\mathbf{v}}_{j} \cdot \nabla, \underbrace{\mathbf{u}}_{\ell},] \qquad (\underbrace{\mathbf{u}}_{\ell},)_{n} = [\underbrace{\mathbf{u}}_{\ell} \underbrace{\mathbf{v}}_{j} \cdot \nabla, (\underbrace{\mathbf{u}}_{\ell},)_{n-1}]$$

The term p=1 corresponds to the original Green's function. The average of the above commutators is now done using a cumulant expansion^{37,38} which is defined by

$$\langle e^{xt} \rangle_{x} = \exp \{ \Sigma \frac{t^{n}}{n!} K_{n} \}$$

 $K_{1} = \langle x \rangle$
 $K_{2} = \langle x^{2} \rangle - \langle x \rangle^{2}$
 $K_{3} = \langle x^{3} \rangle - 3 \langle x \rangle \langle x^{2} \rangle + 2 \langle x \rangle^{3}$
?or •

. :e + !

1

For simplicity we redefine variables in equation 43.

 $-\langle [e^{\underbrace{\mathbf{u}}_{\ell} \mathbf{j}^{* \nabla}}, \underbrace{\mathbf{u}}_{\ell},] \rangle \equiv + \langle e^{\mathbf{x}} \mathbf{y} \rangle$ $= \frac{\partial}{\partial \lambda} \langle e^{\mathbf{x}} e^{\lambda \underbrace{\mathbf{y}}} \rangle|_{\lambda=0}$ $= \frac{\partial}{\partial \lambda} \langle e^{\underbrace{\mathbf{x}} + \lambda \underbrace{\mathbf{y}} + \lambda \underbrace{\sum}_{j=1}^{\infty} a_{j} \underbrace{\mathbf{y}}_{j} j}_{\lambda=0} \rangle|_{\lambda=0}$

$$= \langle e^{\mathbf{X}} \rangle \sum_{\substack{p=2 \\ p=2}}^{\infty} \frac{\frac{Z_p}{p!}}{p!} + \sum_{\substack{p=1 \\ q=0}}^{\infty} \frac{(-1)^p}{p!} a_q(\underbrace{u_{\ell'}}_{p\ell'})_{p+q}$$
(45)

The coefficients a are defined in theorem 8 (Appendix A). Note because of the evaluation at $\lambda=0$ only terms linear in y survive. Z_n contains the terms of the $n\frac{th}{dt}$ cumulant function which are linear in y.

The equation of motion becomes:

$$\underset{\alpha\beta}{\overset{..}{\mathfrak{G}}} (t) = -2\pi \ \delta(t) \ \delta_{\ell\ell}, \delta_{\alpha\beta} - \sum_{j} \overset{u}{\overset{l}{\mathfrak{f}}} \frac{1}{2} \overset{\nabla}{\overset{\nabla}{\mathfrak{f}}} \{ \sum_{p=2}^{\infty} \langle Z_p \rangle \rangle_{\alpha} + \frac{1}{2}$$

$$\sum_{\substack{p=1\\q=0}}^{\infty} \frac{(-1)^p}{p!} a_q^{<<} (u_{\ell},)_{\alpha p+q}^{>>} \nabla_{\beta} V_{j\ell}$$
(46)

$$\langle Z_n \rangle = -i\Theta(t) \langle Z_n \rangle$$

The term p+q=2 represents cubic anharmonicity. The term p+q=n-1 represents $n\frac{th}{t}$ order anharmonicity.

We now keep only the term p=1, q=0, the first two cumulants of the exponential average, and Fourier transform the result.

$$-\omega^{2} m_{\ell} G_{\ell \ell}^{(\omega)} = -\delta_{\ell \ell}, \delta_{\alpha\beta} - \sum_{j\alpha} e^{A_{\ell j} \cdot \nabla + D_{\ell j} \cdot \nabla \nabla} \nabla_{\ell j}^{\alpha} \nabla_{\ell j}^{\gamma} \nabla_{\ell j}^{\gamma} V_{\ell j} G_{j\ell},$$

$$+ \sum_{j\ell} e^{A_{\ell j} \cdot \nabla + D_{\ell j} \cdot \nabla \nabla} \nabla_{\ell j}^{\alpha} \nabla_{\ell j}^{\gamma} \nabla_{\ell j}^{\gamma} V_{\ell j} G_{\ell \ell}, \qquad (47)$$

Besides being an exact approach the calculational methods derived here have the advantage that they are good for finite temperatures and also include long-range order. Nosanow's variational theory suffers in all these respects.

$$\vec{A}_{lj} = \langle \vec{u}_{lj} \rangle$$
(48)

$$D_{lj} = \frac{1}{2} \{ \langle u_{l\alpha} \ u_{l\beta} \rangle + \langle u_{j\alpha} \ u_{j\beta} \rangle - \langle u_{l\alpha} \ u_{j\beta} \rangle - \langle u_{j\alpha} \ u_{l\beta} \rangle \}$$
(49)

$$-\langle \mathbf{u}_{l\alpha} \rangle \langle \mathbf{u}_{l\beta} \rangle - \langle \mathbf{u}_{j\alpha} \rangle \langle \mathbf{u}_{j\beta} \rangle + \langle \mathbf{u}_{j\alpha} \rangle \langle \mathbf{u}_{l\beta} \rangle + \langle \mathbf{u}_{l\alpha} \rangle \langle \mathbf{u}_{j\beta} \rangle \}$$

The vector A represents the mean displacement of an atom from its lattice site. In the pure crystal this should be zero. If not it can be made zero, because of translation symmetry, by a translation or uniform dilation of the lattice coordinates. A strain field corresponding to nonzero A can accompany a substitutional defect. This is considered in more detail in Appendix B. The bilinear terms in D are determined from the Green's function.

$$\langle \mathbf{u}_{\boldsymbol{l}\alpha}\mathbf{u}_{\boldsymbol{j}\beta} \rangle = \liminf_{\delta \to 0} \frac{\mathbf{i} \not{\boldsymbol{l}}}{2\pi} \int_{-\infty}^{\infty} \frac{1}{e^{\beta \omega} - \mathbf{l}_{\boldsymbol{\ell}}} \begin{bmatrix} G_{\boldsymbol{l}\boldsymbol{j}}(\omega + \mathbf{i}\delta) & -G_{\boldsymbol{l}\boldsymbol{j}}(\omega - \mathbf{i}\delta) \end{bmatrix} d\omega$$
$$= \liminf_{\delta \to 0} \frac{2 \not{\boldsymbol{l}}}{2\pi} \operatorname{Im} \int_{-\infty}^{\infty} \operatorname{coth} \left(\frac{\beta \omega}{2}\right) G_{\boldsymbol{l}\boldsymbol{j}}(\omega + \mathbf{i}\delta) d\omega$$
(50)

In matrix notation the equation of motion becomes

$$+m\omega^2 G = 1 + \Phi G \tag{51}$$

$$G = (m\omega^2 \underline{1} - \Phi)^{-1}$$
 (52)

Force Constants

The Green's function matrix G, unit matrix \underline{l} , and force constant matrix phi have dimensions 3N, where N is the number of lattice sites. If the exponential operator in the force constant expression (equation 47) is neglected the classical harmonic force constant remains. The present result is more clearly understood by Fourier transforming to an integral operator.

$$\Phi_{\mu\mu}, = e^{\mathbf{A} \cdot \nabla + \underline{\mathbf{D}} : \nabla \nabla} \nabla^{\alpha} \nabla^{\beta} \mathbf{V}(\mathbf{R}_{\mu\mu},)$$

$$= \frac{1}{(2\pi)^{3}} \int_{-\infty}^{\infty} d^{3} \mathbf{q} e^{i\underline{\mathbf{Q}} \cdot \mathbf{R}_{\mu\mu}} \int_{-\infty}^{\infty} e^{-i\underline{\mathbf{Q}} \cdot \mathbf{R}} d^{3} \mathbf{R} e^{-\underline{\mathbf{Q}} \cdot \underline{\mathbf{D}} \cdot \underline{\mathbf{Q}}} e^{-\mathbf{A}_{\mu\mu}} \cdot \frac{\mathbf{Q}}{2} \nabla^{\alpha} \nabla^{\beta} \mathbf{V}(\mathbf{R})$$

$$= \frac{1}{(2\pi)^{3}} \int_{-\infty}^{\infty} d^{3} \mathbf{R} \nabla^{\alpha} \nabla^{\beta} \mathbf{V}(\mathbf{R}) \int_{-\infty}^{\infty} d^{3} \mathbf{q} e^{-\underline{\mathbf{Q}} \cdot (\mathbf{R}_{\mu\mu}, -\mathbf{R} - \mathbf{A})} e^{-\underline{\mathbf{Q}} \cdot \underline{\mathbf{D}}_{\mu\mu}} e^{-\underline{\mathbf{Q}} \cdot \underline{\mathbf{D}}_{\mu\mu}} \cdot \underline{\mathbf{Q}}$$

$$= \frac{1}{(2\pi)^{3}} \int_{-\infty}^{\infty} d^{3} \mathbf{R} \nabla^{\alpha} \nabla^{\beta} \mathbf{V}(\mathbf{R}) \int_{-\infty}^{\infty} d^{3} \mathbf{q} e^{-\underline{\mathbf{Q}} \cdot (\mathbf{R}_{\mu\mu}, -\mathbf{R} - \mathbf{A})} e^{-\underline{\mathbf{Q}} \cdot \underline{\mathbf{D}}_{\mu\mu}} \cdot \underline{\mathbf{Q}}$$

$$= \frac{1}{(2\pi)^{3}} \int_{-\infty}^{\infty} d^{3} \mathbf{R} \nabla^{\alpha} \nabla^{\beta} \mathbf{V}(\mathbf{R}) \int_{-\infty}^{\infty} d^{3} \mathbf{q} e^{-\underline{\mathbf{Q}} \cdot (\mathbf{R}_{\mu\mu}, -\mathbf{R} - \mathbf{A})} e^{-\underline{\mathbf{Q}} \cdot \underline{\mathbf{D}}_{\mu\mu}} \cdot \underline{\mathbf{Q}}$$

$$= \frac{1}{(2\pi)^{3}} \int_{-\infty}^{\infty} d^{3} \mathbf{R} \nabla^{\alpha} \nabla^{\beta} \mathbf{V}(\mathbf{R}) \int_{-\infty}^{\infty} d^{3} \mathbf{q} e^{-\underline{\mathbf{Q}} \cdot (\mathbf{R}_{\mu\mu}, -\mathbf{R} - \mathbf{A})} e^{-\underline{\mathbf{Q}} \cdot \underline{\mathbf{D}}_{\mu\mu}} \cdot \underline{\mathbf{Q}}$$

$$= \frac{1}{\sqrt{(2\pi)^3 |\underline{D}|}} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell}} \cdot (\underline{u}-\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell}} \cdot (\underline{A}) / 4} \int_{-\infty}^{\infty} d^3 u e^{-(\underline{u}-\underline{A}) \cdot \underline{D}_{\ell}} \cdot (\underline{A}) \cdot \underline{A} - \underline{A}$$

The new force constants are just a spatial average of the old ones. If the mean square displacements of the particles go to zero, D goes to zero and the exponential becomes a delta function. In this limit of stationary particles the classical result is again obtained. The introduction of a force constant change by a mass defect can now be understood as a change in gaussian width D.

$$\delta \Phi \left(\stackrel{\mathbf{R}}{\underset{\mathcal{L}}{\mathcal{L}}} \right) = \Phi - \Phi_{\mathbf{O}} = e^{\nabla \cdot \mathbf{D}^{*} \cdot \nabla} \quad \nabla \nabla \mathbf{V} - e^{\nabla \cdot \mathbf{D} \cdot \nabla} \quad \nabla \nabla \mathbf{V}$$

$$= (e^{\nabla \cdot \delta \mathbf{D}} \cdot \nabla - 1) e^{\nabla \cdot \mathbf{D} \cdot \nabla} \quad \nabla \nabla \mathbf{V}$$

$$= (e^{\nabla \cdot \delta \mathbf{D}} \cdot \nabla - 1) \Phi_{\mathbf{O}} \left(\stackrel{\mathbf{R}}{\underset{\mathcal{L}}{\mathcal{L}}} \right)$$

$$= \{ \frac{1}{\sqrt{(2\pi)^{3} |\delta \mathbf{D}|}} \int_{-\infty}^{\infty} d^{3}u e^{\frac{u' \cdot \delta \mathbf{D}}{\mathcal{L}}} \cdot \frac{u' / 4}{\sqrt{2\pi} + \frac{u'}{2}} - \Phi_{\mathbf{O}} \left(\stackrel{\mathbf{R}}{\underset{\mathcal{L}}{\mathcal{L}}} \right) \right)$$

$$= u - \delta \mathbf{A}$$
(55)

If the change in width δD tends to zero, the gaussian becomes a delta function and the change in force constant disappears.

While the spatial density function for a harmonic oscillator is a gaussian (see Appendix C) the two particle density function for quantum crystals cannot be quite gaussian because of short-range correlations which might arise as a result of a hard core interaction or of fermi statistics. For solid helium the hard-core interaction is responsible for short-range correlations (SRC). For the shortrange correlation function we may either develop the above formalism further (SRC should exist in the neglected terms of the equation of motion) or assume a phenomenological form used by Nosanow. Our objective is to study defect properties; we have therefore done the latter. Nosanow's idea is to use two particle wavefunctions of the form

$$\Psi(\mathbf{R}_{ij}, \mathbf{u}_{ij}) = \Phi_{i} \begin{pmatrix} \mathbf{R}_{i} + \mathbf{u}_{i} \end{pmatrix} \Phi_{j} \begin{pmatrix} \mathbf{R}_{j} + \mathbf{u}_{j} \end{pmatrix} f_{ij} \begin{pmatrix} \mathbf{R}_{ij} + \mathbf{u}_{ij} \end{pmatrix}$$

$$f_{ij} = e^{-KV \begin{pmatrix} \mathbf{R}_{ij} + \mathbf{u}_{ij} \end{pmatrix}}$$
(56)

where Φ is a single particle wavefunction and f_{ij} is the short-range correlation. The product of the single particle gaussians is a result similar to ours (equation 54) except our gaussian width contains long-range correlation effects in addition to single particle effects. Nosanow determined parameter K and the gaussian width by minimizing the total crystal energy. He found K to be the same for many molar volumes and for both isotopes. We therefore accept K as a constant and determine the gaussian width $(D_{\alpha\beta})$ by selfconsistency in equations. Jackson and Feenberg³⁹ have shown how to absorb the SRC effects into an effective potential so that the many-body wavefunction can be approximated by a product of single particle gaussians. This product of gaussians then reduces to our earlier result for the two particle density function in equation 54. The effective interatomic potential becomes³¹

$$V(r) = f^{2}(r) [V(r) - \frac{M^{2}}{2m} \nabla^{2} \ln f(r)]$$
 (57)

The second term is a correlation to the kinetic energy. From equation 52 it is evident that diagonalizing the Green's function is equivalent to diagonalizing the force constant matrix because a unitary transformation which diagonalizes a matrix also diagonalizes its inverse. In the perfect crystal case where translation symmetry exists the force constant matrix can be inverted by the plane wave transformation

$$S = (Nm)^{-\frac{1}{2}} \sigma_{\alpha}^{j}(q) e^{iq \cdot \ell}$$

where sigma is an eigenvector of the dynamical matrix. Different branches of the phonon spectrum are distinguished by index j.

$$\underline{D}_{\alpha\beta}(\underline{q}) \equiv \frac{1}{Nm} \sum_{\substack{\ell \ \ell \\ \kappa \ \kappa}} \Phi_{\ell \ \ell}, \ e^{i\underline{q} \cdot (\ell - \ell')}$$
(58)

$$= \frac{1}{m} \sum_{\substack{\ell=\ell, \\ \kappa=\ell}} \Phi_{\ell\ell}, e^{iq \cdot (\ell-\ell')}$$
(59)

$$\sum_{\beta} \underline{D}_{\alpha\beta}(\underline{q}) \sigma_{\beta}^{j}(\underline{q}) = \omega_{j\underline{q}}^{2} \sigma_{\alpha}^{j}(\underline{q})$$
(60)

$$\sum_{\substack{\ell \\ \ell \\ \alpha\beta}} S_{kj}^{\ell\alpha} \Phi_{\ell}, S_{k}^{\ell'\beta} = \delta_{kk}, \delta_{jj} \Phi_{jk}^{\ell'\beta}$$

Applying the transformation S to the pure crystal Green's function we find

$$G_{kk'} = \sum_{\substack{\ell \ell \\ jj'}} S_{kj}^{\ell\alpha} G_{\ell\ell}^{0} S_{k'j'}^{\ell'\beta} = \frac{\delta_{jj'} \delta_{kk'}}{\omega^2 - \omega_{kj}^2}$$
(61)

The equation of motion can be completed by considering the case of mass and force constant defects in the lattice. Epsilon will denote the negative of the fractional mass change.

$$[m+(m'-m)] \quad \omega^{2}G = 1+(\Phi+\delta\Phi)G$$

$$\varepsilon = (m-m')/m$$

$$(m\omega^{2}-\Phi)G = 1 + [\delta\Phi+m\varepsilon\omega^{2}]G$$

$$= 1 + CG \qquad (62)$$

The matrix C contains all defect information. Multiplying on the left by the perfect crystal Green's function gives a Dyson form and a T-matrix form of the above equation

$$G = G_{O} + G_{O}CG$$
(63)

$$G = G_{O} + G_{O}TG_{O}$$
 $T = C(1-G_{O}C)^{-1}$ (64)

If the above can be solved all of the phonon properties of the imperfect crystal will be known within our selfconsistent approximation.

