ELECTRONS AND PHONONS
IN DISORDERED MEDIA

A thesis presented by
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University of London in application
for the degree of Doctor of Philosophy.

November 1967

Abstract

An investigation of the nature of vibrational modes in a structurally disordered solid and the thermal conduction properties of such a solid is described. Analogies between the vibrational mode problem and the subject of electrons moving in a disordered system of potential wells are discussed and a method for calculating the electronic band structure of perfect solids proposed by Ziman (1965) is interpreted, compared with the A.P.W. method and used to consider the scattering of a Bloch wave from an impurity potential.

Acknowledgements

I am grateful to Dr. Mino Green and Mr. Geoffrey Wexler of Zenith Radio Research Corporation for the encouragement and help they have given me while carrying out the research for this thesis. My thanks are also due to Professor E. Sondheimer for arranging for me to become a part-time research student in his department. Many of the ideas considered here are the result of discussions with Professor J.M. Ziman and this I wish to acknowledge together with my appreciation of the interest he has shown in my work and the encouragement this has given me. I am especially indebted to Grace Minting who has typed this thesis and it is a great pleasure to thank her.

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INTRODUCTION

The nature of the problem

The main theme of this thesis is the development of methods for investigating the nature of the vibrations and the transport of heat in structurally disordered solids. Some of these methods can also be applied to the analogous problem of electrons moving in a disordered system of potential wells; hence the title of this thesis.

The essence of the problem is that the standard perturbation methods of mathematical physics are often not readily applicable. By this we mean that it is not usual to have a set of vibrational modes or wave functions associated with an "unperturbed" Hamiltonion which can be considered to be reasonable approximations to the real modes or wave functions of the disordered system. To take a specific example, it is not feasible to describe the vibrational properties of amorphous Germanium in terms of the modes of perfect crystalline Germanium. Setting aside the question of whether a perturbation expansion in terms of perfect lattice modes would converge, the major obstacle is the fact that there is no simple or unique way of associating an atom in the amorphous structure with a perfect lattice atom. This means that it is difficult to see how to set up a perturbation method based on perfect lattice waves in the first place. A similar difficulty arises when thinking about the properties of electrons in amorphous solids or liquid metals. It is possible in this case to construct wave functions in terms of the Bloch states of some perfect lattice of atoms, but this is mathematically clumsy and unless the potential wells in which the electrons move are weak is not a fruitful approach. In the case of the conduction electrons in a simple liquid metal a free electron wave representation may be used with success for some purposes because the potential wells have a weak effect, but the area of applicability is rather limited.

There is a clear need for the development of new methods particularly in the study of vibrating solids. The theory of electrons in disordered systems is rather more advanced but there is still a large number of unexplored areas.

Examples of disordered systems

There is a vast number of different types of disorder problems. We shall restrict ourselves to those aspects concerned with structural inhomogeneities in the arrangements of atoms rather than the effects of impurities. Broadly speaking the kinds of structural disorder may be divided into three categories corresponding to the presence of (a) long range order, (b) medium range order and (c) only short range order.

In the first category are solids containing dislocations, crystals joined via a grain boundary and solids containing interstitial atoms or vacancies. These three examples come within the scope of this thesis because the solids are not describable as a perturbed or deformed lattice except by rather artificial means. (b) refers to polycrystalline materials where although each crystallite is highly ordered their orientation with respect to each other is random. By far the largest class is (c), encompassing in the solid phase the glasses, many complex organic solids and amorphous films. In addition to these examples there is evidence that liquids behave like "frozen solids" in response to stresses which vary rapidly with time. As far as electrons are concerned there is a rich variety of situations in the liquid phase, including liquid metals, liquid semiconductors and liquid insulators.

This work does not, of course, cover all these situations but the methods, with appropriate modification, should be fairly generally applicable.

Contents

The thesis is divided into two parts, the most important being Part 1 which deals with the modes of vibration and the thermal conductivity of a disordered solid.

The first chapter is a brief outline of previous work in the field and the difficulties which exist. Two simple models are then described in Chapter 2 which have been used to develop the arguments of the subsequent chapters. The first model involves assuming that pairs of atoms are coupled by harmonic and anharmonic forces which are functions only of the relative separation of the two atoms. The second model is called the loaded continuum model and has been extremely useful for testing out ideas and methods. It consists of rigid spheres of mass M embedded in an elastic medium of zero density. The elastic medium provides the restoring forces on the "atoms". (Morgan and Ziman, 1967). Chapter 3 is concerned with the development of methods for calculating the average wave amplitude of a vibrational mode in an amorphous or polycrystalline solid by averaging the equation of motion. Equations for calculating the average Green function are also formulated but no attempt has yet been made to solve them for a specific model of a disordered solid. The most important chapter is 4 which is concerned with the calculation of thermal conductivity. The method proposed is applicable to the three classes of structural disorder discussed in 1.2. It involves making a point transformation of the position and momentum coordinates of the atoms to new collective variables analogous to the use of the Fourier components of the density fluctuations as collective variables in theories of liquids. A Boltzmann type of equation is deduced using this representation and the "collision terms" examined. The final chapter (5) in Part 1 is a discussion of the use of non-orthogonal representations for describing vibrational modes and the construction of biorthogonal functions, the point being that the great majority of mathematical methods used in physics are based on orthogonal transformation and representations.

Chapter 1 in the second part of the thesis is a discussion of how the methods developed for the vibrational problem can be adapted to treat electrons in disordered systems. For example, analogies are drawn between the mathematics describing electrons occupying a tightly bound "band" and that used for investigating vibrational modes. The concluding chapter (2) is divorced to some extent from the main theme of the thesis. It is concerned with the "Greenian" and A.P.W. methods for calculating electron band structures and an approximate method of calculating the scattering of a Bloch wave by an impurity potential.

PART 1.

The vibrational modes and thermal conductivity of a disordered solid.

1.1. Remarks on existing theories of disordered solids.

The purpose of this chapter is to give examples of the kind of problems which have been tackled and the kind of methods which have been used in studies of imperfect solids.

Almost all the work to date has been concerned with the properties of solids containing impurities and simple types of strain field. Such a solid can be described as a perturbed lattice and the vibrational modes as perturbations of perfect lattice states, i.e. either classical lattice waves or phonon states. This means that all the mathematical apparatus of advanced scattering theory and quantum statistical mechanics can be and is being used to investigate the vibrational and transport properties. Machine calculations have been made of the density of states in disordered systems mainly for one-dimensional "solids" where all the difficulties associated with three dimensions are not realised, though recently calculations of the vibrational properties of a model of fused silica have been made, which is a great step forward. Paradoxically, the major developments in the theory of "solids", which cannot be described as perturbed lattices, have been in the theory of collective oscillations in "liquids" when the frequency of the oscillations is sufficiently high for the liquid to be considered as a "frozen solid". Part of this thesis is concerned with the application of similar methods to those used for liquids to the study of general kinds of structural disorder in solids.

The simplest kind of problem which occurs is the presence of an isolated point defect in an otherwise perfect lattice, examples being substitutional impurities or isotopes. Modern interest in this subject was initiated by Lifshitz (1943), although developments had taken place as far back as the last century, (Maradudin, 1965, p.332). In the main, theories have been developed within the framework of the classical equation of motion for a solid which is sufficient for many purposes. Quantum mechanics is necessary for discussing transport and thermodynamic properties at low temperatures but even then the quantization can be done at a late stage rather than at the beginning of a calculation. If $\underline{u}(j)$ denotes the displacement of the j'th atom in a solid from its equilibrium site then the time independent equation of motion takes the form

$$L\,\underline{u}(j) = L^{\circ}\,\underline{u}(j) + L'\,\underline{u}(j) = M_j\,\omega^2\,\underline{u}(j) \qquad (1)$$

where M_j is the mass of the j'th atom, ω is the vibrational frequency, L^{o} is a linear operator characterizing the unperturbed lattice and L' an operator characterizing the perturbation caused by the point defect. Many methods developed for differential equations can be taken over to solve this linear equation and when simple models are used for the atomic interactions exact solutions are obtainable. Two recent reviews of this subject are those by Maradudin (1965, 1966) and Lifshitz and Kosevich (1966).

In the case of extended defects two separate situations arise, (a) when the operator L can be split into an unperturbed lattice operator plus a perturbation operator and (b) when this separation is not possible. As remarked earlier, case (a) has received most attention and the methods used are based on approximation techniques originally developed in other areas of physics. For example, Klemens (1958) and Carruthers (1961) have calculated the scattering of phonons by strain fields using the perturbation methods of quantum field theory and recently Taylor (1967) has calculated the density of vibrational states for a crystal containing large concentrations of impurities using a theory of multiple scattering developed by Lax (1951, 1952) for differential equations. It is far from being simple to obtain accurate solutions in case (a) but at least there is a well developed mathematical background for developing approximations which is absent in case (b). An important piece of recent work on the properties of highly disordered solids is the computer calculations of Dean and co-workers (to be published) of the vibrational modes and density of states in fused silica. Fabricated models have been built to define atomic positions for use in the numerical calculations (1966). Despite the intrinsic worth of these methods they are not substitutes for good analytical approximations when we wish to consider more complicated properties which involve say the density of states. The other major area of research where case (b) has been considered is the theory of collective oscillations in liquids when the periodic time is small compared with the Maxwell relaxation time τ_M. This is the mean time an atom in a liquid stays at an "equilibrium" site before jumping to another one, and is typically of the order $10^{-11} - 10^{-12}$ secs. in liquid metals, (Cocking 1967). The idea that for rapidly varying stresses a liquid can be treated as a "frozen solid" with the instantaneous configuration of atoms in the liquid was first considered in detail by Frenkel (Kinetic Theory of Liquids, 1955) and subsequently by a number of authors, for example, Fisher (Statistical Theory of Liquids, 1964), Schofield (1966) and Schneider and Stoll (1967). Collective oscillations also occur in liquids at low frequencies but this is an even more complicated subject involving the motion of atoms between "equilibrium" sites. A characteristic feature of theories of low frequency oscillations in liquids and gases (e.g. Percus and Yevick, 1958; Tomonaga, 1955 a, b; Mori, 1962) and those for a "frozen solid", is that the Fourier components of the density fluctuations $\rho_{\underline{k}}$ can be introduced as collective coordinates. The $\rho_{\underline{k}}$ are defined by

$$\rho_{\underline{k}} = \frac{1}{N^{\frac{1}{2}}} \sum_{j} e^{i\,\underline{k}\cdot\underline{r}_j} \qquad (2)$$

where N is the number of particles in the system and $\underline{r}_j$ is the position of the j'th particle. To a first approximation each individual coordinate $\rho_{\underline{k}}$ oscillates harmonically with a frequency $\omega(\underline{k})$ which is analogous to the dispersion law for a perfect solid. The success of this kind of approach suggests that analogous transformations should be sought for describing general kinds of structurally disordered solids since in the case of liquids a problem which looks intractable using the real-space coordinates of the atoms becomes much more amenable in terms of the collective coordinates.

The thermal conductivity of a solid is a very important physical parameter and the measurement of it a very useful tool for testing theoretical predictions of the behaviour of waves in disordered solids. Another important transport property in this respect is the contribution to the thermopower of a solid due to phonon-electron interaction, i.e. phonon drag. We will, however, only consider the thermal conduction problem. Most treatments (e.g. Klemens, 1958; Carruthers, 1961) have been within the framework of the phonon Boltzmann equation first developed by Peierls (1929, 1955). Although the mathematical framework for going beyond this simple equation is well understood (e.g. Hardy and Schieve, 1966; Ranninger, 1967), in practice the solving of the Boltzmann equation itself is very difficult, so that further sophistications are often of academic interest. The Boltzmann equation describes heat being transported through a solid by perfect harmonic lattice states which are scattered by the various kinds of imperfection which can occur. The thermal conductivity of a structurally disordered solid cannot therefore be handled by the standard theory. At very low temperatures it is possible to make some very qualitative remarks because only very low frequency modes are excited. If these modes are assumed to be the modes of vibration of an elastic continuum the description of a solid as a discrete structure can be replaced by a continuum description where imperfections are represented by fluctuations in density and elasticity. This approach has been used by Klemens (1965) to discuss amorphous solids but no prescription has been given for calculating the microscopic fluctuations in elasticity. A failing of this method is that it cannot describe anything analogous to the well known "Umklapp" processes which occur in a discrete lattice structure.

The subject of structurally disordered solids is therefore a very challenging one, where it is not possible to proceed by means of mathematical methods already in common use. It is this aspect of the problem which has been found most intriguing.

1.2. Two simple models of disordered solids.

The case for using simple models to develop a theory is that too many complications can obscure the fundamentals. Whilst aware of the shortcomings of the models to be described we consider that they contain the essential features of disordered solids.

1.2.1. The "spring" model.

The traditional development of the theory of a lattice of point atoms begins with the assumption that the total potential energy due to the atomic interactions can be expanded in a Taylor series in terms of the atomic displacements from the perfect lattice sites, (Maradudin, Montroll and Weiss, 1963). The requirement that no net force acts on any atom when all of them are at the equilibrium sites means that terms in the potential energy which are linear in the displacements from equilibrium must vanish. This procedure and conclusion is equally valid for disordered solids. We take the view that the extremely difficult problem of determining how a disordered solid remains stable is outside the scope of this thesis. We therefore assume that the exact equilibrium sites are known and that reasonable approximations can be constructed for the harmonic and anharmonic interactions between the atoms.

In particular we will consider monatomic solids defined by the Hamiltonian

$$H = \sum_{\alpha}\sum_{j} \frac{P_{\alpha}^{2}(j)}{2M} + \frac{1}{2}\sum_{\alpha}\sum_{\alpha'}\sum\sum_{j\neq j'} B_{\alpha\alpha'}(\underline{r}_j-\underline{r}_{j'})\left(u_{\alpha}(j)-u_{\alpha}(j')\right)\left(u_{\alpha'}(j)-u_{\alpha'}(j')\right)$$
$$+\frac{1}{6}\sum_{\alpha}\sum_{\alpha'}\sum_{\alpha''}\sum\sum_{j\neq j'} C_{\alpha\alpha'\alpha''}(\underline{r}_j-\underline{r}_{j'})\left(u_{\alpha}(j)-u_{\alpha}(j')\right)\left(u_{\alpha'}(j)-u_{\alpha'}(j')\right)\left(u_{\alpha''}(j)-u_{\alpha''}(j')\right). \qquad (3)$$

In this expression $\underline{r}_j$ denotes the equilibrium site of the j'th atom, $P_{\alpha}(j)$ and $u_{\alpha}(j)$ denote cartesian components of the momentum and displacement from equilibrium of this atom, and M is the atomic mass. The functions $B_{\alpha\alpha'}(\underline{r}_j-\underline{r}_{j'})$ and $C_{\alpha\alpha'\alpha''}(\underline{r}_j-\underline{r}_{j'})$ are harmonic and anharmonic force constants respectively. It is assumed that the force constants are unaltered by interchange of the subscripts and interchange of j and j'. Quadratic and higher terms in the displacements are assumed negligible.

The form assumed for the harmonic and anharmonic force constants is, of course, a gross simplification. In general they will not be just functions of the separation of a pair of atoms and they will depend on the coordinates of surrounding atoms as well. Equation (3) is valid for solids where the atomic interactions can be described approximately by pair interactions, as for example in ionic solids. This does not mean that if some pair potential function is assumed to calculate the force constants that the conditions for stability will be satisfied. We assume that the structure is stable and merely requires some method for estimating the force constants.

When it is essential to include non-central interactions between atoms it is not possible to devise a Hamiltonion of the form (3) without violating the condition that it should be invariant with respect to rotations of the system, Lax (1963). In any event the methods which will be discussed can be extended to cover more general Hamiltonions but it helps to take a specific simple form.

1.2.2. The loaded continuum model.

The second model is rather different. We make no pretence at physical reality. The model consists of rigid spheres of mass M and radius R_s embedded in an elastic medium of zero density which is assumed to have purely harmonic properties. It is a simple and convenient way of investigating the general properties of a system of masses bound by harmonic forces and is useful for testing out ideas and methods.

We consider the elastic medium to be isotropic and for simplicity take the special choice for the Lamé constants, $\lambda=-\mu$ $(\mu>0)$. Text books on classical elasticity theory show that λ and μ must be greater than zero, (e.g. Sokolinkoff, Mathematical Theory of Elasticity, p.69). However, many of the general features of wave propagation can be investigated by means of this model. It corresponds to making the central and non-central forces of equal strength in a "spring" model of a solid. This unrealistic assumption is quite commonly used to clarify the mathematics in vibration problems. These and related points are discussed in Appendix A. For this special choice of the Lamé constants the elastic wave equation of an isotropic solid reduces to three scalar ones. If $U(\underline{r})$ denotes a cartesian component of the displacement field, then

$$\nabla^2 U(\underline{r}) + V(\underline{r})\, U(\underline{r}) = 0 \tag{4}$$

where $V(\underline{r})$ denotes an operator symbolizing the departure of the system from a structureless elastic medium of zero density, i.e. the presence of rigid spheres. Equation (4) is rather similar in form to Schroedinger's equation for an electron moving in a system of spherical potentials and straightforward adaptations of methods developed for electrons can be used to reformulate this equation.

1.2.2.1. The analogue to the "Greenian" method for electrons.

One of the most successful methods for solving the

Schroedinger equation for perfect lattices is that originally proposed by Korringa (1947) and by Kohn and Rostoker (1954). This method was generalised to arbitrary arrangements of potentials by Phariseau and Ziman (1963) and will be called the "Greenian" method.

Equation (4) can be changed to the integral form

$$U(\underline{r}) = \int G(\underline{r}-\underline{r}')\, V(\underline{r}')\, U(\underline{r}')\, d\underline{r}' \tag{5}$$

where $G(\underline{r}-\underline{r}')$ is the Green function for the Laplace operator, i.e.

$$G(\underline{r}-\underline{r}') = \frac{1}{4\pi|\underline{r}-\underline{r}'|} \quad . \tag{6}$$

It is not necessary to enquire into the precise nature of the operator $V(\underline{r})$ because the problem can be formulated in terms of the displacements on the surfaces of the rigid spheres. A convenient way to do this is by using the condition (Ziman, 1966)

$$\sum_{j'} \int \left\{ G(\underline{\rho}-\underline{\rho}'-\underline{r}_{j'j}) \frac{\partial}{\partial \rho'} U_j(\rho') - U_j(\rho') \frac{\partial}{\partial \rho'} G(\underline{\rho}-\underline{\rho}'-\underline{r}_{j'j}) \right\}_{\rho'=R_s+\epsilon} d\Omega(\underline{\rho}') \tag{7}$$
$$= 0 \quad ,$$

Here $U_j(\underline{\rho})$ is the displacement field around the j'th sphere, ϵ is a positive infinitesimal and

$$\begin{aligned} \underline{r}_{jj'} &= \underline{r}_{j'} - \underline{r}_{j}, \\ \underline{\rho} &= \underline{r} - \underline{r}_{j}, \\ \underline{\rho}' &= \underline{r} - \underline{r}_{j'}, \end{aligned} \tag{8}$$

where $\underline{r}_j$ is the position of the j'th sphere.

In the neighbourhood of the surface of a sphere the displacement field $U_j(\underline{\rho})$ can be expanded in terms of the solutions of Laplace's equation separated in spherical coordinates;

$$U_j(\underline{\rho}) = \sum_{L} \frac{\beta^j_{\ell,m}}{(2\ell+1)} \left(\rho^{-\ell-1} + \gamma_\ell \rho^\ell\right) \mathcal{Y}_{\ell,m}(\underline{\rho}) \quad . \tag{9}$$

The label L denotes collectively the angular label ℓ and the azimuthal label m and $\mathcal{Y}_L(\underline{\rho})$ denotes a real normalised spherical harmonic (Segall and Ham, 1961). The coefficients β^j_L and γ_ℓ are to be determined.

The γ_ℓ can be obtained from the boundary conditions on the surface of a rigid sphere. This information is contained in the equation of motion for the j'th sphere:

$$-M\omega^2 U_j(\underline{s}) = \int \mu \left\{ \nabla U_j(\underline{s}') + U_j(\underline{s}')\nabla - \mathrm{div}\, U_j(\underline{s}') \right\} \cdot d\underline{S}' \tag{10}$$

where $U_j(\underline{s})$ is the displacement component on the surface of the rigid sphere and ω is the vibrational frequency. The right hand side of (10) is the force due to the stress field around the sphere, (see Appendix A)

Substitution of (9) into (10) gives

$$\gamma_0 = \frac{4\pi\mu}{M\omega^2} - \frac{1}{R_s} \, ,$$
$$\gamma_\ell = -\frac{1}{R_s^{2\ell+1}} \quad (\ell > 0). \tag{11}$$

Equations for the β_L^j may now be obtained by substituting from (9) into (7) using the expansion (Morgan and Ziman, 1967)

$$G(\underline{\rho}-\underline{\rho}'-\underline{r}_{j'j}) = -\delta_{jj'}\sum_L \frac{1}{(2\ell+1)} \rho^\ell \rho'^{-\ell-1} \mathcal{Y}_L(\underline{\rho})\mathcal{Y}_L(\underline{\rho}')$$
$$-(1-\delta_{jj'})\sum_{L'}\sum_{L''} B_{L'L''}(\underline{r}_{jj'})\, \rho^{\ell'} \rho'^{\ell''} \mathcal{Y}_{L'}(\underline{\rho})\, \mathcal{Y}_{L''}(\underline{\rho}') \tag{12}$$

where

$$B_{L'L''}(\underline{r}_{jj'}) = 4\pi \sum_L i^{\ell'-\ell-\ell''} \frac{\delta_{\ell'+\ell'',\ell}\,(2\ell+1)!!\; C^L_{L'L''}\; \mathcal{Y}_L(\underline{r}_{j'j})}{(2\ell'+1)!!\,(2\ell''+1)!!\,(2\ell+1)\,|\underline{r}_{j'j}|^{\ell+1}} \tag{13}$$

and

$$C^L_{L'L''} = \int \mathcal{Y}_L(\underline{\rho})\,\mathcal{Y}_{L'}(\underline{\rho})\,\mathcal{Y}_{L''}(\underline{\rho})\, d\Omega(\underline{\rho}) \quad . \tag{14}$$

Using the orthonormal properties of the spherical harmonics we find on substituting from (9) and (12) into (7) that

$$(2\ell+1)^{-1}\gamma_\ell \beta_L^j = \sum_{L'} \sum_{j'\neq j} B_{LL'}(r_{jj'})\beta_{L'}^{j'} . \tag{15}$$

This equation is analogous to the equation of motion for a "spring" model of a solid.

One of the original purposes of investigating this model was to discover whether it would allow direct application of methods developed for electrons in disordered systems. For example, if we consider the problem of an electron in a system of spherical non-overlapping potentials of radius R_s, the wave function within the j'th potential may be written as (Phariseau and Ziman, 1963)

$$\psi_j(\rho) = \sum_L \frac{i^\ell \beta_L^j}{[\mathcal{R}_\ell, j_\ell]} \mathcal{R}_\ell(\rho)\, \mathcal{Y}_L(\rho) \tag{16}$$

where, for emphasis, we use the same symbol as before for the coefficients. The function $\mathcal{R}_\ell(\rho)$ is a solution of the radial Schroedinger equation for the energy $E = \kappa^2$ and

$$\left[\mathcal{R}_\ell, j_\ell\right] = \mathcal{R}_\ell(R_s)\frac{d}{dR_s} j_\ell(\kappa R_s) - j_\ell(\kappa R_s)\frac{d}{dR_s}\mathcal{R}_\ell(R_s) \tag{17}$$

where $j_\ell(\kappa R_s)$ is a spherical Bessel function. In this case the β_L^j satisfy the equation (Phariseau and Ziman, 1963)

$$k(i - \cot\eta_\ell)\beta^j_L = \sum_{L'}\sum_{j'\neq j} B_{LL'}(k, \underline{r}_{jj'})\,\beta^{j'}_{L'} \tag{18}$$

where η_ℓ is the ℓth phase shift for a spherical potential. Equation (18) is rather more complicated than (15) because the matrix on the right hand side is a function of the energy whereas that in (15) is independent of the frequency.

1.2.2.2. A perfect lattice of spheres.

It is desirable at this stage to give a brief discussion of a perfect lattice of spheres showing that the system behaves qualitatively like a "spring" model.

In this case the problem of determining the β^j_L is enormously simplified. The Bloch theorem can be invoked whereby there exists a real wave vector such that

$$\beta^j_L = \beta_L\, e^{i\underline{k}\cdot\underline{r}_j} \tag{19}$$

and equation (15) is simplified to

$$(2\ell+1)^{-1}\gamma_\ell\, \beta_L = \sum_{L'} \mathcal{B}_{LL'}(\underline{k})\,\beta_{L'} \tag{20}$$

where

$$\mathcal{B}_{LL'}(\underline{k}) = \sum_{j'\neq j} B_{LL'}(\underline{r}_{jj'})\, e^{-i\underline{k}\cdot\underline{r}_{jj'}} \quad . \tag{21}$$

It is convenient to take the axis of the spherical harmonics in the direction of $\underline{K}$. The displacement amplitude $u(j)$ of the j'th sphere is obtained from (9);

$$u(j) = (4\pi)^{-\frac{1}{2}} \left(\frac{4\pi\mu}{M\omega^2}\right) \beta^{j}_{00} . \tag{22}$$

To obtain some idea of how the loaded continuum depends on the parameter R_s the limiting behaviour of ω as a function of $\underline{K}$ will be investigated near $|\underline{K}| = 0$ and at the zone boundary for $\underline{K}$ in the (1,1,1) direction of a simple cubic lattice. The spacing between the spheres will be denoted by a. The vibrational frequencies are given by the condition for a non-trivial solution to the simultaneous equations (20) i.e.

$$\det \left| \mathcal{B}_{LL'}(\underline{K}) - (2l+1)^{-1} \gamma_l \, \delta_{LL'} \right| = 0 \tag{23}$$

The $\mathcal{B}_{LL'}(\underline{K})$ are unaltered by adding a reciprocal lattice vector to $\underline{K}$ and therefore $\omega(\underline{K})$ will show the usual periodic properties found in conventional models.

Near $|\underline{K}| = 0$ the elements of the matrix $\mathcal{B}_{LL'}$ may be estimated by replacing the summation in (21) by an integral so that

$$\mathcal{B}_{LL'} \simeq \Delta^{-1} \int B_{LL'}(\underline{r}) \, e^{-i\underline{K}\cdot\underline{r}} \, d\underline{r} \tag{24}$$

where $\Delta = a^3$. In this limit

$$\mathcal{B}_{LL'}(\underline{k}) \propto |\underline{k}|^{l+l'-2} . \tag{25}$$

Using (25) it can readily be ascertained that for small $|\underline{k}|$ the only important spherical harmonics in determining $\omega(\underline{k})$ are those with $l=0$ and $l=1$. Furthermore, along the (1,1,1) direction symmetry arguments may be used to show that only spherical harmonics with

$$m = 0 , +3 , +6 ----- \tag{26}$$

need be retained in the expansion (9). (Segall and Ham, 1961). The determinantal condition then gives

$$\omega^2(\underline{k}) = \frac{4\pi\mu R_s}{M}\left(1 + R_s \mathcal{B}_{00,00} - \frac{3R_s^4 \mathcal{B}_{10,00}\mathcal{B}_{00,10}}{1 + 3R_s^3 \mathcal{B}_{10,10}}\right)^{-1} \tag{27}$$

where

$$\mathcal{B}_{00,00}(\underline{k}) = 4\pi C^{00}_{00,00} \sum_{j'\neq j} \frac{e^{-i\underline{k}\cdot\underline{r}_{jj'}}}{|\underline{r}_{jj'}|} \mathcal{Y}_{00}(\underline{r}_{jj'}) \simeq \frac{4\pi}{\Delta|\underline{k}|^2} ,$$

$$\mathcal{B}_{10,00}(\underline{k}) = -\mathcal{B}_{00,10}(\underline{k}) = \frac{4\pi}{3} C^{10}_{10,00} \sum_{j'\neq j} \frac{e^{-i\underline{k}\cdot\underline{r}_{jj'}}}{|\underline{r}_{jj'}|^2} \mathcal{Y}_{10}(\underline{r}_{j'j})$$

$$\simeq \frac{4\pi i}{3^{\frac{1}{2}}\Delta|\underline{k}|} , \tag{28}$$

$$\mathcal{B}_{10,10}(\underline{k}) = -\frac{4\pi}{3} C^{20}_{10,10} \sum_{j'\neq j} \frac{e^{-i\underline{k}\cdot\underline{r}_{jj'}}}{|\underline{r}_{jj'}|^3} \mathcal{Y}_{20}(\underline{r}_{j'j}) \simeq \frac{8\pi}{\Delta} .$$

In the small $|\underline{k}|$ limit

$$\omega^2(\underline{k}) \simeq \frac{\mu}{D}\left(\frac{1+2\nu/\Delta}{1-\nu/\Delta}\right)|\underline{k}|^2 \tag{29}$$

where ν is the volume of a sphere and D is the mean density, M/Δ. The model therefore behaves like an elastic continuum with an effective elastic constant

$$\mu_{\text{eff.}} = \mu\left(\frac{1+2\nu/\Delta}{1-\nu/\Delta}\right) . \tag{30}$$

The value of ω at the band edge may also be obtained in a simple way by writing

$$\underline{k} = \frac{\pi}{a}\left(\hat{x}+\hat{y}+\hat{z}\right) - \underline{k}' \tag{31}$$

where $\hat{x}$, $\hat{y}$ and $\hat{z}$ are unit vectors along the cube axes. We then find that

$$\mathcal{B}_{LL'}(\underline{k}) \propto |\underline{k}'|^{l+l'} , \tag{32}$$

This conclusion is arrived at by splitting the summation (21) into positive and negative parts using (31) and replacing the sums by integrals. Only the $l=0$ harmonic need be retained to determine the band edge frequency. At the band edge we find

$$\mathcal{B}_{00,00} = -\frac{\zeta}{a} \simeq -\frac{1.75}{a} \tag{33}$$

where ζ is Madelung's constant for an Na-Cl type lattice. The band edge frequency ω_{b} is therefore defined by

$$\omega_D^2 = \frac{4\pi\mu R_s}{M}\left(1 - \frac{\zeta R_s}{a}\right)^{-1}. \tag{34}$$

These limiting formulae for $\omega(k)$ indicate that the loaded continuum behaves like a lattice of point masses coupled by harmonic springs. For example, the ratio of ω_D to the frequency ω_D' which would be obtained without dispersion is

$$\frac{\omega_D}{\omega_D'} = \left\{\frac{4R_s(1-\nu/\Delta)}{3\pi a(1+2\nu/\Delta)(1-\zeta R_s a)}\right\}^{\frac{1}{2}}. \tag{35}$$

The parameter R_s can be chosen to give a value of this ratio typical of the values found for more conventional models.

1.3. Averaged equations of motion for disordered solids.

When a measurement is made of a physical property of a disordered system, an averaged result is frequently obtained for one of two reasons. First, a measurement made on a single specimen can involve sampling of a whole ensemble of sub-systems; for example, the velocity of sound in a glass would be the average of the velocity in different parts of the specimen and providing it is large enough one would not expect different results for two specimens prepared in identical manners. Secondly, the structure of the system may be changing with time, so that a measurement of say the density of electronic states in a liquid metal is time averaged.

This means that in many cases of interest the result of a measurement on a single system can be equated to the average of measurements on a very large number of systems. This is very important because instead of trying to calculate say the density of vibrational states of a single amorphous solid we can try to calculate the average density of states, and this is often a simpler problem.

Foldy (1945) was one of the first to use this idea. He constructed equations for the average amplitude and intensity of a wave scattered by a system of random point scatterers. Foldy's basic method has since been developed by many authors (e.g. Lax, 1951,1952; Waterman and Truell, 1961; Ziman, 1966), and applied to many types of wave propagation problems in continuous media. Recently it has also been used in an investigation of vibrational waves in lattices containing large concentrations of impurities, (Taylor, 1967).

These ideas are particularly valuable for studying structurally disordered solids where there is a dearth of alternative methods.

1.3.1. The average wave amplitude.

We begin by considering how the use of averaging methods can help determine the general shape of the vibrational modes in amorphous and polycrystalline solids.

The idea here is that, although the fine details of waves in disordered systems depend on the microscopic nature of the medium in which the waves travel, there exist grosser features of the waves which are insensitive to the precise details of the structure. For example, we know that at least some of the low frequency modes of a glass are just the elastic waves of an isotropic continuum. We now consider a whole ensemble of disordered systems where the microscopic structure of every member of the ensemble differs from other members of the ensemble. If the volume of each member is large enough it is reasonable to assume that the eigen frequencies of vibration form a continuum of states so that for a particular frequency there exists a mode of vibration for every member of the ensemble. To compare waves in different systems we must first insist that the phase of the time dependence of the waves is identical for every member of the ensemble, and secondly that each member is operating under the macroscopic boundary conditions. For example, we could consider rectangular blocks of amorphous solids (there will be microscopic surface irregularities, of course), with the condition that surface atoms are held fixed; or another possibility is a semi-infinite material with a prescribed driving force applied to the surface.

The basic technique of averaging methods is to seek an equation for the average quantity itself. In this case we are interested in the average displacements from equilibrium of the atoms in a disordered solid.

In 1.2.1. we denoted a cartesian component of the displacement of the j'th atom by $u_\alpha(j)$. The time independent equation of motion for $u_\alpha(j)$ can be written down from (3) using Hamilton's equations,

$$M\omega^2 u_\alpha(j) = 2\sum_{\alpha'}\sum_{j'\neq j} B_{\alpha\alpha'}(\underline{r}_j - \underline{r}_{j'})\left\{u_{\alpha'}(j) - u_{\alpha'}(j')\right\} \qquad (36)$$

where ω is the vibrational frequency with which the atoms oscillate. Anharmonic terms will be omitted in this discussion of averaging methods. The extension of the methods to be described to anharmonic effects should be possible.

The procedure for constructing average quantities is a well established one. Following the notation of Lax (1951) we define $\rho^e(\underline{r}_1\,\underline{r}_2 \cdots \underline{r}_N)$ as the probability of finding the equilibrium site of the first atom at $\underline{r}_1$ in $d\underline{r}_1$, the equilibrium site of the second atom at $\underline{r}_2$ in $d\underline{r}_2$ and so on. For convenience the system is considered to have unit volume and contains N atoms. The conditional probability $\rho^e(\underline{r}_{s+1} \cdots \underline{r}_N | \underline{r}_1 \cdots \underline{r}_s)$ denotes the probability of finding the $(s+1)$'th site at $\underline{r}_{s+1}$ in $d\underline{r}_{s+1}$ etc. when sites $1 \cdots s$ are definitely at $\underline{r}_1 \cdots \underline{r}_s$. A useful relation between the conditional probabilities is

$$\rho^e(\underline{r}_{s+1} \cdots \underline{r}_N | \underline{r}_1 \cdots \underline{r}_s) = \rho^e(\underline{r}_{s+1} | \underline{r}_1 \cdots \underline{r}_s)\,\rho^e(\underline{r}_{s+2} \cdots \underline{r}_N | \underline{r}_1 \cdots \underline{r}_{s+1}). \qquad (37)$$

The simplest kind of average amplitude which can be constructed is the average value of $u_\alpha(j)$ when there is definitely an atom $\underline{r}_j$ but the other atoms can have any distribution which is consistent with there being an atom at $\underline{r}_j$. A convenient notation for this quantity is $\langle u_\alpha(\underline{r}_j)\rangle$ and it is defined by

$$\langle u_\alpha(\underline{r}_j)\rangle = \int\cdots\int u_\alpha(j)\, \rho^e(\underline{r}_1 \overset{\prime}{\cdots} \underline{r}_N \mid \underline{r}_j)\, d\underline{r}_1 \overset{\prime}{\cdots} d\underline{r}_N \tag{38}$$

where $u_\alpha(j)$ is to be understood as being dependent on all the atomic coordinates and where the prime indicates omission of an atomic coordinate, in this case $\underline{r}_j$. A general type of average amplitude contains more information than $\langle u_\alpha(\underline{r}_j)\rangle$ and is defined by

$$\langle u_\alpha(\underline{r}_j \mid \underline{r}_{j'} \cdots)\rangle = \int\cdots\int u_\alpha(j)\, \rho^e(\underline{r}_1 \overset{\prime\prime\cdots}{\cdots} \underline{r}_N \mid \underline{r}_j\, \underline{r}_{j'} \cdots)\, d\underline{r}_1 \overset{\prime\prime\cdots}{\cdots} d\underline{r}_N \tag{39}$$

and is interpreted as the average value of $u_\alpha(j)$ when there are also atoms definitely at $\underline{r}_{j'}, \underline{r}_{j''}, \cdots$.

This is the mathematical apparatus for constructing average quantities. Our task now is to obtain equations for them. If we set $j = 1$ in (36), multiply by $\rho^e(\underline{r}_2 \cdots \underline{r}_N \mid \underline{r}_1)$ and integrate over $\underline{r}_2 \cdots \underline{r}_N$ then the left hand side is just

$$M\omega^2 \langle u_\alpha(\underline{r}_1)\rangle \quad . \tag{40}$$

The right hand side is not so simple. Taking a single term from the sum, say $j' = s$ then we have to consider

$$2\sum_{\alpha'}\int\cdots\int B_{\alpha\alpha'}(\underline{r}_1-\underline{r}_s)\{u_{\alpha'}(1)-u_{\alpha'}(s)\}\,p^e(\underline{r}_2\cdots\underline{r}_N|\underline{r}_1)\,d\underline{r}_2\cdots d\underline{r}_N \quad . \tag{41}$$

Using the fact that

$$p^e(\underline{r}_2\cdots\underline{r}_s\cdots\underline{r}_N|\underline{r}_1)=p^e(\underline{r}_s|\underline{r}_1)\,p^e(\underline{r}_2\cdots{}'\cdots\underline{r}_N|\underline{r}_1\underline{r}_s) \tag{42}$$

then (41) is simply

$$2\sum_{\alpha'}\int B_{\alpha\alpha'}(\underline{r}_1-\underline{r}_s)\,p^e(\underline{r}_s|\underline{r}_1)\{\langle u_{\alpha'}(\underline{r}_1|\underline{r}_s)\rangle-\langle u_{\alpha'}(\underline{r}_s|\underline{r}_1)\rangle\}\,d\underline{r}_s \quad . \tag{43}$$

This quantity is independent of $\underline{r}_s$ and so the sum over j' can be replaced by $(N-1)$ yielding the equation

$$M\omega^2\langle u_\alpha(\underline{r}_1)\rangle =$$
$$(N-1)\sum_{\alpha'}\int B_{\alpha\alpha'}(\underline{r}_1-\underline{r}_2)\,p^e(\underline{r}_2|\underline{r}_1)\{\langle u_{\alpha'}(\underline{r}_1|\underline{r}_2)\rangle-\langle u_{\alpha'}(\underline{r}_2|\underline{r}_1)\rangle\}\,d\underline{r}_2 \tag{44}$$

where we have set $s=2$ for convenience. This cannot be called an equation for $\langle u_\alpha(\underline{r}_1)\rangle$ since it contains another unknown function $\langle u_\alpha(\underline{r}_2|\underline{r}_1)\rangle$. This is a characteristic feature of averaging methods. If instead we multiply equation (36) by $p^e(\underline{r}_3\cdots\underline{r}_N|\underline{r}_1\underline{r}_2)$ and integrate over $\underline{r}_3\cdots\underline{r}_N$ then

$$\begin{aligned} M\omega^2\langle u_\alpha(\underline{r}_1|\underline{r}_2)\rangle &= \sum_{\alpha'} B_{\alpha\alpha'}(\underline{r}_1-\underline{r}_2)\left\{\langle u_{\alpha'}(\underline{r}_1|\underline{r}_2)\rangle-\langle u_{\alpha'}(\underline{r}_2|\underline{r}_1)\rangle\right\} \\ &+(N-2)\sum_{\alpha'}\int B_{\alpha\alpha'}(\underline{r}_1-\underline{r}_3)\,\rho^{e}(\underline{r}_3|\underline{r}_1\underline{r}_2)\left\{\langle u_{\alpha'}(\underline{r}_1|\underline{r}_2\underline{r}_3)\rangle-\langle u_{\alpha'}(\underline{r}_3|\underline{r}_1\underline{r}_2)\rangle\right\}d\underline{r}_3 . \end{aligned} \qquad (45)$$

Thus every equation we construct by this means contains an unknown function of a higher order. After going through this hierarchy of equations we obtain the equation for a particular configuration of atoms, i.e. equation (36).

Before investigating these equations in detail it is convenient to state how the idea of averaging the equation of motion differs from previous applications of this technique to wave propagation in continuous media and waves in lattices containing impurities. The most important point is that the equation of motion leaves the boundary conditions unstated. This is to be contrasted with work on electron waves in disordered systems of potentials where instead of averaging Schroedinger's differential equation an equivalent integral equation is averaged which implicitly states the boundary conditions imposed on the system.

For example, in Waterman and Truell's work (1961) the problem is considered of a free electron wave impinging on a semi-infinite region of disordered potentials. This is also the problem considered by Phariseau and Ziman (1963) and Ziman (1966) though this fact is somewhat veiled in these papers. Recently Taylor (1967) has considered the multiple scattering of vibrational waves by impurities in a lattice and again the formulation is in terms of an integral equation. This is a very convenient procedure but the reason we are unable to follow it directly in the case of structurally disordered solids is the basic difficulty that we do not have a set of waves which we can use as a representation and it is difficult to develop an integral equation formulation without introducing a representation.