CHAPTER III

APPLICATIONS

Pure Crystal Properties

Before beginning the calculation of defect properties our formalism should be tested by a calculation of perfect crystal properties. We calculate some Debye temperatures and later some phonon dispersion curves.

The Debye temperatures are determined by equating the mean square lattice frequency calculated in a force constant model with the same quantity in the Debye model. A calculation of Debye temperature has also been done by de Wette, Nosanow, and Werthamer.⁴⁰ Their calculation used Nosanow's variational parameters which were found by minimizing the ground state energy. Our self-consistent calculation is compared for reasonableness with experiment and Nosanow's results in Table 2.

$$\langle \omega^2 \rangle = \frac{1}{3N} \sum_{k} \omega_{k}^2$$

= $\frac{3}{5} \omega_{D}^2$ Debye model

$$= \frac{1}{3N} \sum_{\substack{q \\ q \\ \chi \alpha}} \sum_{\substack{\ell \alpha \\ \ell \alpha}} (1 - e^{iq \cdot \ell}) \frac{\int_{\alpha \alpha}^{\Phi_{0}}}{m} \text{ force constant model}$$

We use the following definitions:

- 1. $N(\lambda)$ is the number of lattice sites in shell λ .
- 2. The volume per mole of a crystal is V.

3.
$$\mathbf{x}_{\lambda} = q_{\max} R_{\lambda} = (6\pi^2/V)^{1/3} R_{\lambda}$$

- 4. The $n \frac{th}{dt}$ spherical Bessel function is j_n .
- 5. The average of the force constants linking the $\lambda \frac{\text{th}}{\lambda}$ shell of atoms to the origin is $\Phi_{\alpha\alpha}(\lambda)$.

$$\omega_{\rm D}^2 = \frac{5}{3m} \sum_{\lambda\alpha} \Phi_{\alpha\alpha}(\lambda) N(\lambda) \quad (\frac{1}{3} - \frac{j_1(x_{\lambda})}{x_{\lambda}})$$
(65)

$$\Phi_{\alpha\alpha}(\lambda) = \frac{1}{N(\lambda)} \sum_{\substack{\ell \Rightarrow \lambda \\ \alpha\alpha}} \Phi_{0}_{\ell}$$

On the following pages are some phonon dispersion curves calculated using equation 60. The upper curves are longitudinal modes and the lower curves (often degenerate in these symmetry directions) are the two transverse modes for B.C.C. helium three. The purpose of their presentation is to show that the self-consistent harmonic approximation produces normal innocuous phonons, in contrast to the unstable modes with imaginary energies found by Nijboer and de Wette. Figure 5 shows the real and imaginary parts of the perfect crystal displacement Green's function. TABLE 2

³ HE
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PERFECT

Specific Volume	NN Distance	Theta (exp)	Theta (Nelson)	Theta (Nosanow)	Dol αα (Nelson)	Dol αα (Nosanow)
24.49 cc/mole	3.75 Å	17.5 K	25.7 K	25.6 K	.395 å ²	.385 Å ²
22.58	3.65	21.3	28.2	28.8	.361	.352
20.77	3.55	27.8	30.2	32.5	.331	.324
19.91	3.50	28.2	31.9	ł	.318	ł
19.07	3.45	ł	33.1	36.9	.306	.304



FIGURE 3. PHONON DISPERSION FOR HELIUM-THREE (Molar Volume 24.5 (cm³)





Defect Calculation

The second derivative of the potential can be conveniently written in terms of derivatives with respect to the interparticle distance. For completeness higher derivatives are also listed.

$$\begin{split} \nabla^{\alpha} \nabla(\mathbf{r}) &= \frac{\mathbf{r}_{\alpha}}{\mathbf{r}} \nabla^{(1)} \\ \nabla^{\alpha}_{\mathbf{r}} \nabla^{\beta}_{\mathbf{r}} \nabla(\mathbf{r}) &= \frac{\mathbf{r}_{\alpha} \mathbf{r}_{\beta}}{\mathbf{r}^{2}} (\nabla^{(2)} - \frac{\nabla^{(1)}}{\mathbf{r}}) + \delta_{\alpha\beta} \frac{\nabla^{(1)}}{\mathbf{r}} \\ &= \frac{\mathbf{r}_{\alpha} \mathbf{r}_{\beta}}{\mathbf{r}^{2}} (\mathbf{R} - \tau) + \delta_{\alpha\beta} \tau \\ \nabla^{\alpha} \nabla^{\beta} \nabla^{\lambda} \nabla(\mathbf{r}) &= \frac{\mathbf{r}_{\alpha} \mathbf{r}_{\beta} \mathbf{r}_{\lambda}}{\mathbf{r}^{3}} [\nabla^{(3)} - \frac{3}{\mathbf{r}} \nabla^{(2)} + \frac{3}{\mathbf{r}^{2}} \nabla^{(3)}] \\ &+ (\delta_{\alpha\beta} \frac{\mathbf{r}}{\mathbf{r}^{2}} + \delta_{\beta\lambda} \frac{\mathbf{r}}{\mathbf{r}^{2}} + \delta_{\alpha\lambda} \frac{\mathbf{r}}{\mathbf{r}^{2}}) (\nabla^{(2)} - \frac{1}{\mathbf{r}} \nabla^{(1)}) \\ \nabla^{\alpha} \nabla^{\beta} \nabla^{\lambda} \nabla^{\partial} \nabla(\mathbf{r}) &= \frac{\mathbf{r}_{\alpha} \mathbf{r}_{\beta} \mathbf{r}_{\lambda} \mathbf{r}_{\partial}}{\mathbf{r}^{4}} [\nabla^{(4)} - \frac{6}{\mathbf{r}} \nabla^{(3)} + \frac{15}{\mathbf{r}^{2}} \nabla^{(2)} - \frac{15}{\mathbf{r}^{3}} \nabla^{(1)}] \\ &+ (\mathbf{r}_{\alpha} \mathbf{r}_{\beta} \delta_{\lambda\partial} + \mathbf{r}_{\beta} \mathbf{r}_{\lambda} \delta_{\partial\alpha} + \mathbf{r}_{\alpha} \mathbf{r}_{\lambda} \delta_{\beta\partial} + \mathbf{r}_{\alpha} \mathbf{r}_{\partial} \delta_{\beta\lambda} + \mathbf{r}_{\beta} \mathbf{r}_{\partial} \delta_{\alpha\lambda} + \mathbf{r}_{\lambda} \mathbf{r}_{\partial} \delta_{\alpha\beta}) \times \\ &\left[\frac{1}{\mathbf{r}^{3}} \nabla^{(3)} - \frac{3}{\mathbf{r}} \nabla^{(2)} + \frac{3}{\mathbf{r}^{2}} \nabla^{(1)}\right] + (\delta_{\alpha\beta} \delta_{\lambda\partial} + \delta_{\beta\lambda} \delta_{\alpha\partial} + \delta_{\alpha\lambda} \delta_{\beta\partial}) \times \\ &\frac{1}{\mathbf{r}^{2}} (\nabla^{(2)} - \frac{1}{\mathbf{r}} \nabla^{(1)}) \end{split}$$

The superscript indicates the order of the derivative which is evaluated at the interparticle distance. The ratio of the first derivative to the interparticle spacing

is the tangential (τ) force constant. The second derivative with respect to interparticle distance is known as the radial force constant $(\mathbf{\hat{R}})$. The radial force constant as a function of gaussian width is shown in Figure 6, which has several physically interesting interpretations. The ordinate intercept is the bare force constant, that is the second derivative of the interatomic potential appropriate for two free atoms with no spatial averaging. Note that the bare force constant is negative implying lattice instability. The maximum divides the curve into two parts. To the left of the maximum short range correlations are not very important; increasing the gaussian width allows a particle to sample more of the region of positive curvature of the bare interatomic potential yielding a larger force constant. То the right of the maximum however the short range correlation function prevents the gaussian from any further sampling of the positive curvature portion of the bare potential. In fact since the wavefunction is spatially expanding with increasing width more of the negative portion is now sampled and the force constant decreases. The decreasing portion is roughly linear, a fact which is exploitable for numerical calculations. The effect of a mass defect on the force constant depends upon which portion of figure represents the lattice involved. The helium solids all lie to the right of the maximum. A helium four substitutional defect in a helium three lattice will decrease the amplitude of atomic vibration and cause a force constant increase.

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HELIUM FORCE CONSTANTS (Molar Volume = 24.5 (cm)³ FIGURE 7.

43

The calculation of the defect lattice Green's function involves the inversion of some large matrices. We divide the crystal into a defect subspace and a complementary subspace. The defect subspace is modified due to a crystal defect. The dimension of the matrix requiring inversion is three times the number of atoms in the defect subspace. This can be demonstrated by writing the equation of motion in T-matix form.

$$G = G^{\circ} + G^{\circ} TG^{\circ}$$

$$\underline{G} = \begin{pmatrix} G^{\circ}_{11} & G^{\circ}_{12} \\ G^{\circ}_{21} & G^{\circ}_{22} \end{pmatrix} + \begin{pmatrix} G^{\circ}_{11} & G^{\circ}_{12} \\ G^{\circ}_{21} & G^{\circ}_{22} \end{pmatrix} \begin{pmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{pmatrix} \begin{pmatrix} G^{\circ}_{11} & G^{\circ}_{12} \\ G^{\circ}_{21} & G^{\circ}_{22} \end{pmatrix}$$
(66)

Elements 11 refer to the defect subspace, 22 identifies the complementary region of the lattice, 12 and 21 denote the coupling between the defect subspace and its complement.

$$T = C(1-G^{O}C)^{-1}$$

$$(1-G^{O}C)^{-1} = \begin{pmatrix} 1-G_{11}^{O}C_{11} & G_{21}^{O}C_{11} \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} (1-G_{11}^{O}C_{11})^{-1} & 0 \\ -G_{21}^{O}C_{11}(1-G_{11}^{O}C_{11})^{-1} & 1 \end{pmatrix}$$

$$T = \begin{pmatrix} C_{11}(1-G_{11}^{O}C_{11})^{-1} & 0 \\ 0 & 0 \end{pmatrix} = \begin{pmatrix} T_{11} & 0 \\ 0 & 0 \end{pmatrix}$$
(67)

The T-matrix has elements in the defect subspace only and the matrix to be inverted involves only elements in the defect subspace. One should not construe this to mean the remainder of the lattice is unaffected. Equation 66 shows that the perturbation introduced by the defect is coupled to the whole crystal. Note that the perturbation of each element of the matrix G is quadratic in G.

Because the off-diagonal elements $(G_{\ell\ell}^{O})$ of the perfect crystal Green's function fall off as $\left|\frac{1}{r_{\ell\ell}}\right|$ for large $|r_{\ell\ell}|$ the perturbations of the diagonal elements of the Green's function far from the defect subspace fall off as $\frac{1}{r^2}$ and the off-diagonal perturbations as $\frac{1}{r}$.

$$\underline{G} = \underline{G}^{\circ} + \begin{pmatrix} G_{11}^{\circ} T_{11} G_{11}^{\circ} & G_{11}^{\circ} T_{11} G_{12}^{\circ} \\ G_{21}^{\circ} T_{11} G_{11}^{\circ} & G_{21}^{\circ} T_{11} G_{12}^{\circ} \end{pmatrix}$$
(68)

The necessary matrix inversions have been done by three methods all of which give qualitatively similar results for the perturbed force constant. First we used an Einstein approximation for the Green's function. This reduces the behemoth to a 3X3 matrix. The second method used an approximation to the off-diagonal elements which allowed the inversion to be done by hand, and the third method used a computer to do an exact inversion. Since the matrix must be inverted many times in seeking a selfconsistent result the third method is computationally too expensive to be practical, especially when many shells of neighbors are considered.

As a simple example of the effects resulting from an isotopic defect we consider an Einstein oscillator approximation to the equation of motion where the particles are taken to be independent oscillators. Independent oscillators imply that the Green's function is diagonal on site indices. The change in two particle force constant will be written in two parts, the first resulting from the vibrational properties of the new mass and the second from static relaxation of the cage of neighbors around the defect. It was noted earlier that the interatomic force constants were roughly linear in the gaussian width (D). This will be exploited by using the change in D as an expansion parameter. In this Einstein model all perturbed quantities will be expanded to first order in the change in the width parameter and the resulting equations solved for the perturbed gaussian widths.

The following symbols are used:

- τ = tangential force constant, first derivative intersite potential divided by the intersite distance
- D = width of two particle gaussian D_0 = width in unperturbed crystal $V^{(n)} = n\frac{th}{derivative}$ of intersite potential

In general we have that

$$(1-\epsilon_{\ell}) m\omega^{2}G_{\ell\ell} = \delta_{\ell\ell} + \sum_{\ell} (\Phi_{\ell\ell} + \delta\Phi_{\ell\ell})G_{\ell\ell}$$

But in the Einstein model,

$$(1-\epsilon_{\ell}) m \omega^{2} G_{\ell \ell} = 1 + (\Phi_{\ell \ell} + \delta \Phi_{\ell \ell}) G_{\ell \ell}$$

or

$$G_{\ell \ell} = \frac{1}{2m(1-\epsilon_{\ell})\omega} \left(\frac{1}{\omega+\omega_{\ell}} + \frac{1}{\omega-\omega_{\ell}}\right)$$
(69)

where

$$\omega_{\ell} = \sqrt{\frac{\Phi_{\ell\ell} + \delta \Phi_{\ell\ell}}{m(1 - \epsilon_{\ell})}} = \sqrt{\frac{\Phi_{\ell\ell}}{m(1 - \epsilon_{\ell})}} (1 - \frac{1}{2} \frac{\delta \Phi_{\ell\ell}}{\Phi_{\ell\ell}})$$

The last expression is the Einstein frequency for site ℓ . The expansion makes less than one-half of one percent error in frequency if $\frac{\delta\Phi}{\Phi}$ is less than twenty percent.

$$\langle \mathbf{u}_{\ell\alpha}(t) \mathbf{u}_{\ell\alpha}(0) \rangle = -\lim_{\delta \to 0} \frac{\cancel{\mu}}{\pi} \underbrace{\int_{-\infty}^{\infty} [n(\omega) + 1]}_{\alpha \alpha} \operatorname{Im} \operatorname{G}_{\substack{\ell \ell \\ \alpha \alpha}} (\omega + i\delta) e^{-i\omega t} d\omega$$

$$= -\lim_{\delta \to 0} \frac{\cancel{\mu}}{\pi} \operatorname{Im} \underbrace{\int_{-\infty}^{\infty}} e^{-i\omega t} \operatorname{coth} (\frac{\beta \omega}{2}) \frac{1}{2m(1 - \epsilon_{\ell})\omega} (\frac{1}{\omega - \omega_{\ell} + i\delta} + \frac{1}{\omega + \omega_{\ell} + i\delta}) d\omega$$

$$= \underbrace{\cancel{\mu} \cos(\omega_{\ell} t)}_{m(1 - \epsilon_{\ell})\omega_{\ell}} \operatorname{coth} (\frac{\beta \omega_{\ell}}{2})$$

$$(70)$$

We can consider the change in force constants due to relaxation. We do a cubic average of force constants.

$$\Phi_{\lambda} = \frac{1}{N(\lambda)} \sum_{\substack{\ell \gg \lambda}} \Phi_{0\ell} = \langle \frac{xy}{r^2} \rangle (\hat{R}_{\lambda} - \tau_{\lambda}) + \delta_{xy}$$

For the first shell of a BCC lattice the force constant becomes

$$\Phi_1 = (\hat{R}_1 + 2\tau_1)/3 \tag{71}$$

$$\delta \Phi_{\text{relax}} = \eta \left[V^{(3)} + \frac{2}{r} (f_{r-\tau}) \right] / 3$$
(72)

Eta is the relaxation of the nearest neighbors of the defect. This effect is considered in detail in Appendix B and can be written here as

$$\eta = \frac{V^{(1)} - V_{o}^{(1)} + 2(D_{o}V_{o}^{(3)} - DV^{(3)})}{\Re + \Re_{o}}$$

$$= \frac{\frac{\partial V^{(1)}}{\partial D} + 2\left[-V_{O}^{(3)} - \frac{\partial V^{(3)}}{\partial D} D_{O}\right]}{2\Re} \delta D$$

$$\delta \Phi_{relax} \equiv \rho \delta D$$

The effect of the change in mass on the intersite potential is taken as the slope of the effective interatomic potential versus D.