Returning to the first of the averaged equations of motion (44) we can make as a first step the "quasi-crystalline" approximation due to Lax (1952). This consists of writing

$$\langle u_\alpha(\underline{r}_2|\underline{r}_1)\rangle \simeq \langle u_\alpha(\underline{r}_2)\rangle . \qquad (46)$$

This means that (44) is simplified to an equation containing a single function $\langle u_\alpha(\underline{r}_1)\rangle$ namely

$$M\omega^2\langle u_\alpha(\underline{r}_1)\rangle =$$

$$(N-1)\sum_{\alpha'}\int B_{\alpha\alpha'}(\underline{r}_1-\underline{r}_2)\,\rho^e(\underline{r}_2|\underline{r}_1)\{\langle u_{\alpha'}(\underline{r}_1)\rangle-\langle u_{\alpha'}(\underline{r}_2)\rangle\}\,d\underline{r}_2 \quad . \tag{47}$$

Approximation (46) states that the average value $\langle u_\alpha(\underline{r}_1|\underline{r}_2)\rangle$ is insensitive to the fact that there is definitely an atom at $\underline{r}_2$. We would expect this to be so when $\underline{r}_1$ and $\underline{r}_2$ are far apart and hence would expect this approximation to be particularly good when the force constants $B_{\alpha\alpha'}(\underline{r}_1-\underline{r}_2)$ are of a slowly varying long range nature so that the integrand in (47) is not dominated by the regions of $\underline{r}_2$ near to $\underline{r}_1$

Equation (47) is quite general but we now specialise to the case of homogeneous disorder where

$$\rho^e(\underline{r}_2|\underline{r}_1) = \rho^e(|\underline{r}_2-\underline{r}_1|) \, . \tag{48}$$

The function $\rho^e(|\underline{R}|)$ is the pair distribution function for equilibrium sites. This is not quite the same as the usual pair distribution function $\rho(|\underline{R}|)$ which can be measured by X-ray or neutron diffraction experiments. The function $\rho^e(|\underline{R}|)$ is the probability of finding an equilibrium site in $d\underline{R}$ when there is another site at $\underline{R}$, whereas $\rho(|\underline{R}|)$ is the probability of finding an atom in $d\underline{R}$ when there is another atom at $\underline{R}$. The typical form of $\rho(|\underline{R}|)$ in an amorphous solid is sketched in Figure 1. The data have been taken from the measurements of and substitution of this into (47) leads to the following equation for the cartesian components $\langle u_\alpha(\underline{k})\rangle$;

$$M\omega^2\langle u_\alpha(\underline{k})\rangle - \sum_{\alpha'} \mathcal{B}_{\alpha\alpha'}(\underline{k})\langle u_{\alpha'}(\underline{k})\rangle = 0 \; . \tag{50}$$

The matrix $\mathcal{B}_{\alpha\alpha'}(\underline{k})$ is analogous to the dynamical matrix in standard lattice dynamics theory (Maradudin, Montroll and Weiss, 1963) and is defined by

$$\mathcal{B}_{\alpha\alpha'}(\underline{k}) = 2(N-1)\int B_{\alpha\alpha'}(\underline{R})\,\rho^e(|\underline{R}|)\{1-\overline{e}^{i\underline{k}\cdot\underline{R}}\}d\underline{R} \; . \tag{51}$$

It is convenient to illustrate the nature of the eigen vectors of equation (50) and the relationship between ω and the wave vector of the average wave, by using a simple model for $\rho^e(|\underline{R}|)$ and $B_{\alpha\alpha'}(\underline{R})$. Let us consider the pair distribution function

$$\rho^e(|\underline{R}|) = \lambda_0\,\delta(|\underline{R}|-r_0) + \lambda_1\,H(|\underline{R}|-r_1) \tag{52}$$

where $H(x)$ is Heaviside's unit function, r_0 is the distance of the nearest neighbour equilibrium sites and r_1 is the closest equilibrium site of any other atom. The parameter λ_0 is chosen so that there are $\bar{n}$ nearest sites on the average, i.e.

$$\lambda_0 = \frac{\bar{n}}{4\pi N r_0^2} = \frac{8 r_0}{3^{3/2}\pi} \tag{53}$$

where N is the number of atoms per unit volume. λ_1 will be taken as unity, i.e. as if all the atoms are distributed at random when $|\underline{R}| \geqslant r_1$. In particular, we consider a hypothetical disordered solid having the same density and coordination numbers as a body centred lattice, i.e. $\bar{n}=8$, $r_1 = \frac{2r_0}{\sqrt{3}}$ and $N = \frac{3^{3/2}}{4r_0^3}$. This function is shown in Figure 2. A simple model for the $B_{\alpha\alpha'}(\underline{R})$ is obtained if we assume central forces

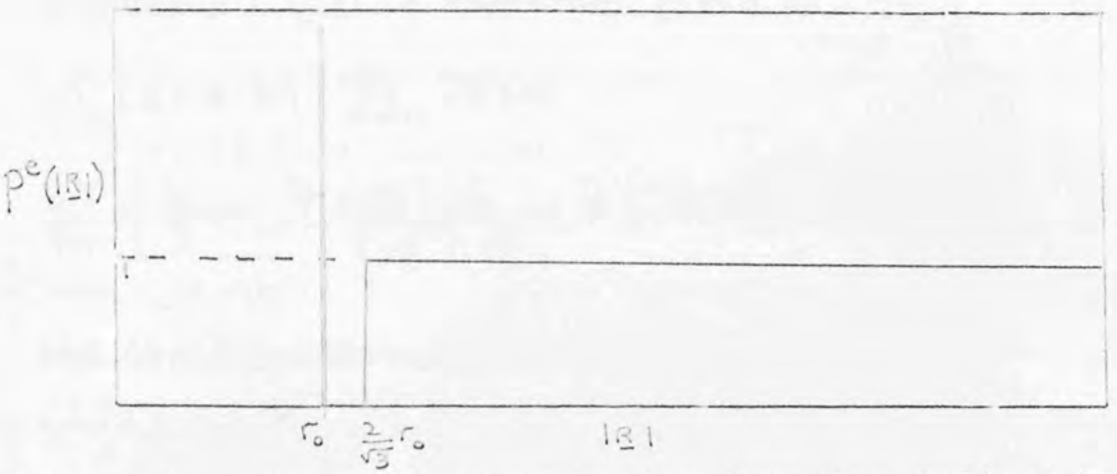


Figure 2. The pair distribution function defined by equation (52).

which are only finite in the region of r_0. Let $\alpha=1$, $\alpha=2$ and $\alpha=3$ correspond to the x, y and z directions respectively, then for $|\underline{r}_{jj'}| = r_0$ we can write the matrix $B_{\alpha\alpha'}(\underline{r}_{jj'})$ as

$$B_{11}(\underline{r}_{jj'}) = \frac{\gamma(x_{jj'})^2}{r_0^2}, \quad B_{12}(\underline{r}_{jj'}) = \gamma\frac{(x_{jj'})(y_{jj'})}{r_0^2}, \quad B_{13}(\underline{r}_{jj'}) = \gamma\frac{(x_{jj'})(z_{jj'})}{r_0^2} \qquad (54)$$

where the remaining elements can be deduced from symmetry arguments, and γ is a constant. It can readily be ascertained that if, say, the x-axis is always rotated to point in the direction of $\underline{k}$ the matrix $\mathcal{B}_{\alpha\alpha'}(\underline{k})$ is diagonal. For any value of $\underline{k}$ the eigen vectors of (50) consist of one longitudinal mode with $\langle \underline{u}(\underline{k}) \rangle$ pointing in the direction of $\underline{k}$ and two transverse modes with $\langle \underline{u}(\underline{k}) \rangle$ perpendicular to $\underline{k}$. The longitudinal frequency $\omega_L(\underline{k})$ is therefore given by

$$\omega^2_L(\underline{k}) = M^{-1}\mathcal{B}_{11}(\underline{k}) = \frac{8\gamma}{M}\left\{\frac{2}{3} - 4\frac{\cos|\underline{k}|r_0}{(|\underline{k}|r_0)^2} - 2\left((|\underline{k}|r_0)^2 - 2\right)\frac{\sin|\underline{k}|r_0}{(|\underline{k}|r_0)^3}\right\} \tag{55}$$

and the degenerate transverse frequencies by

$$\omega_T^2(\underline{k}) = M^{-1}\mathcal{B}_{22}(\underline{k}) = M^{-1}\mathcal{B}_{33}(\underline{k}) = \frac{8\gamma}{M}\left(1 - \frac{\sin|\underline{k}|r_0}{|\underline{k}|r_0}\right) - \frac{1}{2}\,\omega^2_L(\underline{k}). \tag{56}$$

These $\omega(\underline{k})$ relationships are sketched in Figure 3.

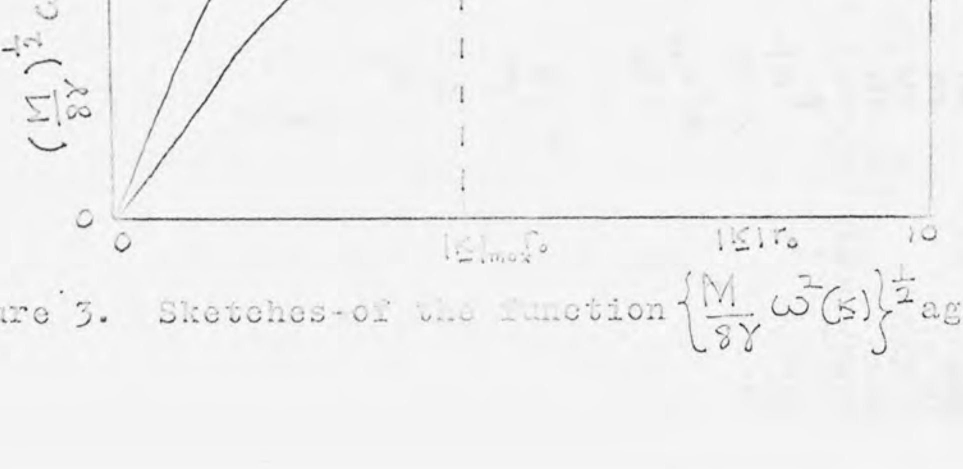


Figure 3. Sketches of the function $\left\{\frac{M}{8\gamma}\,\omega^2(\underline{k})\right\}^{\frac{1}{2}}$ against $|\underline{k}|r_0$

The interpretation of these figures for small values of $|\underline{k}|r_0$ is plain. These modes correspond to the long wavelength acoustic vibrations of an isotropic elastic medium. For $|\underline{k}|r_0$ less than π these results suggest that dispersion occurs just as in a perfect lattice, but they really tell us very little else. It is difficult to believe that the $\omega(\underline{k})$ function for $|\underline{k}|r_0 \gg \pi$ is of any significance since the curves are the product of approximation (46) which is expected to be valid for long wavelength vibrations. For example a large value of $|\underline{k}|r_0$ means that we only have to shift the equilibrium site of an atom a very small distance completely to change its vibrational amplitude which does not seem sensible. If we wish to consider the average waves as crude approximations to the normal modes of a single system then we must introduce a cut-off in the wave vectors just as in the Debye theory of specific heats, that is we choose the wave vectors to lie in a spherical zone with a radius

$$|\underline{k}|_{max.} = 2\pi\left(\frac{3N}{4\pi}\right)^{\frac{1}{3}} = \frac{2\pi}{r_0}\left(\frac{3^{\frac{5}{2}}}{16}\right)^{\frac{1}{3}} = 1\cdot3538\,\frac{\pi}{r_0}\,, \quad (57)$$

In the same way a cut-off would allow us to construct a rough approximation to the density of states from (55) and (56) but this must be viewed as a "last resort" procedure.

It should be stated that these kind of results have also been obtained in studies of the high frequency collective oscillations in liquids, (Schofield, 1966) although the methods used there are rather different. Recently Schneider and Stoll, (1967), have published curves showing the "dispersion" of high frequency waves in a liquid using Schofield's theory. These are very similar to those in Figure 3. A very interesting feature of work on liquids is that neutron scattering experiments have indicated "dispersion" laws like those in Figure 3, (Egalstaff, 1967, Cocking, 1967), and there does seem to be evidence that the $\omega(\underline{k})$ curve has some meaning beyond $|\underline{k}|_{max.}$.

The conclusion we draw from these results is that we must go beyond the "quasi-crystalline" approximation (46) if we are to obtain really useful results. The dispersion laws produced by this approximation can be obtained in a number of different ways, for example by substituting a plane wave trial function into the variational principle for ω^2 (Newell, 1958),

$$\delta[\omega^2] = \delta\left[\frac{\sum_{\alpha}\sum_{\alpha'}\sum\sum_{j\neq j'} \{u^*_\alpha(j) - u^*_\alpha(j')\} B_{\alpha\alpha'}(r_{jj'}) \{u_{\alpha'}(j) - u_{\alpha'}(j')\}}{M \sum_{\alpha}\sum_{j} u^*_\alpha(j)\, u_\alpha(j)} \right] . \qquad (58)$$

Incidentally, this variational argument does give the additional information that the maximum frequency of a disordered solid is greater than or equal to those obtained from equation (47). The usefulness of the averaging method is that we have plenty of room to "manoeuvre" and construct a better approximation than (46). One of the most disappointing features of these results is that equation (47) can be satisfied by plane waves with a purely <u>real</u> propagation constant. This is to be contrasted with work on waves in continuous media (e.g. Foldy, 1945; Lax, 1951, 1952; Waterman and Truell, 1961) where plane wave solutions are found with a complex propagation constant, i.e. the disorder causes the wave to attenuate as it passes through the solid. This failure to find a complex propagation constant is intimately linked with the fact that equation (47) does not contain any information about boundary conditions. We must distinguish between "standing wave" boundary conditions and "outgoing wave" type boundary conditions. In the first category comes the situation where we have a block of material with the surface atoms held fixed. We could satisfy this condition by forming the plane waves into sine and cosine waves but this is not a physically very interesting situation. The second category is usually much more interesting corresponding to waves being produced by some external agency acting on a disordered system. For example it could be a periodic force applied to the surface of a semi-infinite slab of material or perhaps just to a single atom in an infinite system.

The kind of behaviour to be expected for the two types of boundary condition can be guessed at by extrapolating what we know about solids containing impurities to the structurally disordered case. In the first case with the surface atoms held fixed we can think about the modes in terms of (a) perfect lattice waves which are modified to a small extent by the impurities and (b) modes which differ drastically from a single lattice wave. For example, if we introduce a single light isotope into a monatomic lattice most of the modes have an extended form corresponding to modified lattice waves, but in addition a triplet of states is produced which have frequencies greater than any of the lattice waves and these vibrational modes are localised around the isotope. If we now put a lot of isotopes into a solid the same sort of thing happens but the localised vibrations now overlap (if only by a very small amount) giving rise to a band of states whose vibrational modes are extended, even though they are made up of a superposition of localised modes.

On the other hand the case of an applied driving force is rather different. When a periodic force is applied to the surface of a slab of material a wave starts to travel inwards into the solid. The disorder "scatters" this wave so that as it progresses more and more energy is dissipated from the wave front resulting in attenuation of the wave amplitude as it recedes from the surface. This kind of behaviour can often be described in terms of a wave with a complex propagation constant; the imaginary part producing attenuation.

The same general behaviour is to be expected for an amorphous solid. This is why the approximate equation (47) cannot be expected (a) to produce localised vibrational modes and (b) to give attenuated wave solutions (since in the case of (b) there is nothing in the equation which states the inhomogeneous boundary condition). The resolution of these difficulties requires an investigation of Green functions for disordered solids and this is described in the next section.

1.3.2. Green functions

The Green function for a solid, denoted by $G_{\alpha\alpha_0}(j|j_0|\omega)$ is the displacement of an atom at $\underline{r}_j$ in the α direction, when a unit periodic force with frequency ω is applied in the α_0 direction to an atom at $\underline{r}_{j_0}$. This function satisfies the inhomogeneous equation of motion,

$$M\omega^2 G_{\alpha\alpha_0}(j|j_0|\omega) - 2\sum_{\alpha'}\sum_{j'\neq j} B_{\alpha\alpha'}(\underline{r}_{jj'})\left\{G_{\alpha'\alpha_0}(j|j_0|\omega) - G_{\alpha'\alpha_0}(j'|j_0|\omega)\right\}$$
$$= -\delta_{\alpha\alpha_0}\delta_{jj_0}. \tag{59}$$

The Green function is an extremely useful quantity and occupies a central position in any study of the vibrational properties of a solid. For example the displacement field due to a periodic force applied to the surface of a semi-infinite piece of material is obtained by adding up the Green functions originating from every driven atom on the surface. There are other reasons for trying to construct this function. The density of vibrational states $n(\omega)$ may be written as (Edwards, 1961)

$$n(\omega) = \frac{M\omega}{i\pi}\sum_{\alpha}\sum_{j}\left\{G^{+}_{\alpha\alpha}(j|j|\omega) - G^{-}_{\alpha\alpha}(j|j|\omega)\right\} \tag{60}$$

where the positive and negative signs denote "outgoing" and "incoming" Green functions respectively. This means that if $\underline{u}^n(j)$ denotes a normalised eigen function of the homogeneous form of (59) with an eigen frequency ω_n then

$$G^{\pm}_{\alpha\alpha_0}(j|j_0|\omega) = -\sum_{n}\frac{u^n_{\alpha}(j)\,u^n_{\alpha_0}(j_0)}{M(\omega^2 - \omega_n^2 \pm \epsilon)} \tag{61}$$

where ϵ is a positive infinitesimal which indicates how to carry out the "integration" over states near the pole at $\omega_n = \omega$.

The purpose of this chapter is to show that the "average equation of motion method" can be used to calculate average Green functions which behave roughly like $e^{i\kappa|\underline{R}|}/|\underline{R}|$ where $|\underline{R}|$ is the distance from the source and κ is a complex quantity so that the Green function decays exponentially. This work has not yet been applied to a specific realistic model of a disordered solid.

Average Green functions can be defined in precisely the same way as the average amplitudes in the previous chapter. For example $G'_{\alpha\alpha_0}(\underline{r}_2|\underline{r}_1|\omega)$ is defined by

$$G'_{\alpha\alpha_0}(\underline{r}_2|\underline{r}_1|\omega) = \int\cdots\int G_{\alpha\alpha_0}(2|1|\omega)\, p^e(\underline{r}_3\cdots\underline{r}_N|\underline{r}_1\underline{r}_2)\, d\underline{r}_3\cdots d\underline{r}_N \qquad (62)$$

and denotes the average response of an atom definitely at $\underline{r}_2$ when the force is applied to the atom at $\underline{r}_1$.

The average density of states is simply

$$\bar{n}(\omega) = \frac{NM\omega}{i\pi}\sum_{\alpha}\left\{G'^{+}_{\alpha\alpha}(\underline{r}_1|\omega) - G'^{-}_{\alpha\alpha}(\underline{r}_1|\omega)\right\} \qquad (63)$$

where

$$G'_{\alpha\alpha_0}(\underline{r}_1|\omega) = \int G'_{\alpha\alpha_0}(\underline{r}_1|\underline{r}_2|\omega)\, p^e(\underline{r}_2|r_1)\, d\underline{r}_2 \quad : \qquad (64)$$

The function $G'_{\alpha\alpha_0}(\underline{r}_1|\omega)$ is the average displacement of the driven atom when no other atoms are at definite positions, whilst $G'_{\alpha\alpha_0}(\underline{r}_1|\underline{r}_2|\omega)$ is the average displacement when there is definitely another atom at $\underline{r}_2$.

We will be particularly concerned with average equations for the functions $G'_{\alpha\alpha_0}(\underline{r}_2|\underline{r}_1|\omega)$ and $G'_{\alpha\alpha_0}(\underline{r}_1|\underline{r}_2|\omega)$. If j_0 is set equal to 1, j set equal to 2 in (59) and the equation multiplied by $\rho^e(\underline{r}_3 \cdots \underline{r}_N|\underline{r}_1\underline{r}_2)$ then integration over $\underline{r}_3 \cdots \underline{r}_N$ gives

$$M\omega^2 G'_{\alpha\alpha_0}(\underline{r}_2|\underline{r}_1|\omega) - 2\sum_{\alpha'} B_{\alpha\alpha'}(\underline{r}_2-\underline{r}_1)\left\{G'_{\alpha'\alpha_0}(\underline{r}_2|\underline{r}_1|\omega) - G'_{\alpha'\alpha_0}(\underline{r}_1|\underline{r}_2|\omega)\right\}$$
$$-2(N-2)\int\sum_{\alpha'} B_{\alpha\alpha'}(\underline{r}_2-\underline{r}_3)\,\rho^e(\underline{r}_3|\underline{r}_1\underline{r}_2)\left\{G'_{\alpha'\alpha_0}(\underline{r}_2|\underline{r}_1\underline{r}_3|\omega) - G'_{\alpha'\alpha_0}(\underline{r}_3|\underline{r}_1\underline{r}_2|\omega)\right\}d\underline{r}_3 \tag{65}$$
$$= 0$$

where $G'_{\alpha\alpha_0}(\underline{r}_2|\underline{r}_1\underline{r}_3|\omega)$ denotes the average response at when there is an atom definitely at $\underline{r}_3$ in addition to the driven atom which is at $\underline{r}_1$. A different equation to (65) results when $j = j_0 = 1$ then

$$M\omega^2 G'_{\alpha\alpha_0}(\underline{r}_1|\underline{r}_2|\omega) - 2\sum_{\alpha'} B_{\alpha\alpha'}(\underline{r}_1-\underline{r}_2)\left\{G'_{\alpha'\alpha_0}(\underline{r}_1|\underline{r}_2|\omega) - G'_{\alpha'\alpha_0}(\underline{r}_2|\underline{r}_1|\omega)\right\}$$
$$-2(N-2)\int\sum_{\alpha'} B_{\alpha\alpha'}(\underline{r}_1-\underline{r}_3)\,\rho^e(\underline{r}_3|\underline{r}_1\underline{r}_2)\left\{G'_{\alpha'\alpha_0}(\underline{r}_1|\underline{r}_2\underline{r}_3|\omega) - G_{\alpha'\alpha_0}(\underline{r}_3|\underline{r}_1\underline{r}_2|\omega)\right\}d\underline{r}_3 \tag{66}$$
$$= -\delta_{\alpha\alpha_0}\,.$$

Equations (65) and (66) show the characteristic feature of this kind of averaging method, namely they contain higher order average functions, which must be eliminated for any progress to be made. It will be noted that these equations contain three particle correlation functions. These quantities cannot be measured experimentally unlike the simpler two particle correlations. This lack of knowledge of these functions is the major impediment to practical application of the method to be described. We take the view that the construction of theoretical models of correlations in a disordered solid is a question for subsequent study which cannot be avoided. In liquids the situation is simpler because the superposition approximation can often be invoked namely

$$p(\underline{r}_3|\underline{r}_1\underline{r}_2) \simeq p(\underline{r}_3|\underline{r}_1)\,p(\underline{r}_3|\underline{r}_2) \,. \qquad (67)$$

This relation holds for amorphous solids when $\underline{r}_3$, $\underline{r}_2$ and $\underline{r}_1$ are separated by distances larger than a length characterizing the range of order in the solid. This length can be of the order of a few atomic spacings. For closer distances models must be devised to describe the short range correlations. This would not seem to be an insurmountable task, for example in fused silica it is known from the nature of the chemical bond between silicon and oxygen atoms that the oxygen atoms are approximately at the corners of a tetrahedron centred around the silicon atoms. Setting aside the question of the correlation functions we turn to the problem of solving (65) and (66) assuming a model for $\rho^c(\underline{r}_3|\underline{r}_1\underline{r}_2)$ is available.

Clearly the most obvious first step towards solving these equations is the introduction of a quasi-crystalline approximation. In contrast to the simpler equation (44) there is now a choice as to which particle coordinate to drop in the functions under the integral signs in (65) and (66). The simplest procedure is to put

$$G'_{\alpha\alpha_0}(\underline{r}_2|\underline{r}_1\underline{r}_3|\omega) \simeq G'_{\alpha\alpha_0}(\underline{r}_2|\underline{r}_1|\omega) \tag{68}$$

in (65), and in (66)

$$G'_{\alpha\alpha_0}(\underline{r}_1|\underline{r}_2\underline{r}_3|\omega) \simeq G_{\alpha\alpha_0}(\underline{r}_1|\underline{r}_3|\omega) \ . \tag{69}$$

The choice (68) is motivated by the fact that the coordinate of the driven atom must be retained while (69) seems most reasonable in view of the fact that the integrand in (66) will be dominated by values of $\underline{r}_3$ close to $\underline{r}_1$, at least for short range forces. A possible improvement on (69) is

$$G'_{\alpha\alpha_0}(\underline{r}_1|\underline{r}_2\underline{r}_3|\omega) \simeq G'_{\alpha\alpha_0}(\underline{r}_1|\underline{r}_2|\omega) + G'_{\alpha\alpha_0}(\underline{r}_1|\underline{r}_3|\omega) - G'_{\alpha\alpha_0}(\underline{r}_1|\omega) \ , \tag{70}$$

since this has the correct limiting behaviour for $|\underline{r}_3-\underline{r}_1| \gg |\underline{r}_2-\underline{r}_1|$ and also for $|\underline{r}_3-\underline{r}_1| \ll |\underline{r}_2-\underline{r}_1|$.

The consequences of making a quasi-crystalline approximation will be investigated for a very simple model, namely the loaded continuum model for a random distribution of spheres when they have a radius which is small compared with the mean spacing. It will be shown that the quasi-crystalline approach leads to an unattenuated Green function just as was found for the plane wave solution in the previous section. Attenuation can be introduced by using the next equation in the hierarchy of averaged equations. This procedure is much too involved for realistic models but a practical alternative is described at the end of the chapter which will give an attenuated Green function solution.