$$\begin{split} \delta \Phi_{\text{mass}} &= \alpha \delta D \end{split} \tag{73}$$

$$\delta \Phi &= (\rho + \alpha) \delta D \equiv A \delta D \tag{73}$$

$$D &= \frac{1}{2} (\langle u_{0}u_{0} \rangle + \langle u_{1}u_{1} \rangle) = D_{0} + \delta D$$

$$D_{0} + \delta D &= \frac{1}{2} \left\{ \frac{\cancel{\mu} \coth\left(\frac{\beta w_{0}}{2\pi(1 - \varepsilon)}\right)}{2\pi(1 - \varepsilon)w_{b}} + \frac{\cancel{\mu} \coth\left(\frac{\beta w_{1}}{2\pi}\right)}{2\pi w_{1}} \right\}$$

$$\omega_{0} &= \sqrt{\frac{\Phi + 8\delta\phi}{\pi(1 - \varepsilon)}} = \frac{\omega_{E}}{\sqrt{1 - \varepsilon}} (1 - \frac{1}{2} \frac{\delta\phi}{\phi})$$

$$\omega_{1} &= \sqrt{\frac{\Phi + \delta\phi}{\pi}} = \omega_{E} (1 - \frac{1}{16} \frac{\delta\phi}{\phi})$$

$$D_{0} + \delta D &= \frac{\cancel{\mu} \coth\left(\frac{\beta w_{E}}{2}\right)}{4\pi w_{\varepsilon}} \left\{ \frac{(1 - \frac{1}{2} \frac{\delta\phi}{\phi})}{\sqrt{1 - \varepsilon}} \right\}$$

$$\times \left[1 - \frac{\beta \omega_{E} (\sqrt{\frac{1}{1 - \varepsilon}} - 1)^{-\frac{1}{2} \frac{\delta\phi}{\phi} - (\sqrt{\frac{1}{1 - \varepsilon}} - 1) - \frac{1}{2} \frac{\delta\phi}{\phi}}{\cosh\left(\frac{\beta w_{E}}{2}\right)} \right]$$

$$+ (1 - \frac{1}{16} \frac{\delta\phi}{\phi}) \left[1 + \frac{\beta \omega_{E} \delta\phi}{16 \phi} / \left(\cosh\left(\frac{\beta w_{E}}{2}\right) - \sinh\left(\frac{\beta w_{E}}{2}\right)\right) \right] \right\}$$

Using $\delta \Phi = \Delta \delta D$ the above can be solved for δD

$$\delta D = \frac{D_{O}}{2} \frac{\sqrt{\frac{1}{1-\varepsilon}} \left(1 - \frac{\beta \omega_{E} \left[1 - \sqrt{\frac{1}{1-\varepsilon}}\right]}{\cosh \left(\beta \omega_{E/2}\right) \sinh \left(\beta \omega_{E/2}\right)}\right) - 1}{1 + \frac{\Delta D_{O}}{4\phi} \left\{\sqrt{\frac{1}{1-\varepsilon}} + \frac{1}{8} + \frac{\beta \omega_{E} \left[-\frac{1}{8} - \frac{2}{1-\varepsilon} + \sqrt{\frac{1}{1-\varepsilon}}\right]}{\cosh \left(\beta \omega_{E/2}\right) \sinh \left(\beta \omega_{E/2}\right)}\right\}$$

In the low temperature limit $(\beta \omega_E^{>>1})$ the temperature dependence is exponentially small. Taking the zero temperature limit

$$\delta D = \frac{D_{O}}{2} - \frac{\sqrt{\frac{1}{1-\varepsilon} - 1}}{1 + \frac{\Delta D_{O}}{4\phi_{O}} \left(\sqrt{\frac{1}{1-\varepsilon} + \frac{1}{8}}\right)}$$
(74)

The numerator is the result for a mass defect theory and the denominator is the self-consistent renormalization due to quantum mechanical effects (change in shape of the two particle wavefunction). Evaluating the derivatives in equation 73 for a ³He host lattice with molar volume 24.6 cm³ we find a large self-consistency effect. The denominator of equation 74 gives a self-consistent enhancement of sixty-seven percent.

$$\frac{\Delta D_{O}}{4\phi_{O}} = .406 \qquad \qquad \frac{r}{r_{O}} = -1.9\%$$
molar volume = 24.45 (cm)³/mole
$$\frac{\delta D}{D_{O}} = -11.2\%$$

$$\frac{\delta \phi}{\phi_{O}} = \frac{\Lambda \delta D}{\phi_{O}} = 18.1\%$$

$$\Delta = \rho + \alpha$$

Approximate Inversion Scheme

If we consider a model where only force constants which connect an atom to the defect are perturbed and the force constants connecting neighbors of the defect among themselves are unperturbed, $G^{O}C$ can be written as

$$(G^{O}C)_{ij} = (G^{O}_{ii} - G^{O}_{i0})C_{i}\delta_{ij} + (G^{O}_{ij} - G^{O}_{i0})C_{i}(1 - \delta_{ij})(1 - \delta_{j0}) - (\sum_{k} G^{O}_{ik}C_{k0})\delta_{j0}$$
(75)

$$= \begin{pmatrix} (G_{11}^{\circ} - G_{10}^{\circ}) C_{1} & (G_{12}^{\circ} - G_{10}^{\circ}) C_{2} & \dots & -G_{1k}^{\circ} C_{k} \\ (G_{21}^{\circ} - G_{20}^{\circ}) C_{1} & (G_{22}^{\circ} - G_{20}^{\circ}) C_{2} & \dots & -G_{2k}^{\circ} C_{k} \\ \vdots & \vdots & \ddots & \ddots & \vdots \\ (G_{01}^{\circ} - G_{00}^{\circ}) C_{1} & (G_{02}^{\circ} - G_{00}^{\circ}) C_{2} & \dots & C_{i}^{=C}_{i0} \end{pmatrix}$$

$$(80)$$

where the defect has been placed at the origin and C_i is an abbreviation for C_{i0} . For a cubic crystal G_{i1} is diagonal on cartesian coordinates. Taking all matrices to be diagonal on cartesian coordinates the model in equation 80 becomes three one-dimensional models. Now G_{ij}^{O} depends only on |i-j| and within any shell of neighbors about the defect, diagonal elements in $G^{O}C$ are equal. To complete the approximation note that the off diagonal elements $(G_{ij}^{O}-G_{i0}^{O})C_{j}$ are the same except for G_{ij} which is a function connecting different sites within a shell of atoms surrounding the defect. We replace this G_{ij}^{O} by

$$\overline{G_{\lambda}^{O}} = \frac{1}{N\lambda} \sum_{\substack{j \\ j \\ (i,j>\lambda)}} G_{ij}^{O} \longrightarrow \frac{1}{7} (3G_{02}^{O} + 3G_{03}^{O} + G_{04}^{O})$$
(81)

for the first shell of a BCC lattice.

Using one shell of neighbors a force constant defect (C), and a mass defect $m\epsilon\omega^2$, $(1-G_{00}^OC - m\epsilon\omega^2G_{00}^O)$ becomes.

For a BCC lattice and one shell:

$$\lambda = (G_{00}^{O} - G_{10}^{O})C$$

$$\alpha = (\overline{G}^{O} - G_{10}^{O})C$$

$$\gamma = \lambda + 7\alpha - m\varepsilon\omega^{2} G_{01}^{O}$$

$$\gamma_{0} = 1 - 8\lambda - G_{00}^{O} (m\varepsilon\omega^{2})$$

$$(1 - G^{O}C)^{-1} = \frac{1}{Det} B \quad Det = Det(1 - G^{O}C)$$

$$Det(1 - G^{O}C) = (1 - \lambda + \alpha)^{7} (1 - \lambda - 7\alpha)\gamma_{0} - 8(1 - \lambda + \alpha)^{7}\gamma\lambda$$

$$B_{11} = (1 - \lambda + \alpha)^{6} [(1 - \lambda - 6\alpha)\gamma_{0} - 7\gamma\lambda] = B_{11} \quad (i \neq 0)$$

$$B_{12} = (1 - \lambda + \alpha)^{6} (\alpha\gamma_{0} + \lambda\gamma) = B_{11} \quad (i \neq 1), \quad i \neq 0, \quad j \neq 0$$

$$B_{10} = -\lambda (1 - \lambda + \alpha)^{7} = B_{10} \quad (i \neq 0)$$

$$B_{10} = -\gamma (1 - \lambda + \alpha)^{7} = B_{10} \quad (i \neq 0)$$

$$B_{00} + (1 - \lambda + \alpha)^{7} (1 - \lambda - 7)$$

The final defect calculation performed was one using a computer to do the necessary matrix inversions. The defect equation of motion was first rewritten as two equivalent equations because the mass defect equation can be solved exactly and easily. A force constant defect equation of motion was then solved self-consistently using the mass defect Green's functions and equations 84 and 85.

$$G = G^{O} + G^{O} (\delta \Phi + m \varepsilon \omega^{2}) G$$
(83)

$$G_{\rm m} = G^{\rm O} + G^{\rm O} \, {\rm m} \varepsilon \omega^2 \, G_{\rm m} \tag{84}$$

$$G = G_{m} + G_{m} \delta \Phi G$$
(85)

The results of this model are listed below.

Neighbor Number	<u>δD</u> (%) Do	$\frac{\delta\Phi}{\Phi_{O}}$ (%)	<u>δr</u> (%)	Coordinate
1	-9.1	14.0	-1.2	<u>a</u> (111) 8 sites
2	-7.5	3.1	-0.5	(200) 6 sites
3	-6.95	-1.4	-0.2	(220)12 sites

Thermal Conductivity

A number of calculations and experiments on solid helium have been reported. Aside from questions of quantum crystals, solid helium has the historical significance of having been the first solid to exhibit phonon umklapp scattering in 1951, twenty-two years after Peierls' prediction in 1929.⁴¹ A summary of published results of analyzing conductivity experiments is given in Table 3 (in references 42-47 and 52-54). Several difficulties beset the interpretation of experimental results:

- All calculations assume an elastically isotropic and dispersionless solid.
- The necessity for inclusion of three-phonon processes seems understood,^{42,54} however, the various authors differ on the amplitude and

Calculation	т <mark>т</mark> –1*	A/A _K **	<u>C</u> (%)	vol (cm ³ /mole)	Host	T (°K)	Structure	Pressure (atm)	(X°)
Callaway (61)	$B_N \omega^2 T^3$	3.0	.5-2.8	1	⁴ He	1.1+2.1	1	1	1
Berman (65)	B _N ² T ² "	3.1 2.2 1.7	1-11 1-11 1-11 025-16	20.4 19.3 18.1	не в т не не	1-2 1-3 1-3	нсР нсР нсР	60 90 140	28.0 32.3 38.1
Bertman (66)	Β _ω 2 ¹³ Ν"	10.1 20-30	1-50 8-50	19.5 19.5	ане "Не	.5+1.9 .5+1.9	HCP		
Berman (68)		1.5 1.5 1.0		17.3 16.55 13.5 11.65	не не не	1-8 1-8	HCP HCP HCP	190 250 800 1725	43.0 48.25 76.5 104
Berman (70)	B _N ω ² T ² B _N ω ² T ³ ''	1.3 1.2 1.1		19.5 17.6 14.5 12.6	2 = = = 6		HCP HCP HCP	145 250 675 1370	37.3 48.2 76.5 104

THERMAL CONDUCTIVITY EXPERIMENTS

TABLE 3

*Three phonon scattering rate.

******Defect scattering rate/mass defect scattering rate.

frequency dependence of these processes. Herring⁵⁰ has shown that the three phonon scattering rate for long wavelengths is given by

$$\tau^{-1}(k) = k^{S} T^{5-S}$$

where s is usually taken as 2, the value characteristic of longitudinal modes in cubic crystals.

3. The experiments are done principally by two groups. Berman at Oxford University does experiments at constant pressure, while Bertman at Duke University does experiments at constant volume. These different techniques seem to yield different results for the defect scattering rate as shown in Table 3.

Rather than to do the full calculation for the thermal conductivity we shall calculate a scattering amplitude from the scattering T-matrix in Appendix E which can then be compared to experimental values.

The mass defect scattering can be done exactly in the low concentration limit where now noninteracting defects are imagined to exist, while the force constant defect case is a little more complicated. The model used is one where the change in potential between any atom and the defect is proportional to the unperturbed potential.

$$\Phi_{id} - \Phi_{id}^{O} = \Sigma \gamma_{i} \Phi_{id}^{O}$$

$$\alpha\beta \quad \alpha\beta \quad \rho_{\alpha\beta} \rho_{\beta\beta}$$
(86)

If $A_{\alpha\beta}^{}\,(\,\ell\,)$ represents the change in force constants between site ℓ and the defect

$$A_{\ell\ell} = \{-\delta_{\ell d} A_{\alpha\beta}(\ell) - \delta_{\ell' d} A_{\alpha\beta}(\ell') + \delta_{\ell\ell'} A_{\alpha\beta}(\ell)\}\{1 - \delta_{\ell d} \delta_{\ell' d}\}$$
$$+ \sum_{\ell \neq d} A_{\alpha\beta}(\ell)\} \delta_{\ell d} \delta_{\ell' d}$$
(87)

$$A_{qq'} = \sum_{\substack{\ell \ell \\ jj'}} e^{i\underline{q} \cdot \underline{\ell}} \sigma_{\alpha}^{j}(\underline{q}) A_{\ell \ell} e^{-i\underline{q}' \cdot \underline{\ell}} \sigma_{\beta}^{*j'}(\underline{q})$$

$$= [A_{jj'}, (\underline{q}) + A_{jj'}, (-\underline{q}') - A_{jj'}, (\underline{q} - \underline{q}')] e^{i(\underline{q} - \underline{q}') \cdot \underline{d}}$$
(88)

$$\mathbf{A}_{jj}, (\mathbf{q}) \equiv \sum_{\substack{\ell \\ \alpha\beta}} e^{\mathbf{i} \mathbf{q} \cdot (\ell - \ell')} \mathbf{A}_{\ell \ell}, \sigma_{\alpha}^{j}(\mathbf{q}) \sigma_{\beta}^{\star j'}(\mathbf{q})$$

These equations are perfectly general in the case of no perturbation of force constants among the defect neighbors. We now take γ to be a constant independent of site coordinates. This model has been previously considered by Elliott and Taylor.⁵¹ In this scaled force constant model

$$A_{jj}'(q) = \omega_j^2(q) \delta_{jj}'$$
(89)

Using a multiband Debye model and the total perturbation C, the scattering T-matrix can be evaluated.

$$A_{qq'} = \delta_{jj'} 2\gamma V_j^2 q \cdot q' e^{i(q-q') \cdot d}$$
(90)
jj'

 V_j = velocity of sound for branch j

$$C_{\substack{\ell\ell}, = A_{\ell\ell}, + m\varepsilon\omega^2\delta_{\ell}0^{\delta}\ell 0^{\delta}\alpha\beta}$$

$$\alpha\beta \qquad (91)$$

$$T = C (1 - G^{O}C)^{-1}$$
(92)

$$T_{qq'} = \frac{\varepsilon \omega_j^2}{1 - m \varepsilon \omega_j^2 G_{00}^0} + \frac{2\gamma V_j^2 \tilde{q} \cdot \tilde{q}'}{(1 + \frac{2}{3}\gamma) - \frac{23}{3} m \omega^2 G_{00}^0}$$
(93)

The T-matrix can be written as a sum of partial waves provided we take $G^{O}(k)$ to have an isotropic dependence on wave vector.

It is shown by several methods in Appendix E that the lifetime of a phonon with wavevector k is given by equation 94. Va is the atomic volume. x is the concentration of defects.

$$\frac{1}{\tau_{K}} = \frac{\mathbf{x} \, \mathbf{V} \mathbf{a}}{(2\pi)^{2} 4 \omega_{K}^{2}} \int d^{3} \mathbf{K}' \left| \mathbf{T}_{\mathbf{K}\mathbf{K}'} \right|^{2} \, \delta \left(\omega - \omega_{\mathbf{K}}' \right)$$
(94)

$$= \frac{\mathbf{x}}{3} \sum_{j} \frac{\mathbf{V}\mathbf{a}}{4\pi \mathbf{V}_{j}^{3}} |\mathbf{T}_{\mathbf{K}\mathbf{K}'}|^{2}$$
(95)

$$= \frac{\mathbf{x}}{12\pi} \operatorname{Va} \left(\frac{2}{v_{t}^{3}} - \frac{1}{v_{\ell}^{3}} \left\{ \frac{\varepsilon^{2} \omega_{K}^{4}}{\left| 1 - m\varepsilon \omega^{2} G_{00}^{0} \right|^{2} + \frac{4\gamma^{2} \omega^{4}}{\left| 1 + \frac{2\delta}{3} - \frac{2}{3}m\delta \omega^{2} G_{00}^{0} \right|^{2} \right\} (96)$$

Equation 95 was obtained by considering spherical bands and averaging over these bands.