In the case of small spheres the equations for the loaded continuum model (15) may be simplified because only S-waves need be retained in the expansion (9). Writing β^j_{00} as β^j then

$$\gamma_0(\omega)\,\beta^j = \sum_{j' \neq j} \frac{1}{|\underline{r}_j-\underline{r}_{j'}|}\,\beta^{j'}. \tag{71}$$

The corresponding inhomogeneous form of (71) is required when a unit force is applied to the atom j_0 along one of the cartesian axes. Equation (9) must be amended to read (including only S-waves),

$$U_j(\rho) = (4\pi)^{-\frac{1}{2}} \left(\rho^{-1} + \gamma_0(j,\omega) \right) \beta^{jj_0} \tag{72}$$

where $\gamma_0(j,\omega)$ now depends on the position of the atom j. Equation (10) must also be modified if a unit force is applied to the j_0 atom, namely

$$-M\omega^2 U_j(\underline{s}) = \int \mu \left\{ \nabla U_j(\underline{s}') + U_j(\underline{s}')\nabla - \mathrm{div}\, U_j(\underline{s}') \right\} \cdot d\underline{s}' + \delta_{jj_0} . \tag{73}$$

Substitution from (72) into (73) gives

$$\gamma_0(j_0,\omega) = \gamma_0(\omega) + \frac{(4\pi)^{\frac{1}{2}}}{M\omega^2 \beta^{jj_0}} \tag{74}$$

$$\gamma_0(j,\omega) = \gamma_0(\omega) \qquad (j \neq j_0). \tag{75}$$

and using condition (7) we find

$$\gamma_0(\omega)\beta^{jj_0} - \sum_{j' \neq j} \frac{1}{|\underline{r}_j - \underline{r}_{j'}|} \beta^{j'j_0} = -\frac{(4\pi)^{\frac{1}{2}}}{M\omega^2} \delta_{jj_0} \tag{76}$$

The equation for the Green function is obtained by using (22);

$$\gamma_0(\omega) G(j|j_0|\omega) - \sum_{j' \neq j} \frac{G(j'|j_0|\omega)}{|\underline{r}_{j'} - \underline{r}_j|} = -\frac{4\pi\mu}{(M\omega^2)^2} \delta_{jj_0} . \tag{77}$$

It is convenient to consider a force of strength so that the response denoted by $\mathcal{G}(j|j_0|\omega)$ satisfies the equation

$$\gamma_0(\omega)\mathcal{G}(j|j_0|\omega) - \sum_{j' \neq j} \frac{1}{|\underline{r}_j - \underline{r}_{j'}|} \mathcal{G}(j'|j_0|\omega) = -\delta_{jj_0} . \tag{78}$$

The density of states is given in terms of this function by

$$n(\omega) = -\frac{12\mu}{M\omega^3 i} \sum_{j'} \left\{ \mathcal{G}^+(j|j|\omega) - \mathcal{G}^-(j|j|\omega) \right\} . \tag{79}$$

The averaging procedure may now be applied to (78) and the equations analogous to (65) and (66) are

$$\begin{aligned} &\gamma_0(\omega)\, \mathcal{G}'(\underline{r}_2|\underline{r}_1|\omega) - \frac{1}{|\underline{r}_2 - \underline{r}_1|}\, \mathcal{G}'(\underline{r}_1|\underline{r}_2|\omega) \\ &- (N-2) \int \frac{1}{|\underline{r}_2 - \underline{r}_3|}\, \mathcal{G}'(\underline{r}_3|\underline{r}_1 \underline{r}_2|\omega)\, d\underline{r}_3 = 0 \end{aligned} \tag{80}$$

and

$$\begin{aligned} &\gamma_0(\omega)\, \mathcal{G}'(\underline{r}_1|\underline{r}_2|\omega) - \frac{1}{|\underline{r}_1 - \underline{r}_2|}\, \mathcal{G}'(\underline{r}_2|\underline{r}_1|\omega) \\ &- (N-2) \int \frac{1}{|\underline{r}_1 - \underline{r}_3|}\, \mathcal{G}'(\underline{r}_3|\underline{r}_1 \underline{r}_2|\omega)\, d\underline{r}_3 = -1 \end{aligned} \tag{81}$$

where all correlation functions have been replaced by unity corresponding to a completely random distribution of spheres. This is not strictly possible because the spheres have a finite size and cannot overlap but this is of no consequence in the following argument. This pair of equations are a little simpler than the general ones (65) and (66) because only a single function occurs under the integral sign and there is no dilemma as to which particle coordinate to drop. We therefore write

$$\mathcal{G}'(\underline{r}_3|\underline{r}_1\underline{r}_2|\omega) \simeq \mathcal{G}'(\underline{r}_3|\underline{r}_1|\omega) \tag{82}$$

in (80) and (81).

The equations can be decoupled and solved by a combination of the method of Fourier transforms and successive approximation but we will consider only the asymptotic form of $\mathcal{G}'(\underline{r}_2|\underline{r}_1|\omega)$ which can be obtained by a simpler process.

The function $\mathcal{G}'(\underline{r}_1|\underline{r}_2|\omega)$ is not expected to be strongly dependent on $\underline{r}_2$ especially for "large" values of $|\underline{r}_1 - \underline{r}_2|$. We therefore write

$$\mathcal{G}'(\underline{r}_1|\underline{r}_2|\omega) \simeq \mathcal{G}'(\underline{r}_1|\omega) \tag{83}$$

in (80) and solve for $\mathcal{G}'(\underline{r}_2|\underline{r}_1|\omega)$ in terms of $\mathcal{G}'(\underline{r}_1|\omega)$.

We now substitute the trial solution

$$\mathcal{G}'(\underline{r}_2|\underline{r}_1|\omega) = \frac{\alpha\, e^{ik|\underline{r}_2-\underline{r}_1|}}{|\underline{r}_2-\underline{r}_1|} \tag{84}$$

into (80) assuming that k has a small positive imaginary part, and obtain

$$\alpha\left\{\gamma_0(\omega) - \frac{4\pi(N-2)}{k^2}\right\}\frac{e^{ik|\underline{r}_2-\underline{r}_1|}}{|\underline{r}_2-\underline{r}_1|} + \left\{\frac{4\pi(N-2)\alpha}{k^2} - \mathcal{G}'(\underline{r}_1|\omega)\right\}\frac{1}{|\underline{r}_2-\underline{r}_1|} = 0 \tag{85}$$

.

This means that for (85) to be satisfied for all values of $|\mathbf{r}_2 - \mathbf{r}_1|$ we must have

$$\begin{aligned} \kappa^2 &= 4\pi(N-2) \Big/ \left(\frac{4\pi\mu}{M\omega^2} - \frac{1}{R_s} \right), \\ \alpha &= \mathcal{G}'(\mathbf{r}_1|\omega) \Big/ \left(\frac{4\pi\mu}{M\omega^2} - \frac{1}{R_s} \right), \end{aligned} \tag{86}$$

and therefore κ is purely real for $\omega^2 < \frac{4\pi\mu R_s}{M}$ and purely imaginary for $\omega^2 > \frac{4\pi\mu R_s}{M}$ This is just the sort of behaviour found in perfect lattices but in the disordered case we would expect to find a complex κ. This is in fact the problem encountered when solving the homogeneous equation of motion.

Before going on to discuss how the attenuation effects are introduced into the Green function the density of states predicted by this simple approximate solution will be briefly discussed. The first approximation to $\mathcal{G}'(\mathbf{r}_1|\mathbf{r}_2|\omega)$ is obtained by substituting from (84) and (86) into (81) whereby

$$\mathcal{G}'(\mathbf{r}_1|\mathbf{r}_2|\omega) \simeq \gamma_0^{-1}(\omega) \left\{ \frac{\alpha e^{i\kappa|\mathbf{r}_1 - \mathbf{r}_2|}}{|\mathbf{r}_1 - \mathbf{r}_2|^2} - \frac{4\pi(N-2)}{i\kappa}\alpha - 1 \right\} \tag{87}$$

and therefore

$$\mathcal{G}'(\mathbf{r}_1|\omega) \simeq \int \mathcal{G}'(\mathbf{r}_1|\mathbf{r}_2|\omega)\, d\mathbf{r}_2 \simeq -\gamma_0^{-1}(\omega) \left\{ 1 - \frac{4\pi i(N-1)\alpha}{\kappa} \right\}. \tag{88}$$

The constant α can now be determined using (86), namely

$$\alpha = \frac{-\gamma_0^{-2}(\omega)}{\left(1 - \frac{4\pi i(N-1)}{\kappa\, \gamma_0^{2}(\omega)}\right)} . \tag{89}$$

It may be readily ascertained that $\mathcal{G}'(\underline{r}_1|\underline{r}_2|\omega)$ is insensitive to there being an atom at $\underline{r}_2$ especially for low frequencies where the "asymptotic" form holds everywhere except at the driven atom. Better approximations to $\mathcal{G}'(\underline{r}_2|\underline{r}_1|\omega)$ can be obtained by "feeding" (87) back into equation (80) but this will not be considered here.

Using (79), (88) and (89) the normalised density of states is

$$\overline{g}(\omega) = \frac{\overline{n}(\omega)}{3N} = \frac{32\,\mu\,(N-1)\,\pi}{M\omega^3\, \gamma_0^3(\omega)\,|\kappa|\left(1 + \left[\frac{4\pi(N-1)}{|\kappa|\,\gamma_0^2(\omega)}\right]\right)} \tag{90}$$

and this function is sketched in Figure 4.

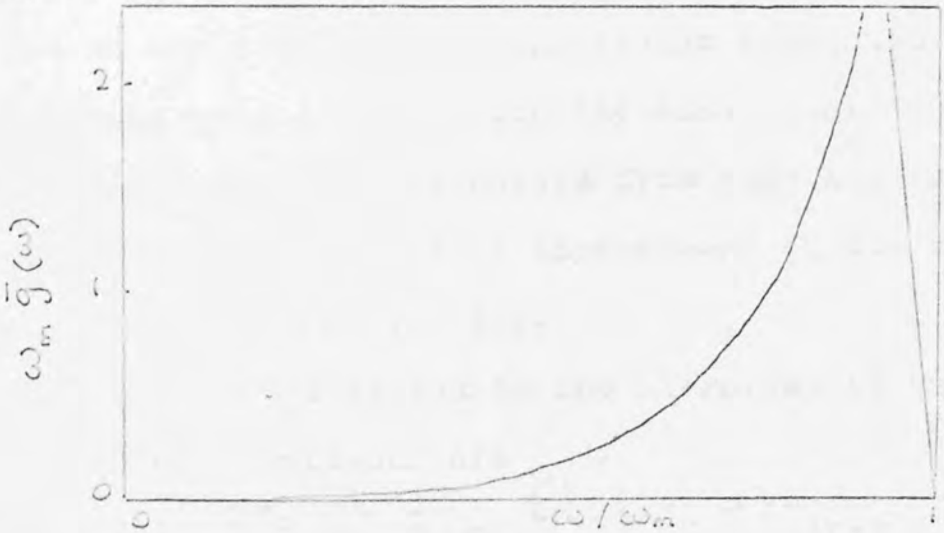


Figure 4. Sketch of $\omega_m \overline{g}(\omega)$ against ω/ω_m where $\omega_m = \sqrt{\frac{4\pi\mu R_s}{M}}$ and R_s has been taken as $\frac{1}{4}(N)^{-\frac{1}{3}}$.

There is little to say about this extremely crude result other than the fact that it is in accord with the intuitive idea that there should be a fairly sharp cut off in the density of states in a disordered system just as in an ordered one. A program could be embarked upon for solving equations (65) and (66) within the quasi-crystalline approximation for a model where a machine calculation has been made but this cannot really be justified in view of the fact that this approximation does not predict any attenuation effect, which is a serious flaw.

An additional reason why it is important to determine the rate at which the Green function attenuates is that this can be measured experimentally. It is also related to the resistance to heat flow in a solid, though not in any simple way. The loaded continuum model will again be used to elucidate the basic features of the problem. The insight gained from this has helped in constructing a practical improvement on the quasi-crystalline approximation.

The next equations in the hierarchy of equations for the loaded continuum are

$$\begin{aligned}&\gamma_0(\omega)\,\mathcal{G}'(\underline{r}_3|\underline{r}_1\underline{r}_2|\omega)-\frac{1}{|\underline{r}_3-\underline{r}_1|}\,\mathcal{G}'(\underline{r}_1|\underline{r}_2\underline{r}_3|\omega)-\frac{1}{|\underline{r}_3-\underline{r}_2|}\,\mathcal{G}'(\underline{r}_2|\underline{r}_1\underline{r}_3|\omega)\\&-(N-3)\int\frac{1}{|\underline{r}_3-\underline{r}_4|}\,\mathcal{G}'(\underline{r}_4|\underline{r}_1\underline{r}_2\underline{r}_3|\omega)\,d\underline{r}_4=0\end{aligned}\qquad(91)$$

and

$$\gamma_0(\omega)\,\mathcal{G}'(\underline{r}_1|\underline{r}_2\underline{r}_3|\omega) - \frac{1}{|\underline{r}_1-\underline{r}_2|}\,\mathcal{G}'(\underline{r}_2|\underline{r}_1\underline{r}_3|\omega) - \frac{1}{|\underline{r}_1-\underline{r}_3|}\,\mathcal{G}(\underline{r}_3|\underline{r}_1\underline{r}_2|\omega)$$

$$-\,(N-3)\int\frac{1}{|\underline{r}_1-\underline{r}_4|}\,\mathcal{G}'(\underline{r}_4|\underline{r}_1\underline{r}_2\underline{r}_3|\omega)\,d\underline{r}_4 = -1\,. \qquad (92)$$

These equations are becoming exceedingly complicated especially when we include the correlation functions. However, the intent here is to show that by obtaining an approximate solution to $\mathcal{G}'(\underline{r}_3|\underline{r}_1\underline{r}_2|\omega)$ in terms of the unknown function $\mathcal{G}'(\underline{r}_3|\underline{r}_1|\omega)$ and by putting this back into (80) an imaginary part is introduced into the propagation constant K.

In (91) we write

$$\mathcal{G}'(\underline{r}_4|\underline{r}_1\underline{r}_2\underline{r}_3|\omega) \simeq \mathcal{G}'(\underline{r}_4|\underline{r}_1\underline{r}_2|\omega) + \mathcal{G}'(\underline{r}_4|\underline{r}_1\underline{r}_3|\omega) - \mathcal{G}'(\underline{r}_4|\underline{r}_1|\omega) \qquad (93)$$

and then substitute

$$\mathcal{G}'(\underline{r}_4|\underline{r}_1\underline{r}_2|\omega) = \mathcal{G}'(\underline{r}_4|\underline{r}_1|\omega) + g'(\underline{r}_4|\underline{r}_1\underline{r}_2|\omega)\,,$$

$$\mathcal{G}'(\underline{r}_1|\underline{r}_2\underline{r}_3|\omega) = \mathcal{G}'(\underline{r}_1|\underline{r}_3|\omega) + g'(\underline{r}_1|\underline{r}_2\underline{r}_3|\omega)\,. \qquad (94)$$

Using (80) equation (91) can then be recast in the inhomogeneous form

$$\gamma_0(\omega)\, g'(\underline{r}_3|\underline{r}_1\underline{r}_2|\omega) - \frac{1}{|\underline{r}_3-\underline{r}_1|}\, g'(\underline{r}_1|\underline{r}_2\underline{r}_3|\omega) - \frac{1}{|\underline{r}_3-\underline{r}_2|}\, g'(\underline{r}_2|\underline{r}_1\underline{r}_3|\omega)$$
$$- (N-3)\int \frac{1}{|\underline{r}_3-\underline{r}_4|}\, g'(\underline{r}_4|\underline{r}_1\underline{r}_2|\omega)\, d\underline{r}_4 = \frac{1}{|\underline{r}_3-\underline{r}_2|}\, \mathcal{G}'(\underline{r}_2|\underline{r}_1|\omega) . \qquad (95)$$

The second and third terms in (95) will be treated as perturbations which can be ignored in a first approximation. Neglecting the second term is justified when $|\underline{r}_2-\underline{r}_1|$ and $|\underline{r}_3-\underline{r}_1|$ are large. If k_0 denotes the propagation constant given by equation (86), then comparison of (95) and (80) shows that an approximate solution to (95) is

$$g'(\underline{r}_3|\underline{r}_1\underline{r}_2|\omega) \simeq \mathcal{G}'(\underline{r}_2|\underline{r}_1|\omega)\, \frac{e^{\pm i k_0 |\underline{r}_3-\underline{r}_2|}}{\gamma_0(\omega)\, |\underline{r}_3-\underline{r}_2|} \qquad (96)$$

or

$$\mathcal{G}'(\underline{r}_3|\underline{r}_1\underline{r}_2|\omega) \simeq \mathcal{G}'(\underline{r}_3|\underline{r}_1|\omega) + \mathcal{G}'(\underline{r}_2|\underline{r}_1|\omega)\, \frac{e^{\pm i k_0 |\underline{r}_3-\underline{r}_2|}}{\gamma_0(\omega)\, |\underline{r}_3-\underline{r}_2|} . \qquad (97)$$

This result has a simple interpretation. The Green function $\mathcal{G}'(\underline{r}_3|\underline{r}_1|\omega)$ travels out from $\underline{r}_1$ through the average medium and is scattered by the departure of the solid from the average, introduced by there being a sphere at $\underline{r}_2$. The approximate result (97) can now be substituted back into (80). If this is carried out and the solution

$$\mathcal{G}'(\underline{r}_2|\underline{r}_1|\omega) = \alpha_1 \frac{e^{i\kappa_1|\underline{r}_2-\underline{r}_1|}}{|\underline{r}_2-\underline{r}_1|} \tag{98}$$

is tried, then instead of (95) we find

$$\begin{aligned} &\alpha_1\left\{\gamma_0(\omega) - \frac{4\pi(N-2)}{\kappa_1^2} - i\kappa_0\right\}\frac{e^{i\kappa_1|\underline{r}_2-\underline{r}_1|}}{|\underline{r}_2-\underline{r}_1|} \\ &+\left\{\frac{4\pi(N-2)\alpha_1}{\kappa_1^2} - \mathcal{G}'(\underline{r}_1|\omega)\right\}\frac{1}{|\underline{r}_2-\underline{r}_1|} = 0 . \end{aligned} \tag{99}$$

Hence

$$\kappa_1^2 = \frac{4\pi(N-2)}{\gamma_0(\omega)-i\kappa_0} = \frac{4\pi(N-2)(\gamma_0(\omega)+i\kappa_0)}{(\gamma_0^2(\omega)+\kappa_0^2)} \tag{100}$$

which can be solved for the real and imaginary parts of κ_1 by writing

$$\kappa_1 = \pm\kappa_r + i\kappa_i . \tag{101}$$

κ_1 is purely imaginary for $\omega/\omega_m > 1$. The values of κ_r and κ_i are plotted out in Figure 5 for $\omega/\omega_m < 1$.

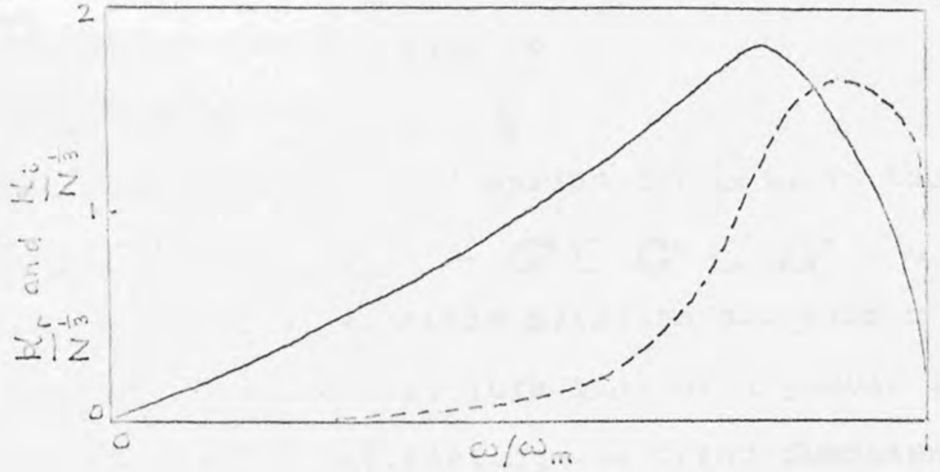


Figure 5. The real and imaginary parts of κ_1. The broken curve represents κ_i.

These results are probably not meaningful near $\omega/\omega_m = 1$ but they indicate the behaviour to be expected for more realistic models. The quantity κ_i is small compared with κ_r for most of the frequency range and then rises rapidly to become roughly equal to κ_r near $\omega = \omega_m$. The procedure used for the loaded continuum model is not likely to be useful in general because it is difficult to see the important features through a maze of correlation functions and various kinds of average Green functions. We now consider an approach which has practical possibilities.

The exact equation for the Green function (59) will be symbolized by

$$L\,G - M\omega^2 G = \delta \tag{102}$$

and we suppose that the operator L can be split into an "unperturbed" part L° plus a perturbation L'. If G° denotes the solution to

$$L^{\circ} G^{\circ} - M\omega^2 G^{\circ} = \delta \tag{103}$$

then the "perturbation" series for G takes the form

$$G = G^{\circ} - G^{\circ} L' G^{\circ} + G^{\circ} L' G^{\circ} L' G^{\circ} - - - \tag{104}$$

where an obvious symbolic notation has been used. It has been stressed that this kind of argument is difficult to use for calculating the Green function for structurally disordered solids because the operator does not split into an L° and L' in any natural way.

However, slight manipulation of this formal expansion makes it possible to generate successive approximations beginning with an arbitrary "guessed" solution.

We first note that G^0 and G must satisfy the conditions

$$G^0 = G^0 - G^0 L^0 G^0 , \qquad \text{(a)}$$
$$G = G - G L G , \qquad \text{(b)} \qquad (105)$$

or

$$G^0 L^0 G^0 = 0 , \qquad \text{(a)}$$
$$G L G = 0 . \qquad \text{(b)} \qquad (106)$$

These conditions (105) have a very simple meaning. The force acting on any atom consists of the applied driving forces plus the forces due to the motion of the atoms to which it is coupled. Thus if a force is applied to one particular atom the response at a second atom is made up of a Green function coming from the driven atom plus secondary sources from every atom in the system. The secondary source Green functions must cancel each other, and this is the interpretation of (106).