In thermal conductivity one is really interested in the rate of loss of forward momentum rather than the total rate of momentum loss. This shortcoming is rectified by the insertion of a $1-\cos(0)$ factor which occurs naturally if one begins with a Boltzmann equation for thermal conductivity.⁵⁵

$$\frac{1}{\tau_{\rm K}} = \frac{\mathbf{x} \, \mathrm{Va}}{(2\pi)^2 \, 4\omega_{\rm K}^2} \int \mathrm{dk'} (1 - \cos\theta) \left| \mathbf{T}_{\rm KK'} \right|^2 \delta(\omega - \omega_{\rm K}') \tag{97}$$

This angular factor couples s and p partial waves and adds to equation 96 a term

$$\frac{\mathbf{x} \mathbf{V} \mathbf{a}}{12\pi} \left(\frac{2}{\mathbf{V}_{t}^{3}} + \frac{1}{\mathbf{V}_{\ell}^{3}} \right) \left\{ \frac{-\frac{2}{3} \mathbf{\gamma} \omega^{4}}{(1 - m \varepsilon \omega^{2} G_{00}^{0}) (1 + \frac{2\gamma}{3} - \frac{2}{3} m \gamma \omega^{2} G_{00}^{0})^{*}} + \text{C.C.} \right\}$$
(98)

The denominators of the scattering rate expressions were checked for possible scattering resonances (vanishing of the real part of the denominator). The resonance condition for the mass defect is shown in Figure 5. A resonance occurs if the curve labeled $1/(\varepsilon \omega^2)$ crosses the real part of the Green's function. The resonance curve for the force constant denominators lie in the upper right some distance off of the graph in Figure 5. The failure of a resonance to occur eliminates these resonances as a possible source of enhanced scattering rate. The total relaxation rate appropriate for thermal conductivity to order ω^4 is then

$$\frac{1}{\tau(\omega)} = \frac{X \operatorname{Va}\omega^{4}}{12\pi} \left(\frac{2}{V_{t}} + \frac{1}{V_{\ell}^{3}} \right) \left\{ \varepsilon^{2} + \frac{4 \gamma^{2}}{3 \left(1 + \frac{2\gamma}{3}\right)^{2}} + \frac{4 \varepsilon \gamma}{3 + 2\gamma} \right\}$$
(99)

In our calculation of a 'He defect in a 'He host we found a value of γ which was approximately minus one-half epsilon. The above equation then implies the scattering rate should be twice the mass defect scattering rate. This result agrees more closely with the experimental analyses of Callaway and Berman than the analysis of Bertman (see Table 3). There are still several scattering mechanisms which we might consider. The helium atoms are only very loosely bound to their lattice sites in the ground state. It may be that higher excited states are not bound and the helium atoms actually become nomadic, allowing inelastic as well as elastic phonon scattering. If the helium four impurity changes the local exchange frequency a change in scattering rate might result.

Defect Specific Heat

A heavy mass defect will increase the density of states at low frequencies and will therefore give an enhanced lattice specific heat at low temperatures. In quantum crystals a mass defect is accompanied by an induced force constant change and we would like to assess the impact of this force constant change on the specific heat. If
there is an increase in force constants for an isotopic defect as in helium there will be a diminution of low temperature specific heat. The force constant change will mask the effect of the mass defect. If a decrease in force constants accompanies a heavy mass defect the opposite effect would be expected. The phonon specific heat is the derivative of the total vibrational energy will respect to temperature. The change in specific heat per mole is then⁵⁶

$$\Delta C(T) = \frac{3N k_B \beta^2}{4} \int_{\infty}^{\infty} \omega^2 \Delta(\omega) \operatorname{csch}^2(\beta \omega/2) d\omega \qquad (100)$$

 $\beta = \mu/kT$

The change in specific heat is expressed in terms of the phonon phase shift (see equation 147) as

$$\Delta \mathbf{g}(\omega) = \frac{\mathbf{x}}{\pi} \frac{\partial \Theta}{\partial \omega} \tag{101}$$

where x is the concentration of defects. The phonon phase shift for a mass defect and for the scaled force constant model (defined in section on thermal conductivity) is

$$\Theta = \tan^{-1} \left(\frac{-\pi \varepsilon \omega^{2} \operatorname{Im} G_{\ell \ell}^{O}}{1 - \pi \varepsilon \omega^{2} \operatorname{Re} G_{\ell \ell \ell}^{O}} \right) + 3 \tan^{-1} \left(\frac{\frac{2}{3} \pi \varepsilon \omega^{2} \operatorname{Im} G_{\ell \ell}^{O}}{1 + \frac{2\gamma}{3} - \frac{2\gamma}{3} \pi \omega^{2} \operatorname{Re} G_{\ell \ell}^{O}} \right)$$
(102)

This expression was evaluated for $\varepsilon = -1/3$ and $\gamma = .15$. The result is displayed in Figure 8. In the very low frequency limit where the density of states is quadratic in frequency



PHONON PHASE SHIFTS (Molar Volume = 24.5 (cm³))

the change in density of states can be found from equation 101 and there is then a simple form for the corresponding very low temperature specific heat.

$$\Delta \mathbf{g}(\omega) = \frac{\mathbf{x}}{\pi} \frac{\partial \Theta}{\partial \omega}$$
(103)

$$= -x\left(\frac{3\varepsilon}{2} + \frac{3\gamma}{1 + \frac{2\gamma}{3}}\right) g(\omega) \qquad \frac{\omega}{\omega_{\rm D}} <<1 \qquad (104)$$

$$\Delta C(T) = -x\left(\frac{3\varepsilon}{2} + \frac{3\gamma}{1 + \frac{2\gamma}{3}}\right) C(T) \qquad \frac{T}{\Theta_D} << 1 \qquad (105)$$

Substitution of the phonon phase shift into equation 100 and an integration by parts gives

$$\Delta C(T) = - \frac{3k_B x N}{\pi} \int_0^\infty d\omega \Theta(\omega) \frac{\beta \omega}{2} \operatorname{csch}^2(\beta \omega/2) \{1 - \frac{\beta \omega}{2} \operatorname{coth} \frac{\beta \omega}{2}\} (106)$$

This expression was evaluated using the phase shift of Figure 8 and at .2 K eighty-one percent of the enhancement due to the mass defect was cancelled. At 1 K seventyfive percent cancellation was found.

The change in the ground state energy was also evaluated and ninety percent of the diminution caused by the mass defect was restored by the induced force constant change.

$$\Delta E(T) = \int_{0}^{\infty} \omega \Delta g(\omega) \, d\omega \, \left(\frac{1}{e^{\beta \omega} - 1} + \frac{1}{2}\right)$$
(107)

integration by parts,

$$\Delta E(T) = \frac{x}{2\pi} \int_{0}^{\infty} \Theta(\omega) \left[\operatorname{coth} \frac{\beta\omega}{2} + \frac{\beta\omega/2}{\sinh\frac{\beta\omega}{2}} \right] d\omega \qquad (108)$$

$$\Delta E(T=0) = -\frac{\mathbf{x}}{2\pi} \int_{0}^{\infty} \Theta(\omega) d\omega$$
 (109)

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CHAPTER IV

CONCLUSIONS

In the preceding developments we have derived a general equation of motion for lattice vibrations which is applicable to all crystals and temperatures but is especially useful in the case of quantum crystals where classical methods fail. The formalism developed is exact and has several advantages over the existing variational theory. The variational theory minimizes the ground state energy and is therefore good at zero temperature and only as good as the trial wavefunctions. This formalism should also be useful in cases where classical calculations are extended by perturbation theory to include anharmonicity. This possibility has recently been proposed by Gillis and Koehler⁵⁷ as a method of treating paraelectric crystals. Spatially averaging the interatomic potential would reduce anharmonicity and provide an alternative to summing many orders of phonon interactions. It has been shown how a force constant change is induced by an isotopic defect and quantitative results were obtained by these methods.

The three methods of calculation consisted of an Einstein model for a solid, an approximate matrix inversion

scheme for calculating the defect crystal Green's function, and an exact computer inversion of the necessary matrices. Although the calculations differed in sophistication the quantitative results were very similar. This can be understood because the results depended on integrals of the phonon spectrum and not on a detailed description of the spectrum.

We can now comment on the experimental effects noted earlier. It was the original expectation that the enhanced spin-lattice relaxation rate which occurs in ³He with only a small addition of isotopic defects could be accounted for by a resonance in the density of states due to a heavy mass defect. While the defect is heavier than the host atoms the fractional mass change is insufficient to cause a resonance; furthermore, the increase which does occur in the density of states is cancelled by the induced force constant change. The effects cancel because an increase in mass enhances the amplitude of low frequency vibrations while diminishing the weight of high frequencies. A force constant increase has an opposite effect. The conclusion is that phonons are unable to explain the spin-lattice relaxation experiments. Other inelastic processes which might account for the experimental spin-lattice relaxation results are enhanced vacancy diffusion and nomadic particles.

The anomaly in thermal conductivity experiments is a phonon scattering rate which exceeds the value given by mass defect theories. By considering the scattering due to

the induced force constant changes, we find a scattering rate which is twice the mass defect prediction. This result is roughly in agreement with most experiments while considerably smaller than the experimental predictions of the Duke University group.

An enhancement of the phonon specific heat of helium because of a heavy mass defect has not been reported. Experiments measuring specific heat have been done in temperature ranges (above isotopic phase separation temperatures but below vacancy generation temperatures) where this effect should be observable. The absence of this observation is explained by the masking of the mass defect by the induced force constant changes.

To complete this work we derive theorems concerning phonon lifetimes and static distortion fields in the appendices. In calculating phonon lifetimes using displacement propagators (descriptor of lattice displacement waves) it is necessary to ascertain the relationship between the phonon propagator and the displacement propagator. This relationship is found as well as the relationship between the associated T-matrices, which are a simple way of expressing phonon lifetimes. Several derivations of phonon lifetimes are given. Lattice distortion near a defect has an important effect on the phonon scattering rates and a simple general method for calculating it is found.

APPENDICES

APPENDIX A

COMMUTATOR THEOREMS

APPENDIX A

COMMUTATOR THEOREMS

Presented here are some theorems used in the derivation of the equation of motion for the displacement Green's function. For two arbitrary operators x and A (which are associative, distributive, but not commutative), we define

$$A_{0} = A$$
 $A_{1} = [x, A]$ $A_{2} = [x, A_{1}]$ $A_{n} = [x, A_{n-1}]$
 $\binom{n}{k} = \frac{n!}{(n-k)! k!}$

Theorem 1

$$A_{n} = \sum_{k=0}^{n} {n \choose k} (-1)^{k} x^{n-k} A x^{k}$$

The proof is by induction. For n = 1 the relation is true. For n = 2, 3, and n + 1:

$$A_2 = [x, [x, A]] = x^2 A - 2xAx + Ax^2$$

$$A_{3} = [x, A_{2}] = x^{3}A - 3x^{2}Ax + 3xAx^{2} - Ax^{3}$$

$$A_{n+1} = [x, A_{n}] = \sum_{k=0}^{n} {n \choose k} (-1)^{k} [x, x^{n-k}Ax^{k}]$$

$$= \sum_{k=0}^{n} {n \choose k} (-1)^{k} x^{n-k+1}Ax^{k} + \sum_{k=1}^{n+1} x^{n-k+1}Ax^{k} {n \choose k-1} (-1)^{k}$$

Q.E.D.
Theorem 2

$$Ax^{n} = \sum_{k=0}^{n} {n \choose k} (-1)^{k} x^{n-k} A_{k}$$

The proof proceeds again by induction.
 $Ax = xA-A_{1}$
 $Ax^{2} = x^{2}A - 2xA_{1} + A_{2}$
 $Ax^{n+1} = \sum_{k=0}^{n} {n \choose k} (-1)^{k} x^{n-k} A_{k} x$
 $= \sum_{k=0}^{n} {n \choose k} (-1)^{k} x^{n+1-k} A_{k} + \sum_{k=1}^{n+1} {n \choose k-1} x^{n+1-k} A_{k} (-1)^{k}$
 $= \sum_{k=1}^{n} {n \choose k} (-1)^{k} x^{n+1-k} A_{k} + \sum_{k=1}^{n+1} {n \choose k-1} x^{n+1-k} A_{k} (-1)^{n+1} A_{n+1}$
 $= \sum_{k=1}^{n} {n \choose k} (-1)^{k} x^{n+1-k} A_{k}$

Q.E.D.

$$(-1)^{k} x^{n-k} A x^{k}$$

$$= \sum_{k=1}^{n} \{ [\binom{n}{k} + \binom{n}{k-1}] (-1)^{k} x^{n-k+1} x^{k} \} + (-1)^{n+1} A x^{n+1} + x^{n+1} A$$
$$= \sum_{k=0}^{n+1} \binom{n+1}{k} (-1)^{k} x^{n-k} A x^{k}$$

=

.

Theorem 3

$$[e^{A},B] = -e^{A} \sum_{p=1}^{\infty} \frac{(-1)^{p}}{p!} B_{p}$$

This relation is derived by expanding the commutators, using theorem 2, and explicit resummation.

$$[e^{A}, B] = \sum_{n=0}^{\infty} \frac{1}{n_{1}} (A^{n}B - BA^{n})$$

$$= -\sum_{n=0}^{\infty} \frac{1}{n_{1}} \sum_{k=1}^{n} {n \choose k} (-1)^{k} A^{n-k} B_{k}$$

$$[e^{A}, B] = -\sum_{n=1}^{\infty} \sum_{k=1}^{n} \frac{(-1)^{k}}{(n-k)! k l} A^{n-k} B_{k}$$

$$-[e^{A}, B] = \frac{(-1)}{0!1!} A^{0} B_{1}$$

$$n = 1$$

$$+ \frac{(-1)^{1}}{1!1!} A^{1} B_{1} + \frac{(-1)^{2}}{0!2!} A^{0} B_{2}$$

$$n = 2$$

$$+ \frac{(-1)^{1}}{2!1!} A^{2} B_{1} + \frac{(-1)^{2}}{1!2!} A^{1} B_{2} + \frac{(-1)^{3}}{0!3!} A^{0} B_{3}$$

$$n = 3$$

$$+ \frac{(-1)^{1}}{3!1!} A^{3} B_{1} + \frac{(-1)^{2}}{2!1!} A^{2} B_{2} + \frac{(-1)^{3}}{1!3!} A^{1} B_{3} +$$

$$\frac{(-1)^{4}}{0!4!} A^{0} B_{4}$$

$$n = 4$$

$$+ \frac{(-1)^{1}}{4!1!} A^{1} B_{1} + \frac{(-1)^{2}}{0!2!} A^{3} B_{2} + \frac{(-1)^{3}}{2!3!} A^{2} B_{3} +$$

$$\frac{(-1)^{4}}{1!4!} A^{1} B_{4} + \frac{(-1)^{5}}{0!5!} A^{0} B_{5}$$

$$n = 5$$

$$+ \ldots$$

$$+ \ldots$$

sum of column
$$1 = \frac{(-1)}{1!} e^{A}B_{1}$$

sum of column $2 = \frac{(-1)^{2}}{2!} e^{A}B_{2}$
sum of column $3 = \frac{(-1)^{3}}{3!} e^{A}B_{3}$
 $[e^{A},B] = -e^{A}\sum_{p=1}^{\infty} \frac{(-1)^{p}}{p!} B_{p}$

Q.E.D.

Theorem 4

If [A,B] = 0 and $A(t) = e^{iHt}Ae^{-iHt}$ then

$$[A(t),B] = -4A(t) \sum_{p=1}^{\infty} \frac{(it)^{p}}{(2p)!} B_{2p} \text{ where } \beta_{1} = [H,B] B_{N} = [H,B_{N-1}]$$

The proof uses several applications of theorem 3.

$$[e^{iHt}Ae^{-iHt},B] = -A(t)\sum_{p=1}^{\infty} \frac{(it)^{p}}{p!} B_{p} - e^{-iHt}\sum_{p=1}^{\infty} \frac{(-it)^{p}}{p!} B_{p}Ae^{-iHt}$$

$$= A(t)\sum_{p=1}^{\infty} \frac{(it)^{p}}{p!} B_{p} - A(t)\sum_{p=1}^{\infty} \frac{(-it)^{p}}{p!} - e^{iHt}A\sum_{p=1}^{\infty} \frac{(it)^{p}}{p!} B_{p}, e^{-iHt}$$

$$= -2(t)\sum_{p=1}^{\infty} \frac{(it)^{2p}}{2p!} B_{2p} + e^{iHt}A(-e^{-iHt})\sum_{p=1}^{\infty} \sum_{q=1}^{\infty} \frac{(it)^{p}it)^{q}}{p!q!} B_{p+q}$$

Coefficients of $t^{p+q}B_{p+q}$ for p+q=N

$$\frac{N-1}{\sum_{\substack{p+q=N\\p+q=N\\p,q=1}}} \frac{(-1)^{p}}{p!q!} = \sum_{\substack{p=1\\p=1}}^{N-1} \frac{(-1)^{p}}{p!(N-p)!} = \frac{1}{N} \sum_{\substack{p=0\\p=0}}^{N} (-1)^{p} \frac{N!}{p!(N-p)!} + \frac{1}{N} - \frac{(-1)^{N}}{N!}$$

$$= 0 + \frac{1-(-1)^{N}}{N!} = \begin{cases} \frac{2}{N} & N \text{ even} \\ 0 & N \text{ odd} \end{cases}$$

$$[A(t),B] = -4A(t) \sum_{p=1}^{\infty} \frac{(it)^{2p}}{(2p)!} B_{2p}$$

Theorem 5

If
$$e^{\mathbf{x}}e^{\mathbf{y}} = e^{\mathbf{z}}$$
 and $y_1 = [\mathbf{x}, y]$ $y_n = [\mathbf{x}, y_{n-1}]$ then
 $\mathbf{z}=\mathbf{x}+\mathbf{y}+\sum_{p=1}^{\infty}a_py_p + \sum_{pq=1}^{\infty}a_{pq}[y_p, y_q] + \sum_{pqr=1}^{\infty}a_{pqr}[y_p[y_q, y_r] + \cdots$
 $=\mathbf{x}+\mathbf{y}+\sum_{p=1}^{\infty}a_py_p + \sum_{q=1}^{\infty}a_{pq}(y_q)_p + \sum_{pqr=1}^{\infty}a_{pqr}((y_p)_q)_r + \cdots$

This is demonstrated by writing

$$e^{tx}e^{ty}=e^{z} \qquad z=\sum_{p=1}^{\infty} z_{p}t^{p}$$

$$\sum_{mn} \frac{x^{m}y^{n}t^{m+n}}{m!n!} = \sum_{n=0}^{\infty} \frac{p=1}{n!}$$
Equating powers of t the above form is found. The coefficients a_{ij} . . are sums of the coefficients a_{k} .