If G^0 is a good approximation to G then

$$G \simeq G^0 - G^0 L' G^0 \qquad (107)$$

and using (106) (a) we can rewrite this as

$$G \simeq G^{0} - G^{0} L \, G^{0} \, . \qquad (108)$$

The beauty of this simple "trick" is that we no longer need to construct an "unperturbed" operator. We guess an appropriate G^{0} and assume that an L^{0} exists such that G^{0} satisfies (103), then an improved approximation to G can be obtained from (108). The success of this approach depends on the initial choice for G^{0} being a good one but it offers great scope when we have an intuitive idea as to the form G should take. We can, of course, repeat the process using (108) as a zeroth approximation to G but this will not be considered further.

This idea is particularly useful for constructing a better approximation than the quasi-crystalline one, using the idea that $G^{1}_{\alpha\alpha_0}(\underline{r}_3|\underline{r}_1\underline{r}_2|\omega)$ is something like $G^{1}_{\alpha\alpha_0}(\underline{r}_3|\underline{r}_1|\omega)$ plus a "scattered" wave originating from $\underline{r}_2$. This work is still at an exploratory stage. We define an unperturbed Green function by

$$G^{0}_{\alpha\alpha_0}(j|j_0|\omega) = G^{j_0}_{\alpha\alpha_0}(\underline{r}_j|\underline{r}_{j_0}|\omega) \qquad (j \neq j_0) \; ;$$

$$G^{0}_{\alpha\alpha_0}(j_0|j_0|\omega) = G^{j_0}_{\alpha\alpha_0}(\underline{r}_{j_0}|\omega) \; ; \qquad (109)$$

that is, we take as the zeroth approximation to the Green function for a particular configuration of atoms the (unknown) average Green function. The first two terms of (108), when written out in full, are

$$G_{\alpha\alpha_0}(j|j_0|\omega) \simeq G^{0}_{\alpha\alpha_0}(j|j_0|\omega)$$

$$-2\sum_{\alpha'}\sum_{j'\neq j''} G^{0}_{\alpha\alpha'}(j|j'|\omega)\sum_{\alpha''}\sum_{j''} B_{\alpha'\alpha''}(\underline{r}_{j'}-\underline{r}_{j''})\left\{G^{0}_{\alpha''\alpha_0}(j'|j_0|\omega)-G^{0}_{\alpha''\alpha_0}(j''|j_0|\omega)\right\} \tag{110}$$

We therefore have an approximation to the Green function for a particular configuration of atoms in terms of average Green functions, so that approximations to the functions $G^{1}_{\alpha\alpha_0}(\underline{r}_3|\underline{r}_1\underline{r}_2|\omega)$ and $G^{1}_{\alpha\alpha_0}(\underline{r}_1|\underline{r}_2,\underline{r}_3|\omega)$ can be obtained by averaging (110). It is confidently expected that these approximations will lead to attenuated Green function solutions when substituted back into (65) and (66). The procedure is complicated but until a particular calculation is attempted it is not possible to say if all the complications are necessary for obtaining a satisfactory picture of Green functions in disordered solids.

This chapter has been written with blithe disregard for the fact that the correlation functions which occur cannot be determined experimentally and, as far as we are aware, there has been no theoretical work on this problem. It is not so much that nothing is known about the structure of disordered solids but that this knowledge is not easily translated into mathematical terms.

The view is taken that the complexities described in this chapter are probably a consequence of the nature of the problem rather than the particular kind of approach. The nature of the correlation functions in a solid must be faced up to and a calculation for a specific model attempted, even if this means taking the retrograde step of working with one-dimensional models in the first instance so that comparison may be made with machine calculations.

1.4. Thermal conduction.

The subject of heat transport in structurally disordered solids is virtually untouched apart from a schematic theory of Klemens (1960, 1965) which involves treating an amorphous solid as an elastic continuum containing fluctuations of density and elasticity (Krumhansl, 1963). This does not mean that there is any basic difference in the nature of heat flow in perturbed lattices and in structurally disordered solids. The problem is to find an adequate mathematical description in the latter case, taking into account the discrete structure of solids.

This frustrating situation has been resolved by transforming from the individual coordinates of the atoms to new collective ones. The kind of transformation is well known in theories of collective oscillations in liquids (e.g. Zubarev,1953; Green,1954; Tomonaga,1955 a,b; Percus and Yevick,1958; Mori,1962) but has not previously been used in the theory of vibrating solids. By this means it is found possible to develop a theory of heat transport within the framework of a Boltzmann equation which is quite analogous to the standard theory and indeed is exactly the same in the limit when atoms occur at lattice sites. This approach is presented in the simplest and most basic form since further sophistications are not justified in general at this stage.

Although this method was developed with the problem of amorphous solids in mind there are a large number of simpler situations where its use is necessary, namely whenever a solid cannot be described easily as a distorted lattice. In addition it is possible to investigate the effect of structural disorder on the traditional three-phonon processes encountered in anharmonic lattices.

The "spring" model of a solid with the Hamiltonion defined by equation (3) is used to develop the argument although more general kinds of Hamiltonion could be dealt with along the same lines.

1.4.1. Point transformations

The form of the Hamiltonion (3), which is expressed in terms of "real-space" coordinates, is inconvenient in general because it does not separate into a part with known eigen functions and a part which may be regarded as a perturbation. One particular way of seeking more attractive forms is by using a point transformation of the type

$$u_\alpha(j) = \frac{1}{N^{\frac{1}{2}}} \sum_s U_\alpha(s)\, \phi_s(j) \tag{111}$$

where the $\phi_s(j)$ denote a complete set of independent functions of the discrete variable j, and S is a label which has just N values, N being the number of atoms in the system being considered. These functions must, of course, satisfy the prescribed boundary placed on the system.

It is not necessary to use an orthonormal set of functions but it is clearly desirable to do so whenever possible and it is usual to employ functions which are approximations to the shape of the normal modes of the system. With regard to structurally disordered solids we do not know functions with both these properties but if the condition of orthonormality is dropped then it is easier to devise functions which have the second property.

New momenta $P_\alpha(s)$ which are canonically conjugate to the "displacements" $U_\alpha(s)$ may be defined by

$$P_\alpha(s) = \frac{\partial \mathcal{L}}{\partial \dot{U}_\alpha(s)} \tag{112}$$

where

$$\dot{U}_\alpha(s) = \frac{d}{dt} U_\alpha(s) , \tag{113}$$

and $\mathcal{L}$ denotes the Lagrangian. From the Hamiltonion (3) we therefore have

$$P_\alpha(s) = \frac{1}{N^{\frac{1}{2}}} \sum_j p_\alpha(j) \, \phi_s(j) \tag{114}$$

and

$$p_\alpha(j) = \frac{1}{N^{\frac{1}{2}}} \sum_s P_\alpha(s) \, \psi^*_s(j) \tag{115}$$

where the $\psi_s(j)$ denote a second set of functions which satisfy

$$\frac{1}{N}\sum_{j}\psi^{*}_{s'}(j)\,\phi_s(j)=\delta_{ss'} \tag{116}$$

and

$$\frac{1}{N}\sum_{s}\psi^{*}_{s}(j')\,\phi_s(j)=\delta_{ss'}\,. \tag{117}$$

The functions $\psi_s(j)$ are said to be biorthonormal to the set $\phi_s(j)$ with respect to the scalar product defined in (116).

We now assume that for most types of structurally disordered solid it is possible to find a set of N independent plane waves such that

$$u_\alpha(j)=\frac{1}{N^{\frac{1}{2}}}\sum_{\underline{k}}U_\alpha(\underline{k})\,e^{i\underline{k}\cdot\underline{r}_j} \tag{118}$$

and that for every value of $\underline{k}$ there is a corresponding value $-\underline{k}$. This is not strictly possible in all cases but should not affect the general conclusions of this chapter. This is discussed in detail later on. The real nature of the atomic displacements is preserved by insisting that

$$U_\alpha(\underline{k})=U^{*}_\alpha(-\underline{k})\,. \tag{119}$$

The difference between (118) and the conventional transformation to normal coordinates for a perfect lattice (Maradudin, Montroll and Weiss, 1963) is the appearance of the actual equilibrium sites instead of perfect lattice sites. A further difference is the use of an unspecified (as yet) set of plane waves rather than wave vectors lying in the first Brillouin zone. The plane waves here are not orthogonal except when the atoms are located on lattice sites.

It is convenient to impose periodic boundary conditions by imagining that the solid considered is part of a super-system of identical adjoining systems. The shape of the normalization volume will, in general, be dictated by the symmetry properties of the solid. For example, in a perfect lattice it is usual to employ a parallelapiped whose edges lie in the same direction as the primitive translation vectors of the lattice. Relatively unimportant considerations such as these will be omitted here and it will be assumed that the normalization volume is a "box" having sides of length L.

The allowed values of from which the N independent waves can be chosen are therefore given by

$$K_\alpha = \frac{2\pi r}{L} \quad ; \quad r = 0, \pm 1, \pm 2 \; ---. \qquad (120)$$

In the limit when the normalization volume $V = L^3$ tends to infinity the wave vectors form a continuum and this is the reason why the shape of the volume is unimportant.

It is not possible to give a precise and unique method for choosing the wave vectors in general but it is clear that the choice should be governed by the following general considerations. First, it is desirable that this theory should yield the familiar results of a perturbed elastic continuum in the limit of long waves and it is therefore reasonable to choose wave vectors within a zone centred about $|\underline{k}| = 0$. The rough limits of this zone are determined by the fact that atoms in a solid cannot approach closer than a minimum distance r_0, hence wave vectors much larger than π/r_0 are not necessary to describe a coarse grained function like $\underline{u}(j)$. Another consideration to be taken into account is that the waves should be chosen such that they are as orthogonal as possible, because the exact normal modes are exactly orthogonal. Finally, symmetry can help in fixing the shape of the zone. For example in a solid having average spherical symmetry (e.g. a vitreous or polycrystalline solid) the wave vectors will be assumed to lie within a spherical zone having a radius

$$|\underline{k}|_{max.} = \frac{2\pi}{L}\left(\frac{3N}{4\pi}\right)^{\frac{1}{3}} \qquad (121)$$

i.e. the wave vectors lie within the Debye sphere. In practice $|\underline{k}|_{max}$ is of the order π/r_0.

In solids retaining a large amount of crystalline orientation one would expect the zone to be roughly the same shape as the Brillouin zone of the corresponding perfect lattice. The question of the zone shape is discussed again in a subsequent section and reasons are put forward as to why the exact details of the short wavelength cut-off should not be of overriding importance in the calculation of thermal conductivity.

1.4.2. The new form for the Hamiltonion.

The basic difficulty with using a non-orthogonal representation lies in constructing the biorthonormal functions which in the case of the plane wave representation are denoted by $\Psi_{\underline{k}}(j)$. If these functions are known then from (114) we may write

$$p_\alpha(j) = \frac{1}{N^{\frac{1}{2}}} \sum_{\underline{k}} P_\alpha(\underline{k}) \Psi^*_{\underline{k}}(j) \tag{122}$$

and using (118) the Hamiltonion may be expressed in terms of the new coordinates by substitution.

In practice it is extremely difficult to generate closed forms for the $\Psi_{\underline{k}}(j)$ and approximations have to be introduced. One method for constructing a series expansion for the $\Psi_{\underline{k}}(j)$ and the practical application of this expansion is discussed in the next chapter.

However, to develop the simple argument of this chapter we adopt an alternative but equivalent approach which avoids introducing the biorthonormal functions explicitly and has rather more physical content.

The kinetic energy terms in (3) may be written as

$$T = \frac{1}{2} \sum_\alpha \sum_{\underline{k}} P_\alpha(\underline{k}) \dot{U}_\alpha(\underline{k}) \tag{123}$$

or using

$$P_{\alpha}(-\underline{k}) = \frac{M}{N} \sum_{\underline{k}'} \dot{U}_{\alpha}(\underline{k}') \sum_{j} e^{i(\underline{k}'-\underline{k})\cdot\underline{r}_j} \tag{124}$$

equation (123) can be rearranged to read,

$$T = \frac{1}{2M} \sum_{\alpha}\sum_{\underline{k}} P_{\alpha}(\underline{k}) P_{\alpha}(-\underline{k}) - \frac{1}{2} \sum_{\alpha}\sum\sum_{\underline{k}\neq\underline{k}'} P_{\alpha}(\underline{k}) \dot{U}_{\alpha}(\underline{k}') \frac{1}{N} \sum_{j} e^{i(\underline{k}'-\underline{k})\cdot\underline{r}_j} . \tag{125}$$

The first term in (125) will be denoted by T° and the second by T'.

The potential energy terms in (3) which will be denoted by V can be expressed in terms of the variables $U_{\alpha}(\underline{k})$ by substituting from (118). We then obtain

$$\begin{aligned} V &= \frac{1}{2} \sum_{\alpha}\sum_{\alpha'}\sum_{\underline{k}} B_{\alpha\alpha'}(\underline{k},-\underline{k})\, U_{\alpha}(\underline{k})\, U_{\alpha'}(-\underline{k}) \\ &+ \frac{1}{2} \sum_{\alpha}\sum_{\alpha'}\sum\sum_{\underline{k}\neq-\underline{k}'} B_{\alpha\alpha'}(\underline{k},\underline{k}')\, U_{\alpha}(\underline{k})\, U_{\alpha'}(\underline{k}') \\ &+ \frac{1}{6} \sum_{\alpha}\sum_{\alpha'}\sum_{\alpha''}\sum_{\underline{k}}\sum_{\underline{k}'}\sum_{\underline{k}''} C_{\alpha\alpha'\alpha''}(\underline{k},\underline{k}',\underline{k}'')\, U_{\alpha}(\underline{k})\, U_{\alpha'}(\underline{k}')\, U_{\alpha''}(\underline{k}'') \end{aligned} \tag{126}$$

where

$$B_{\alpha\alpha'}(\underline{k},\underline{k}') = \frac{1}{N} \sum\sum_{j\neq j'} B_{\alpha\alpha'}(\underline{r}_j-\underline{r}_{j'}) \left(e^{i\underline{k}\cdot\underline{r}_j} - e^{i\underline{k}\cdot\underline{r}_{j'}}\right)\left(e^{i\underline{k}'\cdot\underline{r}_j} - e^{i\underline{k}'\cdot\underline{r}_{j'}}\right) \tag{127}$$

and

$$C_{\alpha\alpha'\alpha''}(\underline{k},\underline{k}',\underline{k}'') = \frac{1}{N} \sum\sum_{j\neq j'} C_{\alpha\alpha'\alpha''}(\underline{r}_j-\underline{r}_{j'}) \left(e^{i\underline{k}\cdot\underline{r}_j} - e^{i\underline{k}\cdot\underline{r}_{j'}}\right)\left(e^{i\underline{k}'\cdot\underline{r}_j} - e^{i\underline{k}'\cdot\underline{r}_{j'}}\right)\left(e^{i\underline{k}''\cdot\underline{r}_j} - e^{i\underline{k}''\cdot\underline{r}_{j'}}\right). \tag{128}$$

The first term in (126) will be denoted by V°, the second by V' and the third by V''.

The merit of this representation is the fact that $H^0 = T^0 + V^0$ is the Hamiltonion of N three-dimensional harmonic oscillators and we now explore the possibility of using the eigen states of H^0 as a basis for the development of conventional perturbation theory. Hamilton's classical equations of motion are

$$\dot{U}_\alpha(\underline{k}) \simeq \frac{\partial H^0}{\partial P_\alpha(\underline{k})} = \frac{1}{M} P_\alpha(-\underline{k}) \tag{129}$$

and

$$\dot{P}_\alpha(\underline{k}) \simeq -\frac{\partial H^0}{\partial U_\alpha(\underline{k})} = -\sum_{\alpha'} B_{\alpha\alpha'}(\underline{k},-\underline{k})\, U_{\alpha'}(-\underline{k}). \tag{130}$$

The combination of these two equations gives

$$M\ddot{U}_\alpha(\underline{k}) = -M\omega^2(\underline{k})\, U_\alpha(\underline{k}) = -\sum_{\alpha'} B_{\alpha\alpha'}(\underline{k},-\underline{k})\, U_{\alpha'}(\underline{k}). \tag{131}$$

The matrix $B_{\alpha\alpha'}(\underline{k},-\underline{k})$ is analogous to the dynamical matrix in standard lattice dynamics and it is convenient to use the terminology of the standard theory. Hence the orthonormal eigen vectors of (131) will be denoted by $\underline{\epsilon}(\underline{k},\rho)$* and the eigen frequencies by $\omega_\rho(\underline{k})$ where ρ is a polarization index.

---

* Since $B_{\alpha\alpha'}(\underline{k},-\underline{k})$ is real and symmetric the eigen vectors $\underline{\epsilon}(\underline{k},\rho)$ can be chosen to be purely real. We will use the convention that (Maradudin, Montroll and Weiss, 1963, p.13) $\underline{\epsilon}(\underline{k},\rho) = -\underline{\epsilon}(-\underline{k},\rho)$, $\omega_\rho(\underline{k}) = \omega_\rho(-\underline{k})$.

For amorphous or polycrystalline systems the solution of (131) is particularly simple. The matrix $B_{\alpha\alpha'}(\underline{k},-\underline{k})$ is identical with the matrix $\mathcal{B}_{\alpha\alpha'}(\underline{k})$ defined by (51) namely,

$$
\begin{aligned}
B_{\alpha\alpha'}(\underline{k},-\underline{k}) &= \frac{1}{N}\sum_{j\neq j'}\sum B_{\alpha\alpha'}(\underline{r}_{jj'})\left(e^{i\underline{k}\cdot\underline{r}_j}-e^{i\underline{k}\cdot\underline{r}_{j'}}\right)\left(e^{-i\underline{k}\cdot\underline{r}_j}-e^{-i\underline{k}\cdot\underline{r}_{j'}}\right) \\
&= 2(N-1)\int B_{\alpha\alpha'}(\underline{R})\, p^c(|\underline{R}|)\left(1-\cos\underline{k}\cdot\underline{R}\right)d\underline{R} = \mathcal{B}_{\alpha\alpha'}(\underline{k}).
\end{aligned} \tag{132}
$$

The eigen frequencies of H^0 are therefore just the same as those obtained from the averaged equation of motion (47). In the case of solids which retain a large amount of crystalline orientation and large areas of perfect crystal the matrix $B_{\alpha\alpha'}(\underline{k},-\underline{k})$ will be virtually the same as that for the perfect crystal.

It is desirable to make a further change of variables which completely diagonalizes H° namely

$$
\begin{aligned}
U_\alpha(\underline{k}) &= \sum_\rho \epsilon_\alpha(\underline{k},\rho)\,\mathcal{U}_\rho(\underline{k}) \\
&= -\sum_\rho i\left(\frac{\hbar}{2M\omega_\rho(\underline{k})}\right)^{\frac{1}{2}}\epsilon_\alpha(\underline{k},\rho)\left\{a^*_\rho(\underline{k})-a_\rho(-\underline{k})\right\}
\end{aligned} \tag{133}
$$

and

$$
\begin{aligned}
P_\alpha(\underline{k}) &= \sum_\rho \epsilon_\alpha(\underline{k},\rho)\,\mathcal{P}_\rho(\underline{k}) \\
&= \sum\left(\frac{\hbar M\omega_\rho(\underline{k})}{2}\right)^{\frac{1}{2}}\epsilon_\alpha(\underline{k},\rho)\left\{a_\rho(\underline{k})+a^*_\rho(-\underline{k})\right\}
\end{aligned} \tag{134}
$$

where the variables $a^*_\rho(\underline{k})$ and $a_\rho(\underline{k})$ are the creation and destruction operators in the quantum limit (Ziman, Electrons and Phonons, p.132), where $a^*_\rho(\underline{k})$ denoting the complex conjugate is replaced by $a^{+}_{\rho}(\underline{k})$ meaning the Hermitian conjugate of $a_{\rho}(\underline{k})$. The variables $\mathcal{U}_{\rho}(\underline{k})$ and $\mathcal{P}_{\rho}(\underline{k})$ transform as

$$\begin{aligned} \mathcal{U}_{\rho}(\underline{k}) &= -\ \mathcal{U}^{*}_{\rho}(-\underline{k}) , \\ \mathcal{P}_{\rho}(\underline{k}) &= -\ \mathcal{P}^{*}_{\rho}(-\underline{k}) . \end{aligned} \tag{135}$$

In terms of the creation and destruction operators (going over to quantum mechanics) the Hamiltonion is

$$\begin{aligned} H = {} & \sum_{\rho}\sum_{\underline{k}} \hbar\,\omega_{\rho}(\underline{k}) \left\{ a^{\dagger}_{\rho}(\underline{k})\, a_{\rho}(\underline{k}) + \tfrac{1}{2} \right\} \\ & + \frac{1}{2} \sum_{\rho}\sum_{\rho'}\sum\sum_{\underline{k} \neq \underline{k}'} \left\{ \sum_{\alpha} \epsilon_{\alpha}(\underline{k},\rho)\, \epsilon_{\alpha}(\underline{k}',\rho')\, \frac{1}{N} \sum_{j} e^{i(\underline{k}'-\underline{k})\cdot \underline{r}_{j}} \right\} \left(\frac{\hbar M \omega_{\rho}(\underline{k})}{2} \right)^{\frac{1}{2}} \\ & \times \left\{ a_{\rho}(\underline{k}) + a^{+}_{\rho}(-\underline{k}) \right\} i \left(\frac{\hbar}{2M\omega_{\rho'}(\underline{k}')} \right)^{\frac{1}{2}} \left\{ \dot{a}^{+}_{\rho'}(\underline{k}') - \dot{a}_{\rho'}(-\underline{k}') \right\} \\ & - \frac{1}{2} \sum_{\rho}\sum_{\rho'}\sum\sum_{\underline{k} \neq -\underline{k}'} \mathcal{B}_{\rho\rho'}(\underline{k},\underline{k}') \left(\frac{\hbar}{2M\omega_{\rho}(\underline{k})} \right)^{\frac{1}{2}} \left\{ a^{+}_{\rho}(\underline{k}) - a_{\rho}(-\underline{k}) \right\} \\ & \times \left(\frac{\hbar}{2M\omega_{\rho'}(\underline{k}')} \right)^{\frac{1}{2}} \left\{ a^{+}_{\rho'}(\underline{k}') - a_{\rho'}(-\underline{k}') \right\} \\ & + \frac{1}{6} \sum_{\rho}\sum_{\rho'}\sum_{\rho''}\sum_{\underline{k}}\sum_{\underline{k}'}\sum_{\underline{k}''} \mathcal{C}_{\rho\rho'\rho''}(\underline{k},\underline{k}',\underline{k}'')\, i \left(\frac{\hbar}{2M\omega_{\rho}(\underline{k})} \right)^{\frac{1}{2}} \left\{ a^{+}_{\rho}(\underline{k}) - a_{\rho}(-\underline{k}) \right\} \\ & \times \left(\frac{\hbar}{2M\omega_{\rho'}(\underline{k}')} \right)^{\frac{1}{2}} \left\{ a^{+}_{\rho'}(\underline{k}') - a_{\rho'}(-\underline{k}') \right\} \left(\frac{\hbar}{2M\omega_{\rho''}(\underline{k}'')} \right)^{\frac{1}{2}} \left\{ a^{+}_{\rho''}(\underline{k}'') - a_{\rho''}(-\underline{k}'') \right\} . \end{aligned} \tag{136}$$

where

$$\mathcal{B}_{\rho\rho'}(\underline{k},\underline{k}') = \frac{1}{N}\sum_{\alpha}\sum_{\alpha'}\sum_{j\neq j'}\sum \epsilon_{\alpha}(\underline{k},\rho)\,\epsilon_{\alpha'}(\underline{k}',\rho')\,B_{\alpha\alpha'}(\underline{r}_{jj'})$$
$$\times\left(e^{i\underline{k}\cdot\underline{r}_j} - e^{i\underline{k}\cdot\underline{r}_{j'}}\right)\left(e^{i\underline{k}'\cdot\underline{r}_j} - e^{i\underline{k}'\cdot\underline{r}_{j'}}\right) \tag{137}$$

and

$$\mathcal{C}_{\rho\rho'\rho''}(\underline{k},\underline{k}',\underline{k}'') = \frac{1}{N^{\frac{3}{2}}}\sum_{\alpha}\sum_{\alpha'}\sum_{\alpha''}\sum_{j\neq j'}\sum \epsilon_{\alpha}(\underline{k},\rho)\,\epsilon_{\alpha'}(\underline{k}',\rho')\,\epsilon_{\alpha''}(\underline{k}'',\rho'')\,C_{\alpha\alpha'\alpha''}(\underline{r}_{jj'})$$
$$\times\left(e^{i\underline{k}\cdot\underline{r}_j} - e^{i\underline{k}\cdot\underline{r}_{j'}}\right)\left(e^{i\underline{k}'\cdot\underline{r}_j} - e^{i\underline{k}'\cdot\underline{r}_{j'}}\right)\left(e^{i\underline{k}''\cdot\underline{r}_j} - e^{i\underline{k}''\cdot\underline{r}_{j'}}\right). \tag{138}$$

This form (136) contains the time derivative of the creation and destruction operators which must be eliminated for further progress to be made. One way of achieving this is by using Heisenberg's equation of motion, namely,

$$\dot{a}_{\rho}(\underline{k}) = \frac{i}{\hbar}\left[H,\ a_{\rho}(\underline{k})\right]\ . \tag{139}$$

The right hand side of (139) still contains $\dot{a}_{\rho}(\underline{k})$ but this equation can be solved by successive approximation beginning by writing

$$H \simeq H^{\circ} = \sum_{\rho}\sum_{\underline{k}} \hbar\omega_{\rho}(\underline{k})\left\{a^{+}_{\rho}(\underline{k})\,a_{\rho}(\underline{k}) + \tfrac{1}{2}\right\}. \tag{140}$$

To a first approximation we then find that

$$\dot{a}_{\rho}(\underline{k}) \simeq -i\,\omega_{\rho}(\underline{k})\,a_{\rho}(\underline{k})\ ,\quad \dot{a}^{+}_{\rho}(\underline{k}) \simeq i\,\omega_{\rho}(\underline{k})\,a^{+}_{\rho}(\underline{k}). \tag{141}$$

This is equivalent to replacing $M\dot{U}_{\alpha}(\underline{k})$ by $P_{\alpha}(-\underline{k})$ in (125).

The subsequent analysis of thermal conductivity will be developed within the limitations of (141) and first order perturbation theory. Successive approximations to $\dot{a}_{\rho}(\underline{k})$ can be generated by iteration of equation (139) but this is a little clumsy to carry out and it is probably best to use the expansion for the functions $\psi_{\underline{k}}(j)$ which is described in the next chapter.

The validity of this simple argument depends on the assumption that the eigen states of H^{o} are reasonable zeroth order approximations and that perturbation methods based on H^{o} are convergent. The validity of the second assumption does not necessarily follow if the first is justified. The evidence that H^{o} is a reasonable choice is that the vibrational frequencies are the same as those predicted by the averaged equation of motion, but this is basically a long wavelength theory. The usefulness of this approach for short wavelength vibration is uncertain but this is not a special feature of this method since the same doubts arise in the standard theory of thermal conductivity.

It is recognised that in general a complete analysis of the perturbation T' will be required; for example, positive density fluctuations should give rise to resonance scattering in the same way that heavy isotopes in a lattice do, (e.g. Takeno, 1963; Morgan, 1966) and first order perturbation theory is inadequate for describing this phenomena. Another situation where first order perturbation theory can be inadequate is when the force constants are locally weaker than the average.

Krumhansl and Mathew (1965) have shown this to be the case for a one dimensional lattice but this will not be so important in three dimensions.

These rather intricate questions are reserved for subsequent study.

1.4.3. The Boltzmann Equation.

We are now in the position of having a set of modes suitable for describing the flow of energy through a structurally disordered solid. Broadly speaking two properties of the representation are required if we wish to use a Boltzmann equation to calculate the thermal conductivity. First, the perturbations to the Hamiltonion H° should have a weak effect and secondly, the energy current operator should be nearly diagonal.

Detailed derivations of transport equations in a perturbed lattice have been given by Hardy (1963, 1965, 1966); Hardy, Swenson and Schieve (1965), and Hardy and Schieve, 1966). The methods of these authors may be readily used to derive the Boltzmann equation for the plane representation, indeed the derivation is identical.

Using the Kubo formalism, Hardy (1965) showed that the thermal conductivity tensor $K^{\alpha\alpha'}$ can be written as

$$K^{\alpha\alpha'} \simeq \frac{V}{k_b T^2} \sum_{\beta} \sum_{\beta'} f(\beta) \, S_d^{\alpha}(\beta) \, S_d^{\alpha'}(\beta') \quad \tilde{P}_3(\beta,\beta') \tag{142}$$

to lowest order in a perturbation parameter λ when the Hamiltonian is assumed to be of the form

$$H = H^{\circ} + \lambda H' . \tag{143}$$

In (141) $\underline{S}_d$ denotes the diagonal part of the energy flux operator in the phonon representation, β labels a "many-phonon" state, f is the equilibrium density matrix, V is the volume of the solid, T is the temperature and k_b is Boltzmann's constant. The quantity $\widetilde{P}_{\eta}(\beta,\beta')$ is defined by

$$\widetilde{P}_{\eta}(\beta,\beta') = \frac{\hbar}{2\pi} \int_0^{\infty} dt \, e^{-\eta t} \left| \langle \beta | e^{-\frac{iHt}{\hbar}} | \beta' \rangle \right|^2 \tag{144}$$

where η is a real positive infinitesimal. Equation (142) is also valid for the representation described in this chapter and in future the eigen states of H^{0} will also be referred to as "phonons".

We now consider the form of the energy flux operator. This quantity has been investigated by a number of authors for liquids and solids, for example, Eisenshitz (1955), Mori (1958), Hardy (1963) and Magid (1964).

Following Hardy's discussion we write

$$\mathcal{V}(j) = \frac{1}{2} \sum_{\alpha} \sum_{\alpha'} \sum_{j' \neq j} B_{\alpha\alpha'}(r_{jj'}) \left(u_{\alpha}(j) - u_{\alpha}(j')\right)\left(u_{\alpha'}(j) - u_{\alpha'}(j')\right) \tag{145}$$

then the mean energy flux is (ignoring anharmonic contributions)

$$\underline{S} = \underline{S}_2 + \underline{S}_3 \tag{146}$$

where $\underline{S}_2$ is quadratic in the particle coordinates and $\underline{S}_3$ is a cubic function of the coordinates, i.e.

$$\underline{S}_2 = \frac{1}{2MV}\sum\sum_{j\neq j'}(\underline{r}_j-\underline{r}_{j'})\sum_{\alpha}\Big\{p_\alpha(j)\frac{1}{i\hbar}\left[p_\alpha(j),\mathcal{V}(j')\right] + \frac{1}{i\hbar}\left[p_\alpha(j),\mathcal{V}(j')\right]p_\alpha(j)\Big\} \tag{147}$$

and

$$\underline{S}_3 = \frac{1}{2V}\Big\{\sum_j\frac{\underline{p}(j)}{M}\Big[\sum_\alpha\frac{p_\alpha^2(j)}{2M}+\mathcal{V}(j)\Big] + \frac{1}{2M}\sum\sum_{j\neq j'}(\underline{u}(j)-\underline{u}(j'))\sum_\alpha\Big(p_\alpha(j)\frac{1}{i\hbar}\left[p_\alpha(j),\mathcal{V}(j')\right] + \frac{1}{i\hbar}\left[p_\alpha(j),\mathcal{V}(j')\right]p_\alpha(j)\Big)\Big\} + \text{H.C.} \tag{148}$$

where H.C. denotes the Hermitian conjugate of the preceding terms. The quantity $\underline{S}_2$ is a quadratic function of the coordinates because

$$(i\hbar)^{-1}\left[p_\alpha(j),\mathcal{V}(j')\right] = -\sum_{\alpha'}B_{\alpha\alpha'}(\underline{r}_j-\underline{r}_{j'})(u_{\alpha'}(j)-u_{\alpha'}(j')). \tag{149}$$

The term $\underline{S}_3$ will be ignored for the reasons given by Hardy (1963). $\underline{S}_3$ can be called the kinetic energy contribution to the energy flux which can be assumed small providing the vibrational amplitudes of the atoms are small compared with the mean spacing. This leaves

$$\underline{S} \simeq \underline{S}_2 = \frac{1}{2MV}\sum_\alpha\sum_{\alpha'}\sum\sum_{j\neq j'}(\underline{r}_j-\underline{r}_j)\Big\{p_\alpha(j)B_{\alpha\alpha'}(\underline{r}_{jj'})(u_{\alpha'}(j)-u_{\alpha'}(j'))+\text{H.C.}\Big\} \tag{150}$$

or in terms of the creation and destruction operators

$$\underline{S} \simeq \frac{1}{NV}\Bigg[\sum_{\rho}\sum_{\underline{k}}\Big\{\sum_{\alpha}\sum_{\alpha'}\sum\sum_{j\neq j'} \epsilon_{\alpha}(-\underline{k},\rho)\,\epsilon_{\alpha'}(\underline{k},\rho)\,B_{\alpha\alpha'}(\underline{r}_{jj'})\left(1-e^{i\underline{k}\cdot\underline{r}_{j'j}}\right)$$

$$\times\left(\underline{r}_j-\underline{r}_{j'}\right)\Big\}\frac{\hbar}{2M\omega_{\rho}(\underline{k})}\left\{\dot{a}^{+}_{\rho}(-\underline{k})-\dot{a}_{\rho}(\underline{k})\right\}\left\{a^{+}_{\rho}(\underline{k})-a_{\rho}(-\underline{k})\right\}$$

$$+\sum\sum_{\rho\neq\rho'}\sum_{\underline{k}}\Big\{\sum_{\alpha}\sum_{\alpha'}\sum\sum_{j\neq j'} \epsilon_{\alpha}(-\underline{k},\rho)\,\epsilon_{\alpha'}(\underline{k},\rho')\,B_{\alpha\alpha'}(\underline{r}_{jj'})\left(1-e^{ik\cdot r_{j'j}}\right)\left(\underline{r}_j-\underline{r}_{j'}\right)\Big\}$$

$$\times\frac{\hbar}{2M}\frac{1}{\left(\omega_{\rho}(\underline{k})\,\omega_{\rho'}(\underline{k})\right)^{\frac{1}{2}}}\left\{\dot{a}^{+}_{\rho'}(-\underline{k})-\dot{a}_{\rho'}(\underline{k})\right\}\left\{a^{+}_{\rho}(\underline{k})-a_{\rho}(-\underline{k})\right\} \tag{151}$$

$$+\sum_{\rho}\sum_{\rho'}\sum\sum_{\underline{k}\neq\underline{k}'}\Big\{\sum_{\alpha}\sum_{\alpha'}\sum\sum_{j\neq j'} \epsilon_{\alpha}(\underline{k},\rho)\,\epsilon_{\alpha'}(\underline{k}',\rho')\,B_{\alpha\alpha'}(\underline{r}_{jj'})\,e^{-i\underline{k}\cdot\underline{r}_j}\left(e^{i\underline{k}'\cdot\underline{r}_j}-e^{i\underline{k}'\cdot\underline{r}_{j'}}\right)$$

$$\times\left(\underline{r}_j-\underline{r}_{j'}\right)\Big\}\frac{\hbar}{2M}\frac{1}{\left(\omega_{\rho}(\underline{k})\,\omega_{\rho'}(\underline{k}')\right)^{\frac{1}{2}}}\left\{\dot{a}^{+}_{\rho}(-\underline{k})-\dot{a}_{\rho}(\underline{k})\right\}\left\{a^{+}_{\rho'}(k')-a_{\rho'}(-k')\right\}$$

$$+\ H.C.\Bigg]$$

The first term in (151) will be denoted by $\underline{S}_d$, the second by $\underline{S}^1_{n.d}$ and the third by $\underline{S}^2_{n.d}$ Invoking approximation (141) and using

$$\omega^2_{\rho}(\underline{k}) = M^{-1}\,\mathcal{B}_{\rho\rho}(\underline{k},-\underline{k}) \tag{152}$$

then it is straightforward to show that

$$\underline{S}_d = V^{-1}\sum_{\underline{k}}\sum_{\rho}\hbar\omega_{\rho}(\underline{k})\frac{\partial\omega_{\rho}(\underline{k})}{\partial\underline{k}}\,a^{+}_{\rho}(\underline{k})\,a_{\rho}(\underline{k}) \quad . \tag{153}$$

Within the limits of approximation (141) both $\underline{S}^1_{n.d}$ and $\underline{S}^2_{n.d}$ are non-diagonal in the creation and destruction operators. The contribution of $\underline{S}^1_{n.d}$ will be assumed small using the argument that if $a^{+}_{\rho}(\underline{k})$ and $a_{\rho}(\underline{k})$ are treated as classical variables with the (approximate) time dependent behaviour.

$$a_\rho(\underline{k}) \propto e^{-i\omega_\rho(\underline{k})t}, \quad a^+_\rho(\underline{k}) \propto e^{i\omega_\rho(\underline{k})t} \tag{154}$$

then if $\omega_\rho(\underline{k})$ and $\omega_{\rho'}(\underline{k})$ are different the time average of $\underline{S}'_{n.d}$ is zero. The special case when $\omega_\rho(\underline{k}) = \omega_{\rho'}(\underline{k})$ causes no difficulty because the contribution to the energycurrent is zero in this situation, (Hardy, 1963).

The neglect of $\underline{S}^2_{n.d}$ is not at all easy to justify. However, even in the extreme case of an amorphous solid it seems reasonable to do so because the configuration average is zero and it is unlikely that it will play a significant role in a thermal conductivity calculation. A precise evaluation of the effect of non-diagonal contributions to the energy flow requires an investigation of their role in higher order equations than the Boltzmann equation.

It is not necessary to go through with Hardy's (1966) derivation of the Boltzmann equation using (142) and (144) because the Hamiltonion (136) is of the same form as that for a perturbed lattice and (153) is also identical with the standard expression for the diagonal contribution to the energy flow in a perturbed lattice. The Boltzmann equation, therefore, also takes the standard form

$$-\frac{\partial}{\partial T}\bar{N}_0(\underline{k},\rho)\frac{\partial\omega_\rho(\underline{k})}{\partial\underline{k}}\cdot\nabla T = -\frac{\partial\bar{N}(\underline{k},\rho)}{\partial t}\Big]_{collisions} \tag{155}$$

where $\bar{N}(\underline{k},\rho)$ is the expected number of phonons in the state $\underline{k}\rho$, ∇T is the temperature gradient and $N_0(\underline{k},\rho)$ is the Bose-Einstein distribution function

$$\bar{N}_0(\underline{k},\rho) = \left\{\exp\left(\frac{\hbar\omega_\rho(\underline{k})}{k_b T}\right) - 1\right\}^{-1}. \tag{156}$$

The heat current is simply

$$\underline{S}_H = V^{-1}\sum_{\underline{k}}\sum_{\rho}\hbar\omega_\rho(\underline{k})\frac{\partial\omega_\rho(\underline{k})}{\partial\underline{k}}\bar{N}(\underline{k},\rho) \tag{157}$$

and the collision term in (155) is to be evaluated from the perturbations to the Hamiltonion H^0 to first order in perturbation theory in the usual manner.

In practice it is reasonable to use equation (155) with the collisions term calculated to an arbitrary order of perturbation theory, providing the scattering is weak. This is sometimes necessary because although a perturbation expansion may diverge, summation of terms in the expansion can give a final result corresponding to weak scattering (e.g. Krumhansl and Mathew, 1965).

1.4.4. Elastic scattering.

The thermal conductivity of a solid is primarily determined by the rate at which phonons are scattered rather than the details of the $\omega_\rho(\underline{k})$ function which is insensitive to the microscopic structure. The form of the collision terms in the Boltzmann equation is precisely the same as those encountered in the standard theory of heat conduction (e.g. Ziman, 1960, Electrons and Phonons) so that attention can be concentrated on the <u>intrinsic</u> transition probabilities. The calculation of these quantities also follows familiar lines so that only a brief outline will be given of the procedure.

We use the general formula

$$P_s^{s'} \simeq \frac{2\pi}{\hbar}\,\delta(E_s - E_{s'})\,\left|\langle s' \,|\, V \,|\, s\rangle\right|^2 \qquad (158)$$

for the transition probability from a state s with energy E_s to a state s', due to a perturbation V. If a many-phonon state is specified by the ket

$$|\cdots\cdots, N(\underline{k}\rho), \cdots N'(\underline{k}'\rho'), \cdots\rangle \qquad (159)$$

where $N(\underline{k},\rho)$ denotes the number of phonons with wave vector $\underline{k}$ and polarization ρ, then using the relations

$$\begin{aligned} a^+_\rho(\underline{k})\,|\cdots N(\underline{k},\rho)\cdots\rangle &= \sqrt{N(\underline{k}\rho)+1}\;\;|\cdots, N(\underline{k},\rho)+1, \cdots\rangle\,, \\ a_\rho(\underline{k})\,|\cdots N(\underline{k},\rho)\cdots\rangle &\;\; \sqrt{N(\underline{k},\rho)}\;\;|\cdots, N(\underline{k},\rho)-1, \cdots\rangle\,, \end{aligned} \qquad (160)$$

it may readily be ascertained that the second and third terms in (136) only cause transitions in which a phonon is destroyed in one state and another is created in a second state. The transition probability $P_{\underline{k}\rho}^{\underline{k}'\rho'}$ may be written as

$$P_{\underline{k}\rho}^{\underline{k}'\rho'} = N(\underline{k},\rho)\left(N(\underline{k}',\rho')+1\right)\, Q_{\underline{k}\rho}^{\underline{k}'\rho'} \qquad (161).$$

where $Q_{\underline{k}\rho}^{\underline{k}'\rho'}$ is called the intrinsic transition probability and is independent of the phonon occupation numbers. This kind of process can be termed "elastic" because phonons are only scattered into other phonon states which have the same frequency.

For these elastic processes we have

$$-\frac{\partial}{\partial t}\bar{N}(\underline{k},\rho)\Big]_{\text{elastic}} = \sum_{\underline{k}'}\sum_{\rho'}\left(\bar{N}(\underline{k}\rho) - \bar{N}(\underline{k}'\rho')\right) Q_{\underline{k}\rho}^{\underline{k}'\rho'} \qquad (162)$$

where

$$Q_{\underline{k}\rho}^{\underline{k}'\rho'} = \frac{2\pi}{\hbar}\,\delta\left(\hbar\omega_\rho(\underline{k}) - \hbar\omega_{\rho'}(\underline{k}')\right)$$

$$\times\left|-\frac{\hbar\omega_\rho(\underline{k})}{2}\,\epsilon(-k,\rho)\cdot\epsilon(\underline{k}'\rho')\,\frac{1}{N}\sum_j e^{i(\underline{k}'-\underline{k})\cdot\underline{r}_j} + \frac{\hbar}{2M\omega_\rho(\underline{k})}\,\mathcal{B}_{\rho\rho'}^{(-\underline{k},\underline{k}')}\right|^2 \qquad (163)$$

A convenient way of writing $\mathcal{B}_{\rho\rho'}^{(-\underline{k},\underline{k}')}$ here is

$$\mathcal{B}_{\rho\rho'}^{(-\underline{k},\underline{k}')} = \frac{1}{N}\sum_j e^{i(\underline{k}'-\underline{k})\cdot\underline{r}_j}\sum_\alpha\sum_{\alpha'}\sum_{j'\neq j}\epsilon_\alpha(-\underline{k}\rho)\,\epsilon_{\alpha'}(\underline{k}'\rho')\,B_{\alpha\alpha'}(\underline{r}_{jj'})\left(1-e^{i\underline{k}\cdot\underline{r}_{jj'}}\right)\left(1-e^{-i\underline{k}'\cdot\underline{r}_{jj'}}\right) \qquad (164)$$

The interpretation of (163) is plain. The first term inside the modulus sign represents scattering due to density fluctuations whilst the second term is the effect of variations in the elastic properties of the solid.

We now consider some situations where this simple formula will be of practical importance and the difficulties involved in evaluating (163).

Amorphous solids.

The low temperature thermal conductivity of amorphous solids should be described quite well in terms of this simple Boltzmann equation approach since in this region the mean free path of the phonons is long, (Klemens, 1960, 1965). Of course, the force constant model used is unrealistic in general but the qualitative features predicted by (163) should be substantially correct. This is the most that can be hoped for in a solid of this complexity.

Although it is possible to replace (163) by its configuration average, this will involve two, three and four particle correlation functions of the equilibrium sites and this information is not available from experiment or theory. This is precisely the problem encountered with the Green functions in the previous chapter and justifies the remark that the need to know these functions is a characteristic feature of disordered solids. However, the position is not quite hopeless.