Q.E.D.

Theorem 6

If we define a symmetry ordering operator S such that

$$S(YX^{n}) \equiv \sum_{\gamma=0}^{n} X^{\gamma} Y X^{n-\gamma}$$

Then

$$Y_{p} x^{n} + xS(Y_{p} x^{n-1}) = S(x^{n}Y_{p}).$$

Corollary

$$x^n Y_p + S(Y_p x^{n-1}) X = S(x^n Y_p)$$

Theorem 7

The difference in ordering of the product of two operators is given by the symmetry ordering operator.

$$Y_{p} x^{n} = x^{n} Y_{p} - S(Y_{p+1} x^{n-1})$$

The proof is an induction proof.
n=1 $Y_{p}x = XY_{p} + (Y_{p}x - XY_{p})$
 $= XY_{p} - Y_{p+1}$
n=2 $Y_{p} x^{2} = XY_{p} x^{-} Y_{p+1} x$
 $= x^{2}Y_{p} + x(Y_{p}x - XY_{p})^{-}Y_{p+1} x$
 $= x^{2}Y_{p} - (XY_{p+1} + Y_{p+1} x)$
 $= x^{2}Y_{p} - S(XY_{p+1})$

Show n+1

$$Y_{p} x^{n} = x^{n} Y_{p} - S(Y_{p+1} x^{n-1})$$

$$Y_{p} x^{n+1} = x^{n} Y_{p} - S(Y_{p+1} x^{n-1}) x$$

$$= x^{n+1} Y_{p} + x^{n}(Y_{p}x - xY_{p}) - S(x^{n} Y_{p+1}) + x^{n} Y_{p+1}$$

$$= x^{n+1} Y_{p} - x^{n} Y_{p+1} - S(x^{n} Y_{p+1}) + x^{n} Y_{p+1}$$

$$= x^{n+1} Y_{p} - S(x^{n} Y_{p+1})$$

$$Q.E.D.$$

Theorem 8

$$\frac{\partial}{\partial \lambda} e^{X} e^{\lambda Y} \Big|_{\substack{\lambda = 0}} \equiv e^{X} Y = \frac{\partial}{\partial \lambda} e^{X + \lambda Z} \Big|_{\substack{\lambda = 0}}$$
where $Z = Y + a_1 Y_1 + a_2 Y_2 + \cdots$

$$= \sum_{j=0}^{\infty} a_j Y_j$$

We prove this by expanding the exponential (e^X) and using the symmetry ordering operator before resumming. First we need the following Lemma.

Lemma 1

$$\frac{x^{n}Y}{n!} = \frac{S(YX^{n})}{(n+1)!} + a_{1} \frac{S(Y_{1} x^{n-1})}{n!} + a_{2} \frac{S(Y_{2} x^{n-2})}{(n-1)!} + a_{n} Y_{n}$$
$$= \sum_{j=0}^{n} a_{j} \frac{S(Y_{j} x^{n-j})}{(n+1-j)!}$$

The proof is by induction.

$$\begin{array}{rcl} \underline{n=1} & xy = \frac{xy + yx + xy - yx}{2} = \frac{S(xy)}{2} + \frac{1}{2} & y_{1} \\ \underline{n=2} & \frac{x^{2}y}{2} = \frac{x + S(xy)}{4} + \frac{1}{4} & xy_{1} \\ & = \frac{S(x^{2}y)}{4} - \frac{y + x^{2}}{4} + \frac{1}{4} & xy_{1} + y_{1}x + xy_{1} - y_{1}x \\ & (Using Theorem 6) \\ & = \frac{S(x^{2}y)}{4} - \frac{x^{2}y}{4} + \frac{S(y_{1}x)}{4} + \frac{1}{8} S(xy_{1}) + \frac{1}{8} & y_{2} \\ & \frac{3}{4} x^{2}y = \frac{S(x^{2}y)}{4} + S(xy_{1}) & \frac{3}{8} + \frac{1}{8} & y_{2} \\ & \frac{x^{2}y}{2} = \frac{S(x^{2}y)}{31} + a_{1} & \frac{S(y_{1}x)}{21} + a_{2}y_{1} \end{array}$$
where $a_{1} = \frac{1}{2} \quad a_{2} = \frac{1}{12} \quad a_{0} \equiv 1$

<u>n+1</u>

$$\frac{x^{n}y}{n!} = \frac{s(x^{n}y)}{(n+1)!} + a_{1} \frac{s(x^{n-1}y_{1})}{n!} + a_{2} \frac{s(x^{n-2}y_{2})}{(n-1)!} \dots a_{n}y_{n}$$

$$\frac{x^{n+1}y}{n!} = \frac{xs(x^{n}y)}{(n+1)!} + a_{1} \frac{xs(x^{n-1}y_{1})}{n!} + \dots a_{n} x y_{n}$$
now use theorem 6
$$\frac{x^{n+1}y}{n!} = \frac{s(x^{n+1}y)}{(n+1)!} + a_{1} \frac{s(x^{n}y_{1})}{n!} + a_{2} \frac{s(x^{n-1}y_{2})}{(n-1)!} + \dots$$

$$- \frac{y x^{n+1}}{(n+1)!} - \frac{a_{1} y_{1} x^{n}}{n!} - a_{2} \frac{y_{2} x^{n-1}}{(n-1)!} - \dots$$

now use theorem 7 $x^{n+1}y \left[\frac{1}{n!} + \frac{1}{(n+1)!}\right] = \frac{S(x^{n+1}y)}{(n+1)!} + a_1 \frac{S(x^ny_1)}{n!} + a_1 \frac{S(x^ny_1)}{n!}$ $a_2 \frac{S(x^{n-1}Y_2)}{(n-1)!} + \cdots$ + $\frac{S(Y_1 X^n)}{(n+1)!}$ - $\frac{a_1Y_1 X^n}{n!}$ - $a_2 \frac{Y_2 X^{n-1}}{(n-1)!}$ --- $x^{n+1}y \frac{n+2}{(n+1)!} = \frac{S(x^{n+1}y)}{(n+1)!} + S(x^{n}y_{1}) [\frac{a_{1}}{n!} + \frac{1}{(n+1)!}] +$ $S(x^{n-1}Y_2) \left[\frac{a_2}{(n-1)!} + \frac{1}{n!}\right] + \dots$ $-\frac{a_1 x'' y_1}{n!} - a_2 \frac{x'' - y_2}{(n-1)!} - a_3 \frac{x'' - y_3}{(n-2)!} - \cdots$ $= \frac{S(X^{n+1}Y)}{(n+1)!} + S(X^{n}Y_{1}) \left[\frac{a_{1}}{n!} + \frac{1}{(n+1)!} - \frac{a_{1}}{(n+1)!}\right]$ + $S(x^{n-1}Y_2) [\frac{a_2}{(n-1)!} + \frac{a_1}{n!} - \frac{a_1^2}{n!} - \frac{a_2}{n!}]$ + S $(x^{n-2}Y_3) \left[\frac{a_3}{(n-2)!} + \frac{a_2}{(n-1)!} - \frac{a_1a_2}{(n-1)!} - \frac{a_3}{(n-1)!}\right]$ + ... $= \frac{S(x^{n+1}Y)}{(n+1)!} + \sum_{K=1}^{n-1} E_{K} \frac{S(x^{n+K-1}Y_{K})}{(n+2-K)!}$ $E_1 = (n+1) + a_0 - a_1$ $E_2 + n a_2 + a_1 - a_1^2 - a_2$ $E_3 = (n-1) a_3 + a_2 - a_1 a_2 - a_2 a_1 - a_3$

$$E_{K} = (n-K+1) a_{K} + a_{K-1} - \sum_{j=1}^{K-1} a_{j} A_{K-j}$$

= (n+2) $a_{K} - (K+1) a_{K} + a_{K-1} - \sum_{j=1}^{K-1} A_{K-j}$
= (n+2) a_{K}

where the recursion relation for the coefficient $\boldsymbol{a}_{K}^{}$ is

(K+1)
$$a_{K} = a_{K-1} - \sum_{j=1}^{K-1} a_{j}a_{K-j}$$

 $a_{0} = 1, a_{1} = \frac{1}{2}, a_{2} + \frac{1}{12}, a_{3} = 0, a_{4} = -\frac{1}{720}, a_{2n+1} = 0$
 $(n \neq 0)$

$$\frac{x^{n+1}y}{(n+1)!} = \frac{S(x^{n+1}y)}{(n+2)!} + \sum_{K=0}^{\infty} \frac{S(x^{n-K-1}y_{K})}{(n+2-K)!}$$

Q.E.D.

The theorem now follows easily. We rewrite the expansion of $e^{X}Y$ in symmetrized form.

$$Y = Y$$

$$X Y = \frac{S(XY)}{21} + a_1Y_1$$

$$\frac{x^2Y}{21} = \frac{S(x^2Y)}{31} + \frac{a_1S(XY)}{21} + a_2Y_2$$

$$\frac{x^3Y}{31} = \frac{S(x^3Y)}{41} + a_1\frac{S(x^2Y)}{31} + a_2\frac{S(XY)}{21} + a_3Y_3$$

In resumming, the RHS is summed by diagonals and we use the definition

$$z = \sum_{j=0}^{\infty} a_j Y_j$$

$$e^{X} Y = Z + \frac{S(ZX)}{2!} + \frac{S(ZX^{2})}{3!} + \frac{S(ZX^{3})}{4!} + \cdots$$

$$e^{X}(1+Y) = 1 + (X+Z) + \frac{X^{2}+S(XZ)}{2!} + X^{3} + \frac{S(ZS^{2})}{3!} + \cdots$$

$$e^{X} Y = \frac{\partial}{\partial \lambda} \frac{e^{X}}{(1+\lambda Y)} |_{\lambda=0} = \frac{\partial}{\partial \lambda} e^{X} e^{XY} |_{\lambda=0}$$

$$= \frac{\partial}{\partial \lambda} \left[1 + \frac{(X+\lambda Z)}{1!} + \frac{(X+\lambda Z)^{2}}{2!} + \frac{(X+\lambda Z)^{3}}{3!} + \cdots\right] |_{\lambda=0}$$

$$= \frac{\partial}{\partial \lambda} e^{X+\lambda Z} |_{\lambda=0}$$

APPENDIX B

STATIC DISPLACEMENTS

APPENDIX B

STATIC DISPLACEMENTS

Static displacements of atoms from the perfect crystal lattice sites resulting from a substitutional impurity are calculated here by minimizing the total Gibbs Free Energy with respect to the atomic positions. Other methods of calculating static displacements will be critized at the end of this appendix. We divide the Gibbs Free Energy into a phonon energy, phonon entropy, configurational entropy and an applied pressure term.

$$G=V_{s}+U_{p}-TS_{p}-TS_{c}+PV$$

$$=V_{s}+F+PV-TS_{c}$$
(110)

where

 V_{g} = static lattice energy

F = Helmholtz Free Energy of phonons

S_c = configurational entropy

If the substitutional defect is not allowed any mobility the configurational entropy may be neglected. Static displacement vectors will be denoted by eta.

$$\begin{aligned} \mathbf{G} = \mathbf{V}_{\mathbf{S}} + \mathbf{F} + \mathbf{PV} \\ \nabla_{\eta} \quad \mathbf{G} = \nabla_{\eta} \nabla_{\mathbf{S}} = \nabla_{\eta} \quad (\mathbf{F}_{0} + \mathbf{PV}) = 0 \quad (\text{perfect lattice}) \\ \frac{\partial}{\partial \mathbf{G}} = \frac{\partial}{\partial \eta} \mathbf{V}_{\mathbf{S}} + \frac{\partial}{\partial \eta} \quad (\mathbf{F} - \mathbf{F}_{0}) \quad (\text{defect lattice}) \quad (111) \\ \text{We consider first the potential term and later the free energy.} \end{aligned}$$

If only the potential term is considered for the present and every atom is required to be in equilibrium we may expand the potential about the perfect crystal lattice sites and determine the static displacement vectors.

$$\Sigma_{j}^{\frac{1}{2}} V(r_{ij}) = 0 \text{ for all } i$$

$$0 = \sum_{j}^{\frac{1}{2}} V(r_{ij}) = \sum_{j} \{\frac{\frac{1}{2}}{r_{ij}} + \frac{\frac{1}{2}}{r_{ij}} + \frac{\frac{1}{2}}{r_{ij}} \cdot n_{ij}\} = \sum_{j}^{\sum_{j} \{V'_{ij} + \Phi_{ij}, n_{ij}\}} i = \sum_{j}^{\sum_{j} \{V'_{ij} + \sum_{j} \Phi_{ij}, n_{i} - \sum_{j} \Phi_{ij}, n_{j}\}} i = \sum_{j}^{\sum_{j} \{V'_{ij} - \sum_{j} \Phi_{ij}, n_{j} = A - \Phi \cdot n\}} (112)$$

Eta may now be found by inverting the force constant matrix (ϕ). This is difficult since ϕ has dimensions 3N X 3N where N is the number of atoms with which any one atom interacts. Assuming the defect is not displaced and does not interact with other defects, it is a center of inversion symmetry and only a spherical distortion

is expected. In this case the number of coordinates involved in the relaxation is just the number of shells of atoms considered. If a vector of direction cosines for atom j of shell λ is defined by Γ_j^{λ} we find a $\lambda_{\max} \propto \lambda_{\max}$ matrix equation.

Many shells of atoms are included here because it if often not possible to consider the relaxation of the nearest neighbors of a defect decoupled from the remainder of the lattice. As a trivial example we consider the case of a single defect in a one-dimensional lattice with nearest neighbor interactions where the first derivative of the potential connecting the defect to its nearest neighbor is changed and no force constants are changed. The effect on an infinite chain is easily visualized to be the displacement of every particle by an amount η_1 towards the defect. For a 2N+1 member chain the equation becomes

$$\begin{bmatrix} 2\Phi & -\Phi & 0 & 0 & \cdots & 0 \\ -\Phi & 2\Phi & -\Phi & 0 & \cdots & 0 \\ 0 & -\Phi & 2\Phi & -\Phi & \cdots & 0 \\ 0 & 0 & -\Phi & 2\Phi & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & 0 & \cdots & -\Phi \\ 0 & 0 & 0 & 0 & 0 & \cdots & 2\Phi \end{bmatrix} \begin{bmatrix} n_1 \\ n_1 \\ n_1 \\ \vdots \\ n_1 \\ \vdots \\ n_1 \\ \vdots \\ n_1 \\ \vdots \\ n_N \end{bmatrix} = \begin{bmatrix} -\delta V_{10} \\ 0 \\ 0 \\ 0 \\ \vdots \\ \vdots \\ 0 \end{bmatrix}$$
(114)

which is easily inverted to give

$$n_{\rm m} = - \frac{({\rm N}+1-{\rm m})}{{\rm N}+1} \frac{\delta V' 10'}{\Phi} \quad ({\rm m} > 0)$$
(115)

which goes to the correct result in the limit $N \rightarrow \infty$. The result of keeping only nearest neighbors is in error by a factor of 2.

Rather than putting all atoms in a shell in equilibrium as in equation 113 it is easier (and equivalent) to put one atom in each shell in equilibrium. The direction cosines for this chosen atom then can be expanded in terms of eta for purposes of iterating equation 112.