In the case of a hypothetical solid with a liquid degree of disorder (164) can be estimated by approximating the sum over j' by its average value. This is justified when the sum for one value of j is uncorrelated with neighbouring ones. We then obtain for long wavelength phonons

$$Q_{\underline{k}\rho}^{\underline{k}'\rho'} \propto \omega^2 a^e(\underline{k}-\underline{k}') \tag{165}$$

where $a^e(\underline{k}-\underline{k}')$ is the two-body correlation function of equilibrium sites defined by

$$\begin{aligned} a^e(\underline{q}) &= \frac{1}{N} \sum_{j} \sum_{j'} e^{i \underline{q} \cdot \underline{r}_{jj'}} - N\,\delta_{q,0} \\ &= 1 + (N-1) \int \rho^e(|\underline{R}|)\, e^{i q \cdot R}\, d\underline{R} - N\,\delta_{q,0}. \end{aligned} \tag{166}$$

This result is equivalent to Rayleigh scatterers distributed at the equilibrium sites. The extreme kind of disorder does not appear to occur in practice but there are cases where groups of atoms are likely to be uncorrelated, for example Klemen's (1965) has suggested that the observed thermal conductivity in amorphous selenium is produced by the structure consisting of spiral chains of atoms which are orientated at random. A simple approach would be to estimate (164) for the atoms in a single chain, assuming that the other chains are randomly orientated, and then average over all directions.

This kind of approach can only give qualitative answers but at least it might be possible to explain the observed variation with temperature of the thermal conductivity of amorphous solids. The merit of (163) is that it provides a simple formula for testing theoretical models. It might be useful to calculate (164) by means of fabricated models of disordered solids, (Dean and Bell, 1966.)

Dislocations.

The thermal resistance due to the presence of dislocations in a solid is anomalous particularly for the alkali halides. Although the experimental data is not conclusive (Moss, 1963) there seems to be large discrepancies between theory and experiment. The theoretical estimates are due to Klemens (1958) and Carruthers (1961), who have, however, only considered the scattering from the long range strain field predicted by classical elasticity theory. Equation (163) enables the core of the dislocation to be treated in a straightforward manner but a model is needed for the atomic positions. Recently computer calculations have been made of the atomic positions in model solids so that in the future it may be possible to compute $Q_{\underline{k}\rho}^{\underline{k}'\rho'}$.

Polycrystalline solids.

When the mean free path due to other effects is large compared with the crystallite dimensions in polycrystalline material, the situation is not very different from the amorphous case but in the more likely event of a short mean free path we must think in terms of the transmission of phonons through a single grain boundary or perhaps an amorphous layer. The problems with evaluating (163) are then essentially the same as those occurring in the case of dislocations.

The difficulties encountered here with making even the simplest estimate of the transition probabilities can be contrasted with the theory of "nearly free" electrons in simple metals (Ziman, 1964) where the pair correlation function is sufficient to obtain a fairly reasonable theory of electrical resistance. The basic reason why this is not possible here is that the "local" elasticity in a solid is in fact not a local property at all at the microscopic level, since it depends on the positions of the surrounding atoms.

1.4.5. Anharmonic scattering.

One of the most important features of the method is that the effect of structural disorder on the well-known "Normal" and "Umklapp" three phonon processes is revealed in a simple way. Three phonon processes are important in the standard theory, not only because U-processes are often the major cause of resistance at high temperatures, but because N-processes affect the low temperature thermal conductivity even though they are not supposed to give rise to thermal resistance on their own. It seems likely that anharmonic effects could play a similar role even in amorphous solids, in spite of the fact that there will be strong elastic scattering due to structural disorder.

The collision term in the Boltzmann equation due to the fourth term in (136) is (Ziman 1960, Electrons and Phonons)

$$-\frac{\partial}{\partial t}\bar{N}(\underline{k},\rho)\Big]_{\text{anharmonic}} = \tag{167}$$

$$\sum_{\rho'}\sum_{\rho''}\sum_{\underline{k}'}\sum_{\underline{k}''}\Big[\Big\{\bar{N}(\underline{k}\rho)\bar{N}(\underline{k}'\rho')\big(\bar{N}(\underline{k}''\rho'')+1\big)-\big(\bar{N}(\underline{k},\rho)+1\big)\big(\bar{N}(\underline{k}'\rho')+1\big)\bar{N}(\underline{k}''\rho'')\Big\}Q^{\underline{k}''\rho''}_{\underline{k}\rho,\underline{k}'\rho'}$$

$$+\frac{1}{2}\Big\{\bar{N}(\underline{k}\rho)\big(\bar{N}(\underline{k}'\rho')+1\big)\big(\bar{N}(\underline{k}''\rho'')+1\big)-\big(\bar{N}(\underline{k}\rho)+1\big)\bar{N}(\underline{k}'\rho')\bar{N}(\underline{k}'',\rho'')\Big\}Q^{\underline{k}'\rho',\underline{k}''\rho''}_{\underline{k}\rho}\Big]$$

where $Q^{\underline{k}'\rho',\underline{k}''\rho''}_{\underline{k}\rho}$ is the intrinsic transition probability for a phonon in $\underline{k}\rho$ to decay into the states $\underline{k}'\rho'$ and $\underline{k}''\rho''$ and $Q^{\underline{k}''\rho''}_{\underline{k}\rho,\underline{k}'\rho'}$ is the probability that phonons in $\underline{k}\rho$ and $\underline{k}'\rho'$ will combine to give a final state with a phonon in $\underline{k}''\rho''$.

The first kind of transition probability is given by

$$Q^{\underline{k}'\rho',\underline{k}''\rho''}_{\underline{k}\rho} = \frac{2\pi}{\hbar}\,\delta\big(\hbar\omega_{\rho}(\underline{k})-\hbar\omega_{\rho'}(\underline{k}')-\hbar\omega_{\rho''}(\underline{k}'')$$
$$\times\frac{\hbar^3}{8M^3\omega_{\rho}(\underline{k})\,\omega_{\rho'}(\underline{k}')\,\omega_{\rho''}(\underline{k}'')}\Big|\,\mathcal{C}^{(-\underline{k},\underline{k}',\underline{k}'')}_{\rho\rho'\rho''}\Big|^2 \tag{168}$$

and the second kind by

$$Q^{\underline{k}''\rho''}_{\underline{k}'\rho,\underline{k}'\rho'} = \frac{2\pi}{\hbar}\,\delta\big(\hbar\omega_{\rho}(\underline{k})+\hbar\omega_{\rho'}(\underline{k}')-\hbar\omega_{\rho''}(\underline{k}'')\big)$$
$$\times\frac{\hbar^3}{8M^3\omega_{\rho}(\underline{k})\,\omega_{\rho'}(\underline{k}')\,\omega_{\rho''}(\underline{k}'')}\Big|\,\mathcal{C}^{(-\underline{k},-\underline{k}',\underline{k}'')}_{\rho\rho'\rho''}\Big|^2. \tag{169}$$

Only (168) will be considered in detail since the same remarks apply to (169).

It is convenient to write $\mathcal{C}_{\rho\rho'\rho''}^{(-\underline{k},\underline{k}',\underline{k}'')}$ as

$$\mathcal{C}_{\rho\rho'\rho''}^{(-\underline{k},\underline{k}',\underline{k}'')} = N^{-\frac{3}{2}} \sum_{j} e^{i(\underline{k}'+\underline{k}''-\underline{k})\cdot\underline{r}_j} \Big\{ \sum_{j'\neq j}\sum_{\alpha}\sum_{\alpha'}\sum_{\alpha''} \tag{170}$$

$$\times\ \epsilon_{\alpha}(-\underline{k},\rho)\,\epsilon_{\alpha'}(\underline{k}',\rho')\,\epsilon_{\alpha''}(\underline{k}'',\rho'')\, C_{\alpha\alpha'\alpha''}(\underline{r}_{jj'})\left(1-e^{i\underline{k}\cdot\underline{r}_{jj'}}\right)\left(1-e^{-i\underline{k}'\cdot\underline{r}_{jj'}}\right)\left(1-e^{-i\underline{k}''\cdot\underline{r}_{jj'}}\right)\Big\}$$

which is a suitable form for making comparisons between the perfect lattice and disordered situations.

We are now faced with the same kind of computational difficulties as occur in the elastic scattering terms. We can, however, isolate one aspect of the change introduced by disorder by replacing the sum over j' in (170) by its average value, namely

$$\mathcal{C}_{\rho\rho'\rho''}^{(-\underline{k},\underline{k}',\underline{k}'')} \simeq N^{-3/2} \sum_{j} e^{i(\underline{k}'+\underline{k}''-\underline{k})\cdot\underline{r}_j} \Big\{ N^{-1} \sum_{j'\neq j''}\sum_{\alpha}\sum_{\alpha'}\sum_{\alpha''}$$

$$\times\ \epsilon_{\alpha}(-\underline{k},\rho)\,\epsilon_{\alpha'}(\underline{k}',\rho')\,\epsilon_{\alpha''}(\underline{k}'',\rho'')\, C_{\alpha\alpha'\alpha''}(\underline{r}_{j'j''})\left(1-e^{i\underline{k}\cdot\underline{r}_{j'j''}}\right)\left(1-e^{-i\underline{k}'\cdot\underline{r}_{j'j''}}\right)\left(1-e^{-i\underline{k}''\cdot\underline{r}_{j'j''}}\right)\Big\} \tag{171}$$

$$\simeq N^{-\frac{3}{2}} \sum_{j} e^{i(\underline{k}'+\underline{k}''-\underline{k})\cdot\underline{r}_j}\, F_{\rho\rho'\rho''}(-\underline{k},\underline{k}',\underline{k}'').$$

This is not intended as a serious approximation to (170) except perhaps in the case of an amorphous solid. We merely wish to show one aspect of how disorder affects the usual selection rules for three phonon processes. In general it will be necessary to add correction terms to (171) which may in fact be more important than the effect which will be discussed.

The intrinsic transition probability is now roughly given by

$$Q_{\underline{k}\rho}^{\underline{k}'\rho',\underline{k}''\rho''} \simeq \frac{2\pi}{\hbar}\,\delta\left(\hbar\omega_{\rho}(\underline{k})-\hbar\omega_{\rho'}(\underline{k}')-\hbar\omega_{\rho''}(\underline{k}'')\right)\frac{\hbar^{3}}{8N^{2}M^{3}\,\omega_{\rho}(\underline{k})\omega_{\rho'}(\underline{k}')\omega_{\rho''}(\underline{k}'')}$$

$$\times\left|\,F_{\rho\rho'\rho''}(-\underline{k},\underline{k}',\underline{k}'')\right|^{2}\left\{N\,\delta_{\underline{k},\underline{k}'+\underline{k}''}+a^{e}(\underline{k}-\underline{k}'-\underline{k}'')\right\}. \qquad (172)$$

The main interest in this expression lies in the terms within the curly brackets, because the other factors will not differ in any radical way from the perfect lattice case.

The quantity

$$N\,\delta_{\underline{k},\underline{k}'+\underline{k}''}+a^{e}(\underline{k}-\underline{k}'-\underline{k}'') \qquad (173)$$

gives "selection rules" for the scattering process. In the case of a perfect lattice it reduces to

$$N\,\delta_{\underline{k},\underline{k}'+\underline{k}''}+N\sum_{\underline{g}\neq 0}\delta_{\underline{k},\underline{k}'+\underline{k}''+\underline{g}} \qquad (174)$$

where $\underline{g}$ is a reciprocal lattice vector. The form of $a^{e}(\underline{q})$ is sketched in Figure 6 for amorphous selenium (uncorrected for thermal effects). It can be seen that disorder causes the sharp selection rules for a perfect lattice to be relaxed, though N-processes represented by $\delta_{\underline{k},\underline{k}'+\underline{k}''}$ persist.

This relaxation means that the observed rise in the thermal conductivity of crystalline solids at low temperatures due to the "freezing out" of U-processes will be strongly damped in amorphous solids, though it may be difficult to disentangle this effect from damping due to elastic scattering. It is possible that interesting

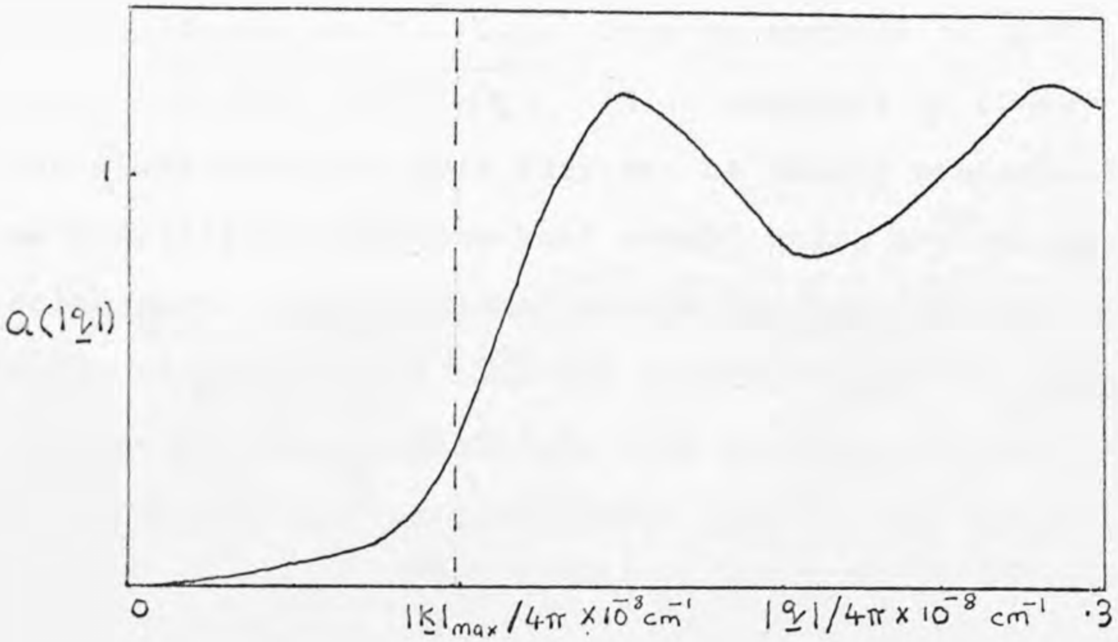


Figure 6. The pair correlation function of the atomic positions in amorphous selenium, taken from the data of Henninger et al (1967).

modifications of the selection rules may be revealed by more precise estimates of (170) for defects like dislocations. In amorphous solids the presence of partial order, such as the chains of atoms in amorphous selenium, should also be taken into account.

These simple arguments indicate that anharmonic processes are likely to be as important for disordered solids as they are for ordered ones.

1.4.6. The choice of plane waves.

The pair correlation function $a^{e}(\underline{k}-\underline{k}')$ is a measure of how two plane waves with wave vectors $\underline{k}$ and $\underline{k}'$

depart from orthogonality. This is because $N^{-1} \sum_{j} e^{i \underline{q} \cdot \underline{r}_j}$ is of the order $N^{-\frac{1}{2}} \sqrt{a^e(\underline{q})}$ It is sensible to choose the plane waves so that they are as nearly orthogonal as possible because the real normal modes are exactly orthogonal. An additional reason for choosing the plane waves in this way is that the scattering due to density fluctuations as predicted by (163) is minimised by making $a^e(\underline{k}-\underline{k}')$ as small as possible.

In practice, however, there are relatively few situations where this criterion can be used to define a short wavelength cut-off precisely. For amorphous and polycrystalline solids $a^e(\underline{q})$ depends only on $|\underline{q}|$ and is only of the order unity at its maximum value, (see Figure 6). We therefore choose the wave vectors to lie within the Debye sphere. In the case of dislocations in an otherwise perfect lattice there is no obvious way of making a unique choice and for some kinds of lattice defect it is not possible to choose N waves which are all nearly orthogonal. For example, if a single interstitial atom is present in a lattice $(N-1)$ wave vectors can be chosen which lie within the first Brillouin zone but any additional wave with a propagation vector outside the zone will be nearly "parallel" to one of the waves inside the zone, and in any case the condition that a negative $\underline{k}$ exists for every positive one cannot be preserved.

In this kind of situation we amend (118) to read

$$u_\alpha(j) = \frac{1}{N^{\frac{1}{2}}} \sum_{\underline{k}} U_\alpha(\underline{k})\, e^{i\underline{k}\cdot\underline{r}_j} + \frac{1}{N^{\frac{1}{2}}} \sum_{s} U_\alpha(s)\, \phi_s(j) \qquad (175)$$

where it is to be understood that the sum over $\underline{k}$ contains N' terms $(N' \leq N)$ and the sum over s just $(N-N')$ terms. It can be assumed that the $\phi_s(j)$ functions are orthogonal to each other and also to the plane waves and that a $-\underline{k}$ value exists for every value $\underline{k}$ without loss of generality. The conclusions of this chapter will not be affected providing the $\phi_s(j)$ are associated with high frequency modes or providing the number $(N-N')$ is small so that these modes carry a negligible amount of heat and have a small effect on the transition rates from plane wave states.

The reason for supposing that the absence of a precise cut-off should not be of critical importance at low temperatures is that only low frequency modes are excited so that high frequency modes associated with high $\underline{k}$ values do not enter the picture in a first-order perturbation theory. If we go to higher orders of perturbation theory they are introduced in two ways. They occur as the intermediate states of virtual processes and they also occur in making corrections to (141). We do not know how to circumvent this problem but it should not be necessary to specify the high frequency modes because the low frequency behaviour of a solid can be described by continuum theory where no cut-off is introduced. It seems likely that in the calculation of say a second-order matrix element between initial and final states of low frequency, the sum over virtual transitions will be sensitive to the details of the high frequency modes.

Above the Debye temperature modes of all frequencies are excited so that the necessity for considering high frequency waves becomes more acute. However in the standard theory of thermal conduction it is often assumed that this is compensated by the fact that high frequency waves travel with a small group velocity and that they tend to be scattered more strongly; thus their contribution to the heat flow might be small, although this has not been demonstrated explicitly. Using this idea thermal conduction data at high temperatures are often analysed in terms of theories using transition probabilities calculated for low frequency waves, ignoring dispersion but putting a Debye cut-off in the spectrum (e.g. Parrott 1963). This reasoning can be invoked to avoid specifying the precise details of the upper limit in the sum over plane waves.

1.4.7. Conclusion.

The simple theory which has been presented can be compared in spirit with the nearly-free electron theory of electrons in simple metals (Ziman 1964). There are many awkward features such as the fact that it is difficult in general to go beyond first order perturbation theory and thereby check the validity of the approximations made. We have to rely on comparisons with experiment and intuition. This is not a special feature of this new approach since the same difficulties already exist in the standard theory. The machinery for constructing an improved theory is there but its use is not justified in general until it is shown that the simplest approach (which is complicated enough) is inadequate. It is remarkable that so much is understood about thermal conduction considering the chain of approximations and assumptions which are necessary to obtain a result.

1.5. Biorthonormal functions.

The perturbation methods of mathematical physics are founded on the properties of orthogonal sets of functions which are usually the eigen functions of some simple equation. It is perfectly possible, however, for a set of functions to be good approximations to the solutions of a given problem without them being orthogonal, but if the exact solutions are known to be orthogonal then the approximate functions must be nearly orthogonal. If full use is to be made of this notion it is necessary to introduce a second set of functions which are biorthonormal to the first set. We consider here the possibility of constructing the functions $\psi_{\underline{k}}(j)$ defined in the previous chapter.

The transformation of the kinetic energy part of the Hamiltonion (3) is formally achieved by writing

$$P_\alpha(j) = \frac{1}{N^{\frac{1}{2}}} \sum_{\underline{k}} P_\alpha(\underline{k})\, \psi^*_{\underline{k}}(j) \tag{176}$$

whence

$$T = \frac{1}{2M} \sum_{\underline{k}} \sum_{\underline{k}'} P_\alpha(\underline{k})\, P_\alpha(-\underline{k}')\, \frac{1}{N} \sum_{j} \psi^*_{\underline{k}}(j)\, \psi^*_{-\underline{k}'}(j) \;, \tag{177}$$

The $\psi_{\underline{k}}(j)$ can be expanded in terms of plane waves, namely

$$\psi^*_{k}(j) = \sum_{\underline{k}'} A(\underline{k},\underline{k}')\, e^{-i\underline{k}'\cdot\underline{r}_j} \tag{178}$$

and using the assumed biorthonormal properties it is easily shown that

$$\frac{1}{N}\sum_{j} \psi^{*}_{\underline{k}}(j)\,\psi^{*}_{-\underline{k}'}(j) = A(\underline{k},\underline{k}') \quad . \tag{179}$$

Therefore attention can be concentrated on determining the amplitudes $A(\underline{k},\underline{k}')$,

If both sides of (178) are multiplied by $N^{-1}e^{i\underline{k}_1\cdot\underline{r}_j}$ and summed over j then we obtain

$$A(\underline{k},\underline{k}_1) = \delta_{\underline{k},\underline{k}_1} - \sum_{\underline{k}'}(1-\delta_{\underline{k}',\underline{k}_1})A(\underline{k},\underline{k}')\frac{1}{N}\sum_{j} e^{i(\underline{k}_1-\underline{k}')\cdot\underline{r}_j} \quad . \tag{180}$$

To determine the amplitudes it is necessary to invert the matrix

$$L_{\underline{k},\underline{k}'} = \delta_{\underline{k},\underline{k}'} + (1-\delta_{\underline{k},\underline{k}'})\frac{1}{N}\sum_{j} e^{i(\underline{k}_1-\underline{k}')\cdot\underline{r}_j} \quad . \tag{181}$$

Although the non-diagonal elements of $L_{\underline{k},\underline{k}'}$ are small compared with the diagonal ones, if the plane waves are nearly orthogonal, $L_{\underline{k},\underline{k}'}$ is not a "diagonally dominant" matrix, namely (Varga 1962, p.23)

$$L_{\underline{k}_1,\underline{k}_1} \not> \sum_{\underline{k}'\neq k_1} |L_{\underline{k}_1\underline{k}'}| \tag{182}$$

or

$$1 \not> \sum_{\underline{k}'\neq\underline{k}_1} N^{-\frac{1}{2}}\sqrt{a^{e}(\underline{k}_1-\underline{k}')} \quad . \tag{183}$$

For example $a^{e}(\underline{q})$ is of the order unity for amorphous solids so that the right hand side of (183) is of the order $N^{\frac{1}{2}}$. This means that if (180) is solved by successive approximation beginning with

$$A(\underline{k},\underline{k}_1) \simeq \delta_{\underline{k},\underline{k}_1} \tag{184}$$

the resulting series

$$A(\underline{k},\underline{k}_1) = \delta_{\underline{k},\underline{k}_1} - (1-\delta_{\underline{k},\underline{k}_1}) N^{-1} \sum_{j'} e^{i(\underline{k}_1-\underline{k})\cdot\underline{r}_{j'}}$$

$$+ N^{-2} \sum_{\substack{\underline{k}'\neq\underline{k}\\ \neq\underline{k}_1}} \sum_{j'} \sum_{j''} e^{i(\underline{k}'-\underline{k})\cdot\underline{r}_{j'}} e^{i(\underline{k}_1-\underline{k}')\cdot\underline{r}_{j''}} \tag{185}$$

$$- N^{-3} \sum_{\underline{k}'\neq\underline{k}} \sum_{\substack{\underline{k}''\neq\underline{k}'\\ \neq\underline{k}_1}} \sum_{j} \sum_{j'} \sum_{j''} e^{i(\underline{k}'-\underline{k})\cdot\underline{r}_{j'}} e^{i(\underline{k}''-\underline{k}')\cdot\underline{r}_{j''}} e^{i(\underline{k}_1-\underline{k}'')\cdot\underline{r}_{j'''}} + \cdots$$

is not likely to be convergent. This lack of convergence is not considered to be an objection to the use of (185) in practice, provided it is used in conjunction with perturbation methods for calculating, say, transition probabilities.