In the following V_{ij} denotes $V(R_{ij})$ where R_{ij} is the vector between sites i and j in the unperturbed lattice and $\cos(A,B)$ is the cosine of the angle between vectors A and B.

$$0 = \sum_{j} \vec{\nabla}_{r_{ij}} V(R_{ij} + \eta_{ij}) = \vec{\nabla}_{r_{ij}} \{V_{ij} + \vec{\nabla}_{r_{ij}} V_{ij} \cdot \eta_{ij}\}$$
$$= \sum_{j} \vec{\nabla}_{r_{ij}} V_{ij} + \vec{\nabla}_{r_{ij}} \frac{\partial V_{ij}}{\partial r_{ij}} \{\cos(ij,i)\eta_{i} - \cos(ij,j)\eta_{j}\}$$
(116)

If the defect is a center of inversion symmetry the sum on j is a radial vector in the direction of site 1. We therefore take the projection of each term along the radial vector and leave vector signs implicit.

$$A_i + z_{ij}\eta_j = 0$$

$$A_{i} = \sum_{j} \frac{\partial V_{ij}}{\partial r_{ij}} \cos(ij,0i)$$
(117)

$$z_{ij} = \begin{cases} \frac{\partial^{2} V_{ij}}{\partial r_{ij}^{2}} \cos(ij,0i) \cos(ij,0j) & i \neq j \\ -\Sigma & \frac{\partial^{2} V_{ij}}{\partial r_{ij}^{2}} \cos^{2}(ij,0i) & i = j \end{cases}$$
(118b)

We again have a $\lambda_{\max} \propto \lambda_{\max}$ system of equations. One can include effects of displacements from shells beyond the λ_{\max} without changing the order of equation by using the elastic limit for these displacements

$$n_{k}(k > \lambda_{max}) = \begin{cases} n_{\ell} \text{ 1 dimension} \\ n_{\ell} \frac{R_{\ell}}{R_{k}} \text{ 2 dimensions} \\ n_{\ell} (\frac{R_{\ell}}{R_{k}})^{2} \text{ 3 dimension} \end{cases}$$
(119)

Phonon Free Energy

If the normal modes of the defect lattice are harmonic phonons the change in the free energy can be written in terms of a density of states $g(\omega)$ or the phonon phase shift $\Theta(\omega)$.

$$\delta F = kT \int_{0}^{\infty} \delta g(\omega) \ln \left[2\sinh\left(\frac{\beta\omega}{2}\right)\right] d\omega \qquad (120)$$

It will be shown in equation 147 that

$$\delta g(\omega) = -\frac{1}{\pi} \frac{\partial}{\partial \omega} \ln |1-GQ| \qquad (121)$$

where Θ is the phonon phase shift, G the defect lattice with no static relaxation, and Q is the change in force constants due to the static relaxations.

$$Q_{ij} = \nabla_{xy}^{2} \nabla_{ij}^{(R+\eta) - \nabla_{xy}^{2}} \nabla_{ij}^{(R)}$$

$$= \frac{xy}{r^{2}} \{ (\nabla^{(3)} - \frac{\nabla^{(2)} - \tau}{r}) (\hat{r} \cdot \eta) + (\nabla^{(4)} - \frac{\nabla^{(3)}}{r} + \frac{\nabla^{(2)} - \tau}{r^{2}}) (\hat{r} \cdot \eta)^{2} \}$$

$$+ \delta_{xy} \{ \frac{\nabla^{(2)} - \tau}{r} \hat{r} \cdot \eta + (\frac{\nabla^{(3)}}{2} - \frac{\nabla^{(2)} - \tau}{r^{2}}) (\hat{r} \cdot \eta)^{2} \}$$

$$\equiv Q^{(1)} \hat{r} \cdot \eta + \frac{1}{2} Q^{(2)} (\hat{r} \cdot \eta)^{2}$$
(122)

 $v^{(n)}$ is the nth derivative of V. Differentiating and performing the integrals the free energy contribution to equation can be found.

$$\Sigma \vec{\nabla}_{\mathbf{r}}_{\mathbf{j}} \delta \mathbf{F} = -2\Sigma Q_{\mathbf{j}}^{(1)} D_{\mathbf{j}}_{\mathbf{\alpha}\beta} \cos(i\mathbf{j},0\mathbf{i}) \hat{\mathbf{r}}_{\mathbf{i}} + \Sigma \{-2D_{\mathbf{j}} Q_{\mathbf{j}}\mathbf{i} - \frac{2\mathbf{N}}{\pi} \int_{0}^{\infty} \mathrm{Im} (\mathbf{G}_{\mathbf{i}}\mathbf{i} \mathbf{G}_{\mathbf{j}} \mathbf{G}_{\mathbf{j}} \mathbf{G}_{\mathbf{i}} \mathbf{G}_{\mathbf{i}}$$

There exist other methods for calculating static relaxations. The method of lattice statics by Hardy⁵⁸ yields displacements in the elastic limit which in general will not be applicable near the defect. The method of lattice statics uses the first two derivatives of the potential and is not easily iterated. Two previous calculations applied to isotopically impure helium used a continuum model. Maradudin and Klemens⁵⁹ neglected the potential energy contribution to the free energy, while Klemens et al.⁵² neglected the possibility of an isotopically dependent potential. Other calculations consider only the potential part of the free energy.^{60,61} APPENDIX C

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HARMONIC OSCILLATORS AND STATISTICS

APPENDIX C

HARMONIC OSCILLATORS AND STATISTICS

The purpose of this section is to further examine the relation of gaussians and harmonic oscillators and then for completeness to gather some statistical relations. The ensemble average of an operator A is given by

$$= tr \rho A = \frac{1}{z} tr \(e^{-\beta H} A\)$$
(124)
$$= \frac{a}{z} \sum_{n} \frac{e^{-\beta \omega} (n + \frac{1}{2})}{2^{n} n! \sqrt{\pi}} (H_{n} (ax) e^{-a^{2} \frac{x^{2}}{2}}, A(x) H_{n} e^{-a^{2} \frac{x^{2}}{2}})$$
$$= \int \{\frac{a}{z} \sum_{n} \frac{e^{-\beta \omega} (n + \frac{1}{2})}{2^{n} n! \sqrt{\pi}} H_{n}^{2} (ax) e^{-a^{2} x^{2}}\} A(x) dx$$
(125)
$$\equiv \int \rho(x) A(x) dx$$
(126)

provided the Hamiltonian is harmonic. H are Hermite polynomials. $\rho(x)$ is an average of field operators

$$\rho(\mathbf{x}) = \langle \Psi^{\dagger}(\mathbf{x}, t^{\dagger}) | \Psi(\mathbf{x}, t) \rangle \qquad (127)$$

The braced quantity can be evaluated using⁶²

$$\sum_{n=0}^{\Sigma} \frac{\frac{H_n(x)H_n(y)}{2^n n!}}{2^n n!} t^n = (1-t^2)^{-1/2} \exp\{\frac{2xyt-(x^2+y^2)t^2}{1-t^2}\}$$
(128)

$$\rho(\mathbf{x}) = \sqrt{\frac{\mathbf{a}^2}{\pi}} \tanh(\beta\omega/2) \exp(-\mathbf{a}^2 \tanh\frac{\beta\omega}{2} \mathbf{x}^2) \quad (129)$$
$$= \sqrt{\frac{1}{2\pi \langle \mathbf{x}^2 \rangle}} \exp(-\mathbf{x}^2/2 \langle \mathbf{x}^2 \rangle)$$
$$\langle \mathbf{x}^2 \rangle = \int \rho(\mathbf{x}) \ \mathbf{x}^2 d\mathbf{x} = \frac{\coth(\beta\omega/2)}{2\mathbf{a}^2}$$

The density function is a gaussian. Note it is also the square of the ground state wavefunction with a temperature dependent width. The density function (or number operator) is the diagonal term of the field theoretic Green's function

$$G = \langle \Psi^{\dagger}(x,t) \Psi(x',t') \rangle \Theta(t-t')$$
 (130)

Using equation 129 we can evaluate G.

$$G = \frac{\phi(t-t')}{z} \sum_{n} e^{[-\beta+i(t-t')][n+\frac{1}{2}]\omega}$$

$$x \frac{Hn(ax)Hn(ax')e^{-\frac{a^{2}x^{2}}{2}}e^{-\frac{a^{2}x'^{2}}{2}}}{2^{n}n!\sqrt{\pi}}$$

$$G(\mathbf{x}\mathbf{t},\mathbf{x}'\mathbf{t}') = \Theta \sqrt{\frac{2a}{\pi}} \frac{\sinh(\beta\omega/2)}{\sinh(\beta\omega-i(\mathbf{t}-\mathbf{t}')\omega)}$$
$$\exp\left\{\frac{-a^2}{2} (\mathbf{x}^2 + \mathbf{x}'^2) \coth[\beta\omega-i(\mathbf{t}-\mathbf{t}')\omega] + \frac{a^2\mathbf{x} \mathbf{x}'}{\sinh[\beta\omega-i\omega(\mathbf{t}-\mathbf{t}')]}\right\}$$

$$G(\mathbf{xt},\mathbf{x't'}) = \sqrt{\frac{2a}{\pi}} \frac{\sinh(\beta\omega/2)\,\Theta(\mathbf{t-t'})}{\sinh(\beta\omega-i(\mathbf{t-t'})\,\omega)}$$
$$\exp\left\{-a^2\mathbf{x}^2 \,\tanh\left[\frac{\beta\omega}{2} - \frac{i(\mathbf{t-t'})}{2}\right]\right\}$$
(131)

Useful statistical functions are the characteristic (χ) , moment generating (M), and cumulant functions (K). Because the density function is a gaussian these properties are easy to calculate and are listed below.

$$\chi(b) = \langle e^{ibx} \rangle = \int e^{ibx} \rho(x) dx = e^{-b^2/4a}$$
 (132)

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$$M(b) = \langle e^{-bx} \rangle = e^{b^2/4a}$$
 (133)

$$K_{r} = \frac{d^{2}}{ds^{2}} \log M(s) \Big|_{s=0} = \frac{1}{2a} \delta_{r,2}$$
(134)

For completeness we include the classical analogs of the above. For an oscillator with fixed energy and amplitude A:

$$P_{C}(\mathbf{x}) = \frac{1}{\pi A} \frac{1}{\sqrt{1 - (\frac{\mathbf{x}}{A})^{2}}}$$
(135)

$$\langle \mathbf{x}^{n} \rangle = \mathbf{A}^{n} \frac{(n-1)!!}{n!!} \qquad \delta_{n, \text{even}}$$

$$\chi(\mathbf{q}) = \Sigma \frac{(\mathbf{iq})^{n}}{n!} \langle \mathbf{x}^{n} \rangle = \mathbf{J}_{0}(\mathbf{Aq})$$

$$K_{r} = (\mathbf{i})^{-r} \frac{\partial^{r}}{\partial q^{r}} \log \chi(\mathbf{q}) |_{q=0} \qquad K_{odd} = 0 \qquad K_{2} = \frac{\mathbf{A}^{2}}{2} \qquad K_{4} = \frac{27\mathbf{A}^{4}}{8}$$

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The quantum and classical statistics are inosculated by considering the classical ensemble average.

$$P_{c}(x) = \sqrt{\frac{m\omega^{2}\beta}{\pi}} e^{-m\omega^{2}\beta x^{2}/2} \equiv \sqrt{\frac{b}{\pi}} e^{-b^{2}x^{2}/2}$$
 (136)

This is similar to the quantum result; the difference is in the inverse width of the distributions.

$$b = \sqrt{\frac{m\omega^2}{kT}}$$
 classical (137a)

$$a = \sqrt{\frac{2m\omega}{M}} (\tanh \frac{M\omega}{2kT})^{+1/2} \quad \text{quantum} \quad (137b)$$

$$\lim_{kT > h\omega} a = \sqrt{\frac{m\omega^2}{kT}}$$
(138)

Equation 138 is a demonstration of the correspondence principle.

APPENDIX D

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DENSITY OF STATES

APPENDIX D

DENSITY OF STATES

We derive here some formulas for the density of phonon states. Q will be a unitary transformation which diagonalizes the product of the diagonal mass matrix and the displacement Green's functions. The eigenstates of the defect crystal will be labeled s.

$$m \varepsilon \omega^{2} G_{\ell \ell} = \delta_{\alpha \beta} \delta_{\ell \ell} + \sum_{\substack{\gamma \ell \\ \gamma \ell}} \Phi_{\ell \ell} G_{\ell} G_{\ell}$$
(139)

$$\sum_{\substack{\boldsymbol{\ell} \\ \boldsymbol{\alpha}\beta \\ \boldsymbol{\gamma}^{3} \\ \boldsymbol{\gamma}^{3}}} \sum_{\boldsymbol{\gamma}^{1}} \sum_{\boldsymbol{\beta}^{1}} \sum_{\boldsymbol{\beta}^{1}}$$

$$\sum_{l\alpha} Q_{s}^{l\alpha} Q_{s'}^{l\alpha} \equiv \delta_{ss'}$$
(141a)

$$\sum_{\mathbf{s}} Q_{\mathbf{s}}^{\boldsymbol{l}\alpha} Q_{\mathbf{s}}^{\boldsymbol{l}'\boldsymbol{\beta}} \equiv \delta_{\boldsymbol{l}\boldsymbol{l}}, \delta_{\boldsymbol{\alpha}\boldsymbol{\beta}}$$
(141b)

$$\sum_{\substack{\ell \\ \ell \\ \alpha\beta}} Q_{s}^{\ell \alpha} \frac{\alpha \beta}{m_{\ell}} Q_{s'}^{\dagger \ell' \beta} \equiv \omega_{s}^{2} \delta_{ss'}$$
(141c)

Using equations 141 in equation 140 we find

$$\frac{1}{3N} \operatorname{tr} \left[\operatorname{QmGQ}^{\dagger} \right] = \frac{1}{3N} \sum_{s} \frac{1}{\omega^{2} - \omega_{s}^{2}}$$

$$\lim_{\delta \to 0} \operatorname{Im} \frac{1}{3N} \operatorname{tr} \left[\operatorname{QmG} (\omega + i\delta) \mathcal{Q} \right] = -\frac{\pi}{3N} \sum_{s} \delta (\omega^{2} - \omega_{s}^{2}) = -\pi g (\omega^{2}) \quad (142)$$

$$g (\omega^{2}) = -\frac{1}{\pi 3N} \sum_{\ell \alpha} m_{\ell} G_{\ell \ell} (\omega + i0^{+}) \quad (143)$$

The last step follows by invariance of the trace to representation.

If we consider a mass defect

$$\Delta g(\omega^{2}) = -\frac{1}{\pi 3N} \sum_{\ell \alpha} \{ m_{\ell}^{\prime} G_{\ell \ell} - m_{G}^{0} \xi_{\ell \ell} \}_{\alpha \alpha}$$
$$= -\frac{1}{\pi 3N} \sum_{\ell \alpha} \{ -m_{\ell} \varepsilon_{\ell} G_{\ell \ell}^{0} + m_{\ell} (1 - \varepsilon_{\ell}) (G^{0} T G^{0}) \xi_{\ell} \}_{\alpha \alpha} \}$$

This result is cumbersome. A more eloquent general result can be found in terms of the phonon phase shift.

where we have used a relation true for a nonsingular A.

$$tr ln A = ln$$
 Det A
Then since

$$\omega_{+}^{2} - \Phi = (\omega_{+}^{2} - \Phi) \{1 - (\omega^{2} - \Phi_{0})^{-1}C\},$$

$$g(\omega^{2}) = -\frac{1}{\pi N} \operatorname{Im} \frac{\partial}{\partial \omega^{2}} \ln \operatorname{Det} \{(\omega_{+}^{2} - \Phi_{0})(1 - G^{0}(\omega_{+}^{2})C)\}$$
(145)

The determinant of the product of two square matrices is the product of the determinants.

$$\Delta g(\omega^2) = -\frac{1}{\pi N} \operatorname{Im} \frac{\partial}{\partial \omega^2} \operatorname{In} \operatorname{Det} \left\{ 1 - G^{\mathsf{O}}(\omega_+^2) C \right\}$$
(146)

$$\Delta g(\omega^2) = -\frac{1}{\pi N} \frac{\partial}{\partial \omega^2} \Theta(\omega_+^2) \quad \Theta(\omega_+^2) \equiv \text{Im In Det } \left| 1 - G^{O}(\omega_+^2) C \right|$$
(147)

This can be rewritten in a form which is sometimes more useful by expanding the determinant and expressing the force constant perturbation in an orthogonal basis.

$$\Delta g(\omega^2) = \operatorname{Im} \frac{1}{\pi} \frac{\partial}{\partial \omega^2} \ln \left| 1 - G^{\circ} C \right|$$
(148)

$$\Delta g(\omega^2) = -\frac{1}{\pi} \frac{\partial}{\partial \omega^2} \sum_{n} \operatorname{tr} \frac{(G^0 C)^n}{n}$$
(149)

using, ln Det A = \sum_{i} ln A_i A_i (eigenvalues) = 1-x_i = \sum_{i} ln(1-x_i) = - \sum_{i} $\sum_{n=1}^{\infty}$ $\frac{(x_1)^n}{n}$ (150) = -tr $\sum_{n=1}^{\infty}$ $\frac{x^n}{n}$

After differentiation equation 149 can be resummed as a geometric series.

$$\Delta g(\omega^2) = -\operatorname{Im} \frac{1}{\pi} \operatorname{tr} \sum_{n=0}^{\infty} (G^{\circ}C)' (G^{\circ}C)^n$$
(151)

$$= -Im \frac{1}{\pi} tr (G^{\circ}C)' (1-G^{\circ}C)^{-1}$$
 (152)

In equation 151 the derivative could be commuted to the left in each term because of the trace operation. The prime denotes differentiation with respect to ω^2 . We now expand the perturbation in an orthogonal basis. Band indices will be labeled j and V is a folded matrix.

$$C_{qq'} = \sum_{ik} V_{ik} \quad \Psi_{i}^{*}(q) \Psi_{k}(q') \qquad (153)$$

$$g(\omega^{2}) = -Im \frac{1}{\pi} tr\{ (G^{\circ}C) \mid_{qq}^{*} + (G^{\circ}C) \mid_{qq_{1}}^{*} G_{q_{1}j_{1}}^{\circ} \int_{1j_{1}}^{*} G_{q_{1}q}^{*} + \dots \}$$

$$= -Im \frac{1}{\pi} tr\{ (\Lambda_{ki} V_{ik}) \mid + (\Lambda_{ki} V_{im}) \mid \Lambda_{mn} V_{nk} + \dots \}$$

$$= -Im \frac{1}{\pi} tr\{ (\Lambda V) \mid (1 - \Lambda V)^{-1} \} \qquad (154)$$

$$\Lambda_{ik} \equiv \delta_{jj}, \Sigma \Psi_{i}(\underline{q}) G_{qj}^{\circ} \Psi_{k}^{*}(\underline{q})$$

$$jj', \overline{q} \qquad (155)$$

Mass Defect Example

$$C_{\ell\ell} = m\varepsilon\omega^2 \, \delta_{\ell\beta} \, \delta_{\ell\beta} \, \delta_{\alpha\beta}$$
(156)

$$C_{qq'} = \sum_{\substack{\elll'\\ jj'}} e^{iq' \ell} e^{-iq' \ell} \sigma_{\alpha}^{j}(q) \sigma_{\beta}^{\star j'}(q) C_{\ell\ell}, \alpha_{\beta}^{\prime}$$

$$= m\epsilon\omega^{2} \delta_{jj}, G_{\ell\ell}^{0}, \beta_{jj}^{\prime}, \alpha_{\beta}^{\prime}, \alpha_{$$

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$$C_{qq'} = V_{jj'} \cdot g \cdot g'$$

$$= qq' V_{jj'} \cdot \frac{2\pi}{3} Y_{11} (g) Y_{11}^{*} (g') + Y_{10} (g) Y_{10}^{*} (g') + Y_{1-1} (g) Y_{1-1}^{*} (g')$$

$$\Lambda_{-10}^{j} \equiv \sum_{g} q Y_{1-1} (g) Y_{10}^{*} (g) G_{gj}^{0}$$

$$\Lambda_{1-1}^{j} = \sum_{g} q^{2} Y_{1-1}^{*} (g) Y_{11} (g) G_{gj}^{0}$$

and V are now 9 X 9 matrices. By imbedding the band indices j into azimuthal matrix elements, we find the following form.

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$$\Lambda \mathbf{v} = \begin{bmatrix} \Lambda_{11} \ \mathbf{v}_{11} & \Lambda_{1-1} \mathbf{v}_{11} & \Lambda_{10} \ \mathbf{v}_{11} \\ \Lambda_{1-1}^{\star} \mathbf{v}_{11} & \underline{\Lambda}_{1-1} \mathbf{v}_{11} & \Lambda_{-10} \mathbf{v}_{11} \\ \Lambda_{10}^{\star} \ \mathbf{v}_{11} & \underline{\Lambda}_{1-1}^{\star} \mathbf{v}_{11} & \Lambda_{-10} \mathbf{v}_{11} \end{bmatrix}$$

In order to find a simple result we consider the case of spherical bands.

$$\Lambda_{\ell m}^{j} = \delta_{\ell m} \sum_{q} q^{2} G_{qj}^{O} = \delta_{\ell m} (1 - m\omega^{2} G_{OO}^{O})$$
(159)
jj

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G is the diagonal element of the real space perfect jj crystal Green's function.

$$\Lambda \mathbf{V} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \begin{array}{c} (1 - m\omega^2 \mathbf{G}_{00}^{\mathbf{O}}) \mathbf{V}_{jj}, \\ jj \end{array}$$

$$\Delta g(\omega) = -\operatorname{Im} \frac{2\omega}{\pi} \sum_{jj'} [(1 - m\omega^2 G_{00}^{0}) V_{jj'}] [-\frac{1}{3} (1 - m\omega^2 G_{00}) V_{jj'}]$$
(160)

If the perturbation does not couple bands and is the same for all bands,

$$V_{jj}, = \delta_{jj}, V$$

$$\Delta g(\omega) = -\operatorname{Im} \frac{2\omega}{\pi} \sum_{j} \frac{[(1-m\omega^2 G_{OO}^{O})V]'}{1-\frac{1}{3}(1-m\omega^2 G_{OO}^{O})V}$$
(161)

APPENDIX E

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SCATTERING

APPENDIX E

SCATTERING

In transport problems the phonon lifetime is required. It will be shown that the phonon lifetime can be calculated from the T-matrix for the displacement Green's function. For structureless scattering centers the lifetime is found to be temperature independent. This appendix begins with the calculation of the phonon Green's functions by several methods, comparison of the various T-matrices, lifetime calculation and finally the connection with phase shifts is given.

Retarded Green's Functions

The displacement Green's function (G) is a linear combination of a phonon Green's function (g_{-}) and a "hole" Green's function (g_{+}) , the propagation of the state with one phonon removed.

$$G_{k}(\omega) = \frac{1}{2\omega} \left(\frac{1}{\omega + \omega_{k}} + \frac{1}{\omega - \omega_{k}}\right) = \frac{1}{2\omega} \left(g_{+k} + g_{-k}\right)$$
(162)

In deriving equations for these Green's functions several definitions are necessary:

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$$g_{+kk'} = -2\pi <> \equiv (-2\pi) [-i\Theta(t)<[a_k^{\dagger}(t),\alpha_{k'}(0)]>]$$
(163a)

$$g_{-kk'} = 2\pi << a_k(t) a_k^{\dagger}(0) >>$$
 (163b)

$$f_{kk'} = 2\pi << a_k^{\dagger}(t) a_{k'}^{\dagger}(0) >>$$
 (163c)

$$h_{kk'} = -2\pi << a_k(t)a_{k'}(0)>>$$
 (163d)

The name of the phonon Green's function is justified by the interpretation of the related correlation function

$$\langle \mathbf{a}_{\mathbf{k}}(t) \ \mathbf{a}_{\mathbf{k}}^{\dagger}(0) \rangle = \lim_{\delta \to 0} \frac{\mathbf{i}}{2\pi} \int_{-\infty}^{\infty} e^{-\mathbf{i}\omega t} \mathbf{g}_{-\mathbf{k}\mathbf{k}}(\omega + \mathbf{i}\delta) \ [\mathbf{n}(\omega) + 1] \ d\omega$$
 (164)

as the probability amplitude for creating a phonon of wavevector k' at time zero and destroying a phonon of wavevector k at time t. In this sense then g_ allows one to follow the evolution of the n+1 phonon state.

The Hamiltonian in momentum states

$$H = \sum_{k} \varepsilon_{k} (a_{k}^{\dagger}a_{k}^{\dagger} + \frac{1}{2}) + \frac{1}{2} \sum_{kk'} V_{kk'} (a_{k}^{\dagger} + a_{k'}) (a_{k'}^{\dagger} + a_{k'})$$
(165)

is found by transforming the real space Hamiltonian

$$H = \frac{P_{\ell\alpha}^2}{2m} + \frac{1}{2} \sum_{\ell\ell} \Phi_{\ell\ell} u_{\ell\alpha} u_{\ell\beta} + \frac{1}{2} \sum_{\ell\ell} C_{\ell\ell} u_{\ell\alpha} u_{\ell\beta}$$
(166)

where

$$P_{l\alpha} = \frac{\sqrt{1}}{3N} \sum_{\substack{k j \\ k j}} i \frac{\sqrt{m\omega_k k}}{\sqrt{2}} \sigma_{\alpha}^{j}(k) (a_{k}^{\dagger} - a_{k}) e^{ik \cdot l}$$
(167a)

$$u_{l\alpha} = \frac{\sqrt{1}}{3N} \sum_{\substack{k \ j}} \sqrt{\frac{\varkappa}{2m\omega_{k}}} (a_{k}^{\dagger} + a_{k}) e^{i \frac{\kappa}{2} \cdot \frac{l}{2}\sigma_{\alpha}^{j}(k)}$$
(167b)

We identify $V_{kk'} = C_{kk'} \frac{1}{4m\sqrt{\omega_k \omega_k'}}$. For a mass defect $V_{kk'} = \frac{1}{4m\sqrt{\omega_k \omega_k \omega_k'}}$

The equation of motion for g_{is} found by taking the time derivative using Heisenberg's equation of motion:

$$i \not i \ \dot{g}_{-kk} = \delta(t) \delta_{kk}, \quad (2\pi \not k) + \varepsilon_k g_{-kk}, \quad + \sum_i v_{ki} (g_{-ik}, +f_{ik}).$$
$$i \not k \ \dot{f}_{ik} = -\varepsilon_i f_{ik}, \quad - \sum_k v_{ik} (f_{kk}, +g_{-kk}).$$

Fourier transforming and solving for g_

$$g_{-} = \{ (1-g_{-}^{o}V) + g_{-}^{o}V (1+g_{-}^{o}V)^{-1} g_{+}^{o}V \}^{-1} g_{-}^{o}$$

Superscript zeros denote unperturbed functions. g₊ is found similarly:

$$i \not h \dot{g}_{+kj} = 2\pi \not h \delta(t) \delta_{kj} - \epsilon_k g_{+kj} - V_{kl} (g_{+lj} + h_{lj})$$
$$i \not h \dot{h}_{lj} = \epsilon_l h_{lj} + V_{lk} (g_{+kj} + h_{kj})$$

Fourier transforming and solving for g₊

$$g_{+} = [(1+g_{+}^{O}V) + g_{+}^{O}V(1-g_{-}^{O}V)^{-1} g_{-}^{O}V]^{-1} g_{+}^{O}$$

Having derived the Green's functions we display the results in closed, Dyson, and T-matrix form.

$$g_{+} = [(1+g_{+}^{O}V) + g_{+}^{O}V(1-g_{-}^{O}V)^{-1} g_{-}^{O}V]^{-1} g_{+}^{O}$$

$$g_{-} = [(1-g_{-}^{O}V) + g_{-}^{O}V(1+g_{+}^{O}V)^{-1} g_{+}^{O}V]^{-1} g_{-}^{O}$$

$$G = (1-G^{O}C)^{-1}G^{O}$$

$$g_{+} = g_{+}^{O} + g_{+}^{O}V(1 + [1 - g_{-}^{O}V]^{-1} g_{-}^{O}V) g_{+}$$

$$g_{-} = g_{-}^{O} + g_{-}^{O}V(1 - [1 + g_{+}^{O}V]^{-1} g_{+}^{O}V) g_{-}$$

$$G_{-} = G_{-}^{O} + G_{-}^{O}CG$$

$$g_{+} = g_{+}^{\circ} + g_{+}^{\circ}t_{+}g_{+}^{\circ}$$
$$g_{-} = g_{-}^{\circ} + g_{-}^{\circ}t_{-}g_{-}^{\circ}$$
$$G = G^{\circ} + G^{\circ}TG^{\circ}$$

T-matrices

$$t^{+} = -V(1 - [1 - g_{-}^{o}V]^{-1}g_{-}^{o}V) \{1 + g_{+}^{o}V(1 - [1 - g_{-}^{o}V]^{-1}g_{-}^{o}V)\}^{-1}$$

$$t_{-} = -V(1 - [1 - g_{+}^{o}V]^{-1}g_{+}^{o}V) \{1 + g_{-}^{o}V(1 - [1 - g_{+}^{o}V]^{-1}g_{+}^{o}V)\}^{-1}$$

$$T = C(1 - G^{o}C)^{-1}$$

C is the force constant perturbation

Note that $g_+(\omega) = -g_-(-\omega)$ $t_+(\omega) = -t_-(-\omega)$

A relation between t_ and T can be found by equating two T-matrix forms for G.

$$G = G^{\circ} + G^{\circ} TG^{\circ} = \frac{1}{2\omega} (g_{+}^{\circ} + g_{-}^{\circ}) = \frac{1}{2\omega} (g_{+}^{\circ} + g_{+}^{\circ} + g_{+}^{\circ} + g_{-}^{\circ} + g_{-}^{\circ} + g_{-}^{\circ})$$

$$G^{\circ} TG^{\circ} = \frac{1}{2\omega} (g_{+}^{\circ} t_{+} g_{+}^{\circ} + g_{-}^{\circ} t_{-} g_{-}^{\circ})$$

$$T_{kk'} = \frac{(\omega - \omega_{k}) t_{+kk'} (\omega) (\omega - \omega_{k'})}{2\omega} + \frac{(\omega + \omega_{k}) t_{-kk'} (\omega) (\omega + \omega_{k'})}{2\omega}$$
(168)
$$= -\frac{(\omega - \omega_{k}) t_{-kk'} (-\omega) (\omega - \omega_{k'})}{2\omega} + \frac{(\omega + \omega_{k}) t_{-kk'} (\omega) (\omega + \omega_{k'})}{2\omega}$$

In the case of elastic scattering $(\omega_k = \omega_k)$, T and t_ are simply related by a factor 2ω .

Time Dependent Scattering

The phonon transition probability will be found to be linear in time. The inverse lifetime is then given by

$$\frac{1}{\tau_{k}} = \sum_{k'} \lim_{t \to 0} \left| \frac{\langle a_{k'}(t) | a_{k}^{\dagger}(0) \rangle}{\sqrt{(n_{k}+1)(n_{k'}+1)}} \right|^{2} \frac{1}{t}$$
(169)

The thermal factors in the denominator normalize the states $a^{\dagger}_{k'}|_{0>}, a^{\dagger}_{k}|_{0>}$.

$$A_{kk} = \langle a_{k}, (t) a_{k}^{\dagger}(0) \rangle = \frac{i}{2\pi} \int_{-\infty}^{\infty} [1-n(\omega)] e^{-i\omega t} g_{-k}, (\omega) t_{-kk}, g_{-k}(\omega)$$
$$= \frac{[n(\omega_{k})+1]}{\omega_{k}-\omega_{k}} t_{-k}, (\omega_{k}) e^{-i\omega_{k}t} + [n(\omega_{k})+1] \frac{t_{-kk}, (\omega_{k})}{\omega_{k}, -\omega_{k}} e^{-i\omega_{k}t}$$

Once $A_{k'k}$ is divided by the nomalizing thermal factors it is independent of temperature. The poles of t have been neglected since these give short transient effects except in the case of a localized mode where its residue must also be included. Performing the square and limiting operation:

$$\frac{1}{\tau_{k}} = 2\pi \sum_{k'} \left| t_{-kk'}(\omega_{k}) \right|^{2} \delta(\omega_{k} - \omega_{k'})$$
(170)

$$= 2\pi \sum_{\mathbf{k}'} \frac{\left| \frac{\mathbf{T}_{\mathbf{k}'\mathbf{k}}(\omega_{\mathbf{k}})}{4\omega_{\mathbf{k}'}^2} \right|^2}{4\omega_{\mathbf{k}'}^2} \delta(\omega_{\mathbf{k}} - \omega_{\mathbf{k}'})$$
(171)

Where equation 168 has been used. If the T-matrix depends on the final wavevector only via the final state energy the delta function may be replaced by the density of final states.

$$\frac{1}{\tau_{k}} = \pi N \frac{g(\omega_{k})}{2\omega_{k}^{2}} \left| T_{kk}, (\omega_{k}) \right|^{2}$$
(172)

$$= - \frac{\mathrm{Nm}}{\omega_{k}} \operatorname{Im} \left[\operatorname{G}_{ll}^{O} \mid T_{k'k}(\omega_{k}) \right]^{2}$$
(173)

Perturbation Scattering Theory

Perturbation techniques make use of the time ordered Green's function

$$i\overline{G}_{k}(t) = \langle T a_{k}(t) a_{k}^{\dagger}(0) \rangle$$
 (174)

which can be related to the advanced and retarded functions via the spectral function. 36

$$g^{R}(k\omega) = \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \frac{\rho(k\omega')}{\omega - \omega' + i\eta}$$
(175a)

$$g^{A}(k\omega) = \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \frac{\rho(k\omega')}{\omega - \omega' - i\eta}$$
(175b)

$$\overline{G} = [1 + e^{-\beta\omega}]^{-1} g^{R}(k\omega) + [1 + e^{\beta\omega}]^{-1} g^{A}(k\omega)$$
(175c)

For real frequencies these reduce to

$$\operatorname{Im} g^{\mathrm{R}}(k\omega) = -\frac{1}{2}\rho(k\omega) \qquad (176a)$$

$$\operatorname{Im} g^{\mathbf{A}}(k\omega) = + \frac{1}{2}\rho(k\omega)$$
 (176b)

$$\operatorname{Im} \overline{G} = -\frac{1}{2} \operatorname{coth} \left(\frac{B\omega}{2}\right) \rho(k\omega)$$
 (176c)

$$\operatorname{Re} \overline{G} = \operatorname{Re} g^{R} = \operatorname{Re} g^{A}$$
 (176d)

These relations permit the calculation of the spectral function from either the time ordered or the retarded Green's functions previously considered. Note that for zero temperature the real and imaginary parts of the time ordered and retarded functions are equal. The imperfect crystal propagator can be expanded in the usual way. 36

$$\overline{G}_{kk'}(t) = -i \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int_0^{\beta} \dots \int_0^{\beta} \dots d\tau d\tau d\tau (\tau_1) \dots V(\tau_n) a_k(t) a_k^{\dagger}(0) > (177)$$

$$\mathbf{v} = \sum_{kk'} \mathbf{v}_{kk'} (\mathbf{a}_{k}^{\dagger} + \mathbf{a}_{k}) (\mathbf{a}_{k'}^{\dagger} + \mathbf{a}_{k'})$$

This potential allows only the following interactions between two phonons (order of operation plotted vertically): $k \land k' \land k' \land k' \land k' \land k' \land k'$

Using Wick's expansion of the ordered product

$$i\overline{G}_{kk'}(t) = \int_{k'}^{k'} \int_{k'}^{k'}$$

Dyson's equation can be employed to simplify the summation by extracting the irreducible self-energy by grouping graphs.

$$\overline{G}^{O} = \overline{G}^{O} + \overline{G}^{O} \Sigma \overline{G} = (1 - \overline{G}^{O} \Sigma)^{-1} \overline{G}^{O}$$
(178)

$$\Sigma = v_{kk} + v_{kk_1} g_{0k_1}^{<} v_{k_1k} + v_{kk_1} g_{0k_1}^{<} v_{k_1k_2} g_{0k_2} v_{k_2k_3} + \dots$$
(179)

$$= V (1 - g_0^{<} V)^{-1}$$
 (180)

$$\overline{G} = -i \langle T a_{k}^{\dagger}(t) a_{k}^{\dagger}(0) \rangle \qquad \overline{G}^{\circ} = g_{o}^{\circ}$$
 (181)

$$g^{<}(kt) = i\Theta(t) < a_{k}^{\dagger}(t) a_{k}(0) > g_{0}^{<}(k\omega) = -\frac{1}{\omega + \omega_{0} - i\delta}$$
 (182)

$$g^{>}(kt) = i\Theta(t) < a_{k}(t) a_{k}^{+}(0) > g_{0}^{>}(k\omega) = \frac{1}{\omega - \omega_{0} + i\delta}$$
 (183)

$$\overline{G} = G^{\circ} + G^{\circ} \Sigma G = g^{\circ} + g^{\circ} \Sigma \overline{G}$$

$$= (1 - g^{\circ} \Sigma) g^{\circ}$$

$$= \{1 - g_{o}^{\circ} V (1 - g_{o}^{\circ} V)^{-1}\}^{-1} g_{o}^{\circ}$$
(184)

Time Independent Scattering

Beginning an equation of motion for displacement waves, we now derive the time independent scattering equations

$$(m\omega^2 - \Phi) | u > = 0, \Phi = \Phi_0 + c$$
 (185)

 Φ are the atomic force constants. The above can be written as a Lippmann-Schwinger equation by use of the displacement Green's function.

$$(m\omega^{2}-\Phi) | u > = c | u >$$

$$|u > = |u_{o} > +G_{o}C | u = |u_{o} > +G_{o}T | u_{o} >$$
(186)

where $T=C(1-G^{\circ}C)^{-1}$

If we consider an incident wave $\langle r | u_0 \rangle = e^{i \frac{k}{c} \cdot r} \sigma_{\alpha}^{j}(k)$ with polarization σ , branch j and wave vector k, the scattering equation in real space becomes

The scattered wave is

$$\Psi(\mathbf{r}_{\ell}) = \sum_{\substack{\beta \neq \ell \\ \ell_2}} G_{\ell \ell}^{\circ} T_{\ell} e^{\mathbf{i}\mathbf{k} \cdot \ell_2} \sigma_{\gamma}^{\mathbf{j}}(\mathbf{k})$$
(188)

and can be written as a spherical wave by expanding the Green's function for large distances from the scattering center.

$$G_{\alpha\beta}^{o}(R\omega) = \frac{1}{3 \text{sNm}} \sum_{\substack{j \\ k}} \frac{\sigma_{\alpha}^{*j}(k) \sigma_{\beta}^{j}(k)}{\omega^{2} - \omega_{jk}^{2}} e^{ik \cdot R}$$
(189)

Using a two band isotropic model the completeness condition may be used to sum the eigenvectors.

$$\sum_{j} \frac{\sigma_{\alpha}^{j} \sigma_{\beta}^{i}}{\omega^{2} - \omega_{jk}^{2}} = \frac{\sigma_{\alpha}^{1} \sigma_{\beta}^{1} + \sigma_{\alpha}^{2} \sigma_{\beta}^{2} + \sigma_{\alpha}^{\ell} \sigma_{\beta}^{\ell}}{\omega^{2} - \omega_{tk}^{2}} + \sigma_{\alpha}^{\ell} \sigma_{\beta}^{\ell} \left[\frac{1}{\omega^{2} - \omega_{\ell k}^{2}} - \frac{1}{\omega^{2} - \omega_{t k}^{2}}\right]$$
$$= \frac{\delta \alpha \beta}{\omega^{2} - \omega_{t k}^{2}} + \frac{k_{\alpha}^{k} \beta}{k^{2}} \left[\frac{1}{\omega^{2} - \omega_{\ell k}^{2}} - \frac{1}{\omega^{2} - \omega_{t k}^{2}}\right]$$
(190)

Equation 189 becomes

$$G_{\alpha\beta}^{o}(\mathbf{R},\omega) = \frac{V}{m(2\pi)^{3}} \int d^{3}\mathbf{k} \ e^{i\mathbf{k}\cdot\mathbf{R}} \sim \left\{ \frac{\delta_{\alpha\beta}}{\omega^{2}-\omega_{tk}^{2}} + \frac{k_{\alpha}k_{\beta}}{k^{2}} \right\}$$
(191)
$$\times \left[\frac{1}{\omega^{2}-\omega_{\ell k}^{2}} - \frac{1}{\omega^{2}-\omega_{t k}^{2}} \right] \right\}$$

In the above equations & labels the longitudinal branch and t labels the degenerate transverse branches.

There are two types of integrals here:

$$I = \int \frac{d^{3}k \ e^{ik \cdot R}}{\omega^{2} - v^{2}k^{2}} \qquad \qquad J = \int \frac{q_{\alpha}q_{\beta}}{q^{2}} \frac{e^{iq \cdot R}}{\omega^{2} - v^{2}q^{2}} \ d^{3}q$$

$$I = 4\pi \int_{0}^{\infty} k^{2} dk \frac{\sin kR}{kR} \frac{1}{\omega^{2} - v^{2}k^{2}}$$

$$J = (-i)^{2} \nabla_{\alpha} \nabla_{\beta} \int_{0}^{\infty} \frac{4\pi}{q^{2}} \frac{\sin qR}{qR} q^{2} dq$$

$$\nabla_{\alpha}\nabla_{\beta} \frac{\sin qR}{qR} = \frac{\delta_{\alpha\beta}}{R^{2}} \cos qR - \frac{2R_{\alpha}R_{\beta}}{R^{4}} \cos qR - \frac{R_{\alpha}R_{\beta}q}{R^{3}} \sin qR - \frac{\sin qR}{R^{3}} - \frac{\sin qR}{R^{3}} + \frac{3R_{\alpha}R_{\beta}}{R^{5}q} \sin qR - \frac{R_{\alpha}R_{\beta}}{R^{4}} \cos qR$$
$$= -\frac{R_{\alpha}R_{\beta}}{R^{2}} \frac{q^{2} \sin qR}{qR} \text{ to order } (\frac{1}{R})$$
$$J = \frac{R_{\alpha}R_{\beta}}{R^{2}} I \text{ to order } (\frac{1}{R})$$

Both integrals reduce to the same form for large R.

$$G_{\alpha\beta}^{o}(R\omega) = \{\delta_{\alpha\beta} I_{t} + \frac{R_{x}R_{y}}{R^{2}}(I_{l}-I_{t})\}\frac{V}{6\pi^{2}m}$$

in terms of a function I which depends on the branch index and which can be evaluated analytically in a Debye model.
$$I_{j} = \int_{0}^{q} \max \frac{\sin qR}{qR} \frac{1}{\omega^{2} - v_{j}^{2}q^{2}} q^{2} dq d\Omega$$

$$= \frac{2\pi}{\alpha} \{ [Ci\alpha(\omega + \omega_{max}^{j}) - Ci\alpha(\omega_{max}^{j} - \omega)] \sin \alpha\omega + [Si\alpha(\omega_{max}^{j} + \omega) + Si\alpha(\omega_{max}^{j} - \omega) - \pi] \cos \alpha\omega \}$$
(192)

Si and Ci are sine and cosine integral functions and α is R/v_j . In the large R limit or more exactly when $\frac{R}{v_j}(\omega_{max}^j \pm \omega) >> 1$ $I_j = -\frac{\pi v_j}{2Rv_j^3} e^{i(R/v_j)\omega}$

$$G_{\alpha\beta}^{0}(\omega R) = -\frac{V_{a}}{4\pi m} \frac{\delta_{\alpha\beta}}{v_{t}^{2}} e^{i(R/v_{t})\omega} + \frac{R_{x}R_{y}}{R^{2}} (\frac{e^{i(R/v_{l})\omega}}{v_{l}^{2}} - \frac{e^{i(R/v_{t})\omega}}{v_{t}^{2}})$$

Using the equalities

1.
$$\lim_{\substack{R \in \mathcal{L} \\ R \neq 1 \\ R \neq 1}} e^{i(R \ell - R \ell_1) (\omega / v_j)} = e^{iR(\omega / v_j)} e^{-k_j \cdot R \ell_1} (k_j - \omega_k \hat{\ell})$$

$$\frac{R_\ell}{R_{\ell_1}} >> 1$$

2.
$$\delta_{\alpha\beta} = \sum_j \sigma_{\alpha}^j \sigma_{\beta}^j$$

amplitude.

$$\Psi_{\alpha}(\mathbf{r}, \ell) = \sum_{J\beta\delta\gamma\ell} G_{\beta\ell} \sigma_{J} \sigma_{\delta}^{J} \sigma_{\delta}^{J} T_{\ell} \sigma_{\gamma}^{J}(\mathbf{k}) e^{i\mathbf{k}\cdot\ell} 2$$

$$= -\frac{\mathbf{v}}{4\pi m} \sum_{j} \frac{\sigma_{\alpha}^{J}}{\mathbf{v}_{J}^{2}} \frac{\mathbf{r}}{\mathbf{v}_{J}} e^{iR_{\ell}\omega\mathbf{v}_{J}}{R} \qquad (193)$$

$$= \sum_{j} \mathbf{f}_{J}(\mathbf{k}, \mathbf{k}') \frac{e^{i\mathbf{k}_{J}^{'R}}}{R} \qquad (194)$$

Where the scattering amplitude is

$$\mathbf{f}_{J}(\Theta_{\mathbf{k}\mathbf{k}},) = -\frac{\mathbf{v}}{4\pi m} \frac{\sigma_{\alpha}^{J}}{\mathbf{v}_{J}^{2}} \mathbf{T}_{\mathbf{k}'\mathbf{k}}$$
(195)

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In finding the total cross section we neglect the rapidly oscillating interference terms between different bands.

$$\frac{d\sigma}{d\Omega} = \left| \sum_{j\alpha} f_{j\alpha} \right|^{2} = \left| f_{\ell} \right|^{2} + 2 \left| f_{t} \right|^{2}$$

$$= 2 \left(\frac{V_{a}}{4\pi m v_{t}^{2}} \right)^{2} \left| T_{k'k} \right|^{2} + \left(\frac{V_{a}}{4\pi m v_{\ell}^{2}} \right)^{2} \left| T_{k'k} \right|^{2}$$
(196)

As an example we may find the phonon lifetime in the case of a mass defect where the T-matrix is easily calculable:

$$T_{kk'} = \frac{m\varepsilon\omega^2 \,\delta_{jj'}}{1 - m\varepsilon\omega^2 G_{oo}^{O}}$$
(197)

$$\frac{1}{\tau(\omega)} = \frac{\mathbf{v}_{s}}{\mathbf{v}_{a}} \sigma_{T} = \frac{\mathbf{v}_{s}}{\mathbf{v}_{a}} \left| \mathbf{f}_{kk} \right|^{2} d\Omega$$
$$= \frac{\mathbf{v}_{a}}{4\pi N} \frac{\varepsilon^{2} \omega^{4}}{1 - m\varepsilon \omega^{2} G^{0}} \frac{1}{3} \left(\frac{2}{\mathbf{v}_{t}^{3}} + \frac{1}{\mathbf{v}_{k}^{3}} \right)$$
(198)

where an average over initial polarizations has been performed.

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Phase Shifts

We write down the expression for phase shifts by analogy with the relation between the T-matrix and phase shifts for particles. So that we may have noninterfering phase shifts, the T-matrix will be considered in an irreducible representation labeled by γ and degeneracy g.

$$T = \frac{e^{i\Theta} \sin\Theta}{Im G} \text{ or equivalently,}$$
(199)

$$\Theta = \tan^{-1} \left(\frac{\operatorname{Im} T}{\operatorname{Re} T} \right)$$
 (200)

The T-matrix was originally defined in equation 64. It can be rewritten for one irreducible representation and the total phase shift found by summing all representations.

$$T = C(1-G^{O}C)^{-1}$$

$$\Theta_{\gamma} = \tan^{-1} \left(\frac{-\operatorname{Im} (G^{O}C)_{\gamma}}{1-\operatorname{Re} (G^{O}C)_{\gamma}}\right)$$
(201)

= Im Det
$$|1-(G^{O}C)_{\gamma}|$$
 (202)

$$\Theta = \sum_{\gamma} g_{\gamma} \Theta_{\gamma} = \text{Im Det } |1 - G^{O}C|$$
(203)

One way to find the T-matrix and phase shifts is to decompose the perturbation on an orthogonal basis and use folded matrices.

$$T_{qq'} = \sum_{q_{1}j_{1}} C_{qq_{1}} (1-G^{\circ}C)_{q_{1}q'}^{-1} (204)$$

$$C_{qq'} = \sum_{ik} v_{ik}^{jj'} \Psi_{i}^{*}(q) \Psi_{k}(q') (205)$$

$$T_{qq'} = \sum_{ik} v_{ik} \Psi_{i}(q) \Psi_{k}^{*}(q') + \sum_{ik} v_{ik}^{jj} \Psi_{i}^{*}(q) \Psi_{k}(q) G_{q_{1}j_{1}}^{o} V_{k}^{j} U_{m}^{j} \Psi_{k}^{*}(q_{1}) \Psi_{m}^{*}(q') + ...$$

$$= \sum_{ik} v_{ik} \Psi_{i}^{*}(q) \Psi_{k}(q') + \sum_{ikm} v_{ik}^{jj} \Lambda_{kk}^{j} v_{km}^{jj} \Psi_{i}^{*}(q) \Psi_{m}(q')$$

$$+ \sum_{im} (v\Lambda v\Lambda v)_{im} \Psi_{i}^{*}(q) \Psi_{m}(q') ...$$

$$= \sum_{im} \{v(1-\Lambda v)^{-1}\}_{jm'_{1}} \Psi_{i}^{*}(q) \Psi_{m}(q') \qquad (206)$$

where

1

$$\Lambda_{kl}^{jj'} = \delta_{jj'} \Sigma f_{k}^{*}(q) G_{qj}^{O} f_{l}(q)$$
(207)

In a mass defect example the function indices i,m do not occur.

$$C_{qq'} = m\varepsilon\omega^2 \delta_{jj'} = \delta_{jj'} V_{00}$$
(208)
jj'

$$\Lambda = \Sigma G_{qj}^{o} = G_{ll}^{o}$$
 (Real space Green's function)
q jj

.

$$T_{qq'} = \frac{m\varepsilon\omega^{2} \delta_{jj'}}{1-m\varepsilon\omega^{2} \sum_{j} G_{ll}^{0}}$$

$$T_{qq'} = \frac{m\varepsilon\omega^{2} \delta_{jj'}}{1-m\varepsilon\omega^{2} G_{ll}^{0}} \quad \text{or} \quad \Theta = \arg (1-m\varepsilon\omega^{2} G_{ll}^{0}) \quad (210)$$

$$\alpha\alpha$$

p wave example:

$$C_{qq'} \equiv v_{jj'} q q'$$
(211)
$$= \frac{4\pi}{3} v_{jj'} qq' \{ y_{1-1}^{\star}(q) \ y_{1-1}(q') + y_{11}^{\star}(q) y_{11}(q') + y_{10}^{\star}(q) y_{10}(q') \}$$
$$V_{10} = \frac{4\pi}{3} v_{jj'}$$
$$\Lambda_{1-1}^{j} = \sum_{q} q^{2} y_{11}^{\star}(q) \ y_{1-1}(q) \ P_{qj}$$

 Λ and V are now written in folded form; each matrix element below represents a 3X3 matrix of band coordinates. The indices below are azimuthal labels.

$$\Lambda^{j} = \begin{bmatrix} \Lambda_{11}^{j} & \Lambda_{1-1}^{j} & \Lambda_{10}^{j} \\ \Lambda_{1-1}^{j} & \Lambda_{-1-1}^{j} & \Lambda_{-10}^{j} \\ \Lambda_{10}^{j} & \Lambda_{-10}^{j} & \Lambda_{00}^{j} \end{bmatrix} \quad V_{jj}, = \frac{4\pi}{3}v_{jj}, \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$T = \begin{bmatrix} q & Y_{11} & (q) \\ q & Y_{1-1} & (q) \\ q & Y_{10} & (q) \end{bmatrix}^{\frac{4\pi}{3}} V_{jj}, \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\times \begin{bmatrix} \Lambda_{11} & V_{11} & \Lambda_{1-1} & V_{11} & \Lambda_{10} & V_{11} \\ 1 & -\Lambda_{1-1} & V_{11} & \Lambda_{-1-1} & V_{11} & \Lambda_{-10} & V_{11} \\ \Lambda_{10} & V_{11} & \Lambda_{-10} & V_{11} & \Lambda_{00} & V_{11} \end{bmatrix} = \begin{bmatrix} q' & Y_{11} & (q') \\ q' & Y_{1-1} & (q') \\ q' & Y_{10} & (q') \end{bmatrix}$$

If we now consider spherical bands, Λ is diagonal on azimuthal indices.

$$T_{qq'} = \frac{4\pi}{3} \sum_{j_1} v_{jj_1} \{1 - \Lambda_{11} v_{11}\}_{j_1j'}^{-1} qq' \sum_{\ell=-1}^{1} Y_{1\ell}^*(q) Y_{1\ell}(q')$$

$$T_{qq'} = \sum_{j_1, j_1} v_{j_1} \{1 - \Lambda_{11} v_{11}\}_{j_1j'}^{-1}, q'q'$$

If the perturbation is diagonal on band indices

$$T_{qq'} = \delta_{jj'} \frac{q \cdot q' \cdot v_{j'j}}{(1 - \Lambda_{11} v_{11})}$$

 $\Theta = \arg(1 - V_{11}V_{11})$ (212)

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