The reason for this supposition, which we have not yet proved in general, comes from the theory of scattering of elastic waves in a continuum containing density fluctuations. The kinetic energy can be expressed in the form

$$T = \frac{1}{2} \sum_{\alpha'} \int \frac{P_\alpha(\underline{r})\, P_\alpha(\underline{r})}{\rho(\underline{r})}\, d\underline{r} \tag{186}$$

where $P_\alpha(\underline{r})$ denotes a component of the momentum density at $\underline{r}$ and $\rho(\underline{r})$ is the mass density. (Ziman, Electrons and Phonons, p.50). The momentum variables $P(\underline{r})$ can be expanded in plane waves;

$$P_\alpha(\underline{r}) = \frac{1}{\sqrt{V}} \sum_{\underline{k}} P_\alpha(\underline{k})\, e^{-i\underline{k}\cdot\underline{r}} \tag{187}$$

where the sum runs over an infinite set of wave vectors which are chosen to satisfy periodic boundary conditions. In this continuum theory the plane waves are orthogonal with respect to <u>integration</u>;

$$\frac{1}{V}\int e^{i\underline{q}\cdot\underline{r}}\,d\underline{r} = \delta_{\underline{q},0} \quad . \tag{188}$$

The kinetic energy is now

$$T = \frac{1}{2}\sum_{\alpha}\sum_{\underline{k}} \frac{P_{\alpha}(\underline{k})P_{\alpha}(-\underline{k})}{\bar{\rho}} + \frac{1}{2}\sum_{\alpha}\sum_{\underline{k}}\sum_{\underline{k}'} P_{\alpha}(\underline{k})\,P_{\alpha}(-\underline{k}')\,\frac{1}{V}\int\left(\frac{1}{\rho(\underline{r})}-\frac{1}{\bar{\rho}}\right)e^{i(\underline{k}-\underline{k}')\cdot\underline{r}}\,d\underline{r} \tag{189}$$

where $\bar{\rho}$ is the mean density. The first term in (189) is analogous to T_0 in equation (125). The creation and destruction operator formalism can now be introduced as an aid to carrying out perturbation theory, but the interesting thing about (189) is the form of the second term which is to be regarded as a perturbation. We can write

$$\frac{1}{\rho(\underline{r})} - \frac{1}{\bar{\rho}} = \frac{\bar{\rho}-\rho(\underline{r})}{\bar{\rho}\,\rho(\underline{r})} = -\frac{1}{\bar{\rho}}\,\frac{\frac{\Delta\rho(\underline{r})}{\bar{\rho}}}{1+\frac{\Delta\rho(\underline{r})}{\bar{\rho}}} \tag{190}$$

then the Fourier transform of this quantity occurs s times in the s'th order term of the perturbation series for the scattering matrix. If however the scattering of an elastic wave is considered by using the elastic wave equation the terms in the standard perturbation series contain the Fourier transform of $\frac{\Delta\rho(\underline{r})}{\bar{\rho}}$ instead, but the two kinds of series must give the same final result if the perturbation series are carried to infinite order.

They will, however, not be the same to any finite order in perturbation theory. The fact that the perturbation series for the scattering of lattice waves from an isotope can be arranged either as powers of $\frac{\Delta M}{M}$ or $\frac{\Delta M}{M} / (1 - \frac{\Delta m}{M})$ has been pointed out by Liftshitz and Kosevich (1966, p.222). ΔM is the difference between the isotope mass and the host atom mass M. The point is that the low frequency scattering is given correctly by first order perturbation theory using an expansion in $\frac{\Delta \rho(\underline{r})}{\bar{\rho}}$ or $\frac{\Delta M}{M}$ because higher order terms are proportional to higher powers of the frequency.

With this hindsight it is therefore sensible to write

$$\frac{\frac{\Delta \rho(r)}{\bar{\rho}}}{1 + \frac{\Delta \rho(\underline{r})}{\bar{\rho}}} = \frac{\Delta \rho(\underline{r})}{\bar{\rho}} \left\{ 1 - \frac{\Delta \rho(\underline{r})}{\bar{\rho}} + \left(\frac{\Delta \rho(\underline{r})}{\bar{\rho}} \right)^2 - - - \right\} \tag{191}$$

which can be a divergent series in general. We know, however, that if this expansion is combined with perturbation theory the divergent terms must be cancelled.

To calculate the scattering using the creation and destruction operators to first order in perturbation theory we therefore write

$$\frac{\frac{\Delta \rho(r)}{\bar{\rho}}}{1 + \frac{\Delta \rho(r)}{\bar{\rho}}} \simeq \frac{\Delta \rho(\underline{r})}{\bar{\rho}} \tag{192}$$

and if the local mass density is expressed in terms of the atom positions as

$$\rho(\underline{r}) = \frac{M}{V}\sum_{j} \delta^{c}(\underline{r}-\underline{r}_{j}) \quad , \qquad (193)$$

where $\delta^{c}(\underline{r})$ is a coarse grained delta function (Green 1954), it may be readily ascertained that this gives the same estimate of the scattering due to density fluctuations as found in equation (163).

These are the reasons why the divergent nature of (185) is not considered to be serious. The properties of this series are being considered in more detail at the present time.

PART 2.

ELECTRONS

2.1. Possible methods for electrons in a disordered system of potentials.

In this chapter we wish to indicate where the ideas about phonons should be applicable to the motion of electrons in disordered (frozen) configuration of potentials. The understanding of electrons is more advanced mainly because they can propagate in empty space and a free electron representation can be used which is independent of the structure. The state of the theory of electrons has recently been reviewed by Mott (1967)

The analogies between electrons and vibrational waves will not be laboured. The differences are more important. We will consider how the method of averaging which we were forced to adopt for vibrational waves can be of use in the electron problem.

The equation of motion for a harmonic solid is a difference equation while electrons are described by Schroedinger's differential equation. They are both linear equations however so that methods developed for one problem can often be translated and applied to the other. The possibility of interchanging methods becomes particularly obvious when Schroedinger's equation is transformed to a discrete variable or finite difference equation.

2.1.1. The tight binding method.

One of the earliest schemes for calculating the band structure of a perfect lattice was the "linear combination of atomic orbitals" method or as it is more simply known, the tight binding method. This method is also useful for thinking about disordered systems because of its simplicity. The basic idea of this approach is to approximate the wave functions in a solid by a superposition of atomic wave functions for the isolated atoms. Let $\phi(\underline{r}-\underline{r}_j)$ denote an eigen function of an isolated potential at $\underline{r}_j$ with an eigen value E_0 where the level E_0 is assumed to be widely separated in energy from neighbouring ones. The function $\phi(\underline{r}-\underline{r}_j)$ satisfies the equation

$$\frac{\hbar^2}{2m}\nabla^2\phi(\underline{r}-\underline{r}_j) - v(\underline{r}-\underline{r}_j)\,\phi(\underline{r}-\underline{r}_j) = E_0\,\phi(\underline{r}-\underline{r}_j) \tag{194}$$

where $v(\underline{r}-\underline{r}_j)$ is an atomic potential. We now suppose that the total potential for a collection of atoms may be written as

$$v_T(\underline{r}) = \sum_j v(\underline{r}-\underline{r}_j) + \sum_j \Delta v(\underline{r}-\underline{r}_j) \tag{195}$$

where $\Delta v(\underline{r}-\underline{r}_j)$ is a small correction to $v(\underline{r}-\underline{r}_j)$. Schroedinger's equation is therefore

$$\frac{\hbar^2}{2m}\nabla^2\psi(\underline{r}) - v_T(\underline{r})\psi(\underline{r}) = E\,\psi(\underline{r}) \tag{196}$$

and we can attempt to construct approximate solutions for values of E close to E_0 by writing

$$\psi(\underline{r}) = \sum_j \alpha_j\,\phi(\underline{r}-\underline{r}_j) \tag{197}$$

where the coefficients are to be determined. In the case of a crystalline solid

$$\alpha_j \propto e^{i\underline{k}\cdot\underline{r}_j} \tag{198}$$

and the single level of an isolated atom is broadened to form a band which can accommodate just N electrons. If E_0 is widely separated from neighbouring levels of the isolated atom this band does not overlap other ones.

Substituting from (197) into (194) and using (196), we obtain

$$\sum_{j'\neq j''}\sum \alpha_{j'}\phi(\underline{r}-\underline{r}_j)v(\underline{r}-\underline{r}_{j''}) + \sum_{j'}\sum_{j''}\alpha_{j'}\,\phi(\underline{r}-\underline{r}_{j'})\Delta v(\underline{r}-\underline{r}_j) = (E-E_0)\sum_{j'}\alpha_{j'}\phi(\underline{r}-\underline{r}_{j'}). \tag{199}$$

The essential assumption of the tight binding method, as the name implies, is that for a low lying level of the isolated atom the wave functions fall off rapidly away from the origin. Thus if we multiply (199) by $\phi^*(\underline{r}-\underline{r}_j)$ and integrate over $\underline{r}$, "three-centre" integrals like

$$\int \phi^*(\underline{r}-\underline{r}_j)v(\underline{r}-\underline{r}_{j'})\phi(\underline{r}-\underline{r}_{j''})\,d\underline{r} \tag{200}$$

can be assumed to be negligible. We may normalise the $\phi(\underline{r}-\underline{r}_j)$ such that

$$\int \phi^*(\underline{r}-\underline{r}_j)\,\phi(\underline{r}-\underline{r}_j)\,d\underline{r} \quad . \qquad (201)$$

The coefficients α_j satisfy the equation

$$\begin{aligned}
&\alpha_j\left\{\int \phi^*(\underline{r}-\underline{r}_j)\sum_{j'\neq j} v(\underline{r}-\underline{r}_{j'})\,\phi(\underline{r}-\underline{r}_j)\,d\underline{r}\right\}\\
&+\alpha_j\left\{\int \phi^*(\underline{r}-\underline{r}_j)\sum_{j'} \Delta v(\underline{r}-\underline{r}_{j'})\,\phi(\underline{r}-\underline{r}_j)\,d\underline{r}\right\}\\
&+\sum_{j'\neq j}\alpha_{j'}\left\{\int \phi^*(\underline{r}-\underline{r}_j)\,v(\underline{r}-\underline{r}_j)\,\phi(\underline{r}-\underline{r}_{j'})\,d\underline{r}\right\}\\
&+\sum_{j'\neq j}\alpha_{j'}\left\{\int \phi^*(\underline{r}-\underline{r}_j)\,\Delta v(\underline{r}-\underline{r}_{j'})\,\phi(\underline{r}-\underline{r}_{j'})\,d\underline{r}\right\} \qquad (202)\\
&+\sum_{j'\neq j}\alpha_{j'}\left\{\int \phi^*(\underline{r}-\underline{r}_j)\,\Delta v(\underline{r}-\underline{r}_{j})\,\phi(\underline{r}-\underline{r}_{j'})\,d\underline{r}\right\}\\
&=(E-E_0)\alpha_j+(E-E_0)\sum_{j'\neq j}\alpha_{j'}\left\{\int \phi^*(\underline{r}-\underline{r}_j)\,\phi(\underline{r}-\underline{r}_{j'})\,d\underline{r}\right\} .
\end{aligned}$$

In practice it is also usual to neglect the second term on the right hand side of (202) and some of the terms on the right hand side may also be neglected in the first instance, e.g. by putting $\Delta v(\underline{r})=0$. The equation then has the form

$$\sum_{j'} X(\underline{r}_j-\underline{r}_{j'})\,\alpha_{j'} = (E-E_0)\,\alpha_j \qquad (203)$$

which is analogous to the equation of motion for a harmonic lattice, though it is a little simpler because the α_j are scalars.

This kind of equation has recently been investigated by De Dycker and Phariseau (1967, a,b) using the method of averaging described in 1.3.1, and the quasi crystalline approximation. The procedure for improving on the quasi crystalline approximation suggested in 1.3.2. may be particularly useful in the case of electrons in liquids, (treating the atoms as a frozen configuration) because the superposition approximation may often be used to overcome the difficulties with high particle correlation functions.

2.1.2. The Greenian Method.

One of the merits of the tight binding method is that it takes into account from the start the fact that the potential wells in a real solid are very deep, because the functions $\phi(\underline{r}-\underline{r}_j)$ satisfy the Schroedinger equation within the deep potentials. Another more general procedure which also achieves this is the Greenian method which can describe electrons of all energies. However some sacrifice of reality has to be made for this method to be used for liquids and amorphous solids.

In the case of a crystalline solid it is possible to approximate to the lattice potential by a lattice of spherical non-overlapping potentials (Ham and Segall,

1961) which has come to be known as a "muffin tin" potential. This is a great simplification when formulating methods for solving Schroedinger's equation and it is usual to assume that the potentials in a disordered solid or liquid are also of a spherical non-overlapping kind. The error made by this assumption is likely to be more serious in this case (Ziman, 1966) but until the simplified situation is better understood there is little point in considering these refinements.

The principles of the Greenian method have been dealt with briefly in 1.2.2, which deals with the loaded continuum model. This method will be described in more detail here because some rather subtle points arise with regard to electrons in disordered systems.

We begin with Schroedinger's differential equation for an infinite system of spherical non-overlapping potentials

$$\nabla^2 \psi(\underline{r}) + \kappa^2 \psi(\underline{r}) = \sum_j u(\underline{r}-\underline{r}_j)\, \psi(\underline{r}) \qquad (204)$$

where κ^2 denotes the energy (in units of $\frac{2m}{\hbar^2}$) and $u(\underline{r}-\underline{r}_j)$ denotes a spherical potential centred at $\underline{r}_j$. The energy scale is chosen such that the potential energy in between the wells is zero. If there are no electron sources or sinks within the system the integral equation equivalent of (204) is

$$\psi(\underline{r}) = \sum_{j} \int G(\underline{r},\underline{r}')\, u(\underline{r}'-\underline{r}_j)\, \psi(\underline{r}')\, d\underline{r}' \tag{205}$$

where $G(\underline{r}\,\underline{r}')$ is a Green function satisfying

$$\nabla^2 G(\underline{r},\underline{r}') + k^2 G(\underline{r},\underline{r}') = \delta(\underline{r}-\underline{r}') \tag{206}$$

and the same boundary condition imposed on $\psi(\underline{r})$.

There are three kinds of solution to (206) for an infinite medium, namely

$$G^{+}(\underline{r},\underline{r}') = -\frac{1}{4\pi}\,\frac{e^{ik|\underline{r}-\underline{r}'|}}{|\underline{r}-\underline{r}'|}\,, \tag{207}$$

$$G^{-}(\underline{r},\underline{r}') = -\frac{1}{4\pi}\,\frac{e^{-ik|\underline{r}-\underline{r}'|}}{|\underline{r}-\underline{r}'|}\,, \tag{208}$$

$$G^{s}(\underline{r},\underline{r}') = -\frac{1}{4\pi}\,\frac{\cos k\,|\underline{r}-\underline{r}'|}{|\underline{r}-\underline{r}'|}\,. \tag{209}$$

When k is purely real (energy positive), $G^{+}(\underline{r},\underline{r}')$ corresponds to an outgoing flux of particles, $G^{-}(\underline{r},\underline{r}')$ to an incoming flux and $G^{s}(\underline{r},\underline{r}')$ to a zero flux. Since we have stipulated that there are no sources or sinks in the system $G^{s}(\underline{r},\underline{r}')$ must be the correct choice for positive energies. When k is purely imaginary (energy negative) these three Green functions give rise to a zero flux but if we examine their behaviour for large values of $|\underline{r}-\underline{r}'|$ both $G^{-}(\underline{r},\underline{r}')$ and $G^{s}(\underline{r},\underline{r}')$ diverge which would result in the wave function $\psi(\underline{r})$ being non-normalisable so that $G^{+}(\underline{r},\underline{r}')$ is the correct choice for negative energies since it tends to zero as $|\underline{r}-\underline{r}'|$ tends to infinity.

The wave function within the j'th potential may be expressed in the general form

$$\Psi_j(\underline{\rho}) = \sum_L i^\ell \frac{\beta_L^j}{[\mathcal{R}_\ell, j_\ell]} \mathcal{R}_\ell(\rho) \mathcal{Y}_L(\underline{\rho}) \tag{210}$$

where $\mathcal{R}_\ell(\rho)$ is a solution of the radial Schroedinger equation for a single potential, corresponding to an energy $E=\kappa^2$. The quantity $[\mathcal{R}_\ell, j_\ell]$ is included for convenience to tidy up the subsequent algebra and is defined by

$$[\mathcal{R}_\ell, j_\ell] = \mathcal{R}(R_s)\frac{d}{dR_s} j_\ell(\kappa R_s) - j_\ell(\kappa R_s)\frac{d}{dR_s} \mathcal{R}_\ell(R_s), \tag{211}$$

R_s being the radius of the potential wells and $j_\ell(\kappa R_s)$ is a spherical Bessel function.

The procedure for obtaining an equation for the coefficients β_L^j follows the pattern described for the loaded continuum. Our interest lies in the form of the equations so that only the essential steps will be sketched. First a condition analogous to (7) can be written down in which the Green function for the Laplace operator is replaced by $G^s(\underline{r},\underline{r}')$ or $G^+(\underline{r},\underline{r}')$ depending on whether the energy is positive or negative, and $U_j(\underline{\rho})$ is replaced by $\Psi_j(\underline{\rho})$. Substitution from (210) and use of standard expansions for the Green function (Phariseau and Ziman, 1963) in terms of spherical harmonics and Bessel functions leads to the equations

$$\sum_{L'}\sum_{j'\neq j} B'_{LL'}(\kappa,\underline{r}_{jj'})\,\beta^{j'}_{L'} + \kappa \cot\eta_\ell\,\beta^{j}_{L} = 0 \quad (E>0)\,, \tag{212}$$

$$\sum_{L'}\sum_{j'\neq j} B_{LL'}(\kappa,\underline{r}_{jj'})\,\beta^{j'}_{L'} + \kappa(\cot\eta_\ell - i)\,\beta^{j}_{L} = 0 \quad (E<0). \tag{213}$$

η_ℓ is the ℓ'th phase shift for a spherical potential at the energy E, defined by

$$\cot\eta_\ell = \frac{\mathcal{R}_\ell(R_s)\frac{d}{dR_s}n_\ell(\kappa R_s) - n_\ell(\kappa R_s)\frac{d}{dR_s}\mathcal{R}_\ell(R_s)}{\mathcal{R}_\ell(R_s)\frac{d}{dR_s}j_\ell(\kappa R_s) - j_\ell(\kappa R_s)\frac{d}{dR_s}\mathcal{R}_\ell(R_s)} = \frac{[\mathcal{R}_\ell, n_\ell]}{[\mathcal{R}_\ell, j_\ell]} \tag{214}$$

where $n_\ell(\kappa R_s)$ is a spherical Neumann function. The matrixes $B'_{LL'}(\kappa,\underline{r}_{jj'})$ and $B(\kappa,\underline{r}_{jj'})$ are defined by

$$B'_{LL'}(\kappa,\underline{r}_{jj'}) = 4\pi \sum_{L''} C^{L''}_{LL'}\, i^{-\ell''}\,\kappa\, n_\ell(\kappa|\underline{r}_{jj'}|)\, Y_{L''}(\underline{r}_{jj'})\,, \tag{215}$$

and

$$B_{LL'}(\kappa,\underline{r}_{jj'}) = 4\pi \sum_{L''} C^{L''}_{LL'}\, i^{-\ell''-1}\,\kappa\, h_\ell(\kappa|\underline{r}_{jj'}|)\, Y_{L''}(\underline{r}_{jj'})\,, \tag{216}$$

$h_\ell(\kappa|\underline{r}_{jj'}|)$ being a spherical Hankel function and the coefficients $C^{L''}_{LL'}$ are defined in equation (14).

As pointed out before these equations differ slightly in form from the equation of motion for a harmonic solid because the matrix operator is a function of the energy. This does not lead to any special difficulties, except that (212) and (213) cannot be solved explicitly and some adjustments are necessary to derive expressions for the density of states from the solutions of inhomogeneous forms of (212) and (213). Before going on to discuss how this representation of Schroedinger's equation may be used to calculate the density of states in a disordered system it is desirable to digress a little to emphasize how equations (212) and (213) differ from those considered by Phariseau and Ziman (1963).

These authors used the Green function $G^{+}(\underline{r},\underline{r}')$ both for positive and negative energies, but although this seems at first sight to be incorrect, it is in fact a very fruitful procedure. This leads to a modification whereby equation (212) is supposed to hold for both negative and positive energies. This has no effect in the case of a perfect lattice but for a disordered system it has quite a profound effect.

If the equation

$$\sum_{L'}\sum_{j'\neq j} B_{LL'}(\kappa,\underline{r}_{jj'})\,\beta^{j'}_{L'} + \kappa(\cot\eta_\ell - i)\,\beta^{j}_{L} = 0 \qquad (217)$$

is averaged as described in 1.3.3, then we obtain

$$(N-1)\sum_{L'}\int B_{LL'}(\kappa,\underline{r}_1-\underline{r}_2)\,p(\underline{r}_2|\underline{r}_1)\langle\beta_{L'}(\underline{r}_2|\underline{r}_1)\rangle\,d\underline{r}_2 \qquad (218)$$
$$+\kappa(\cot\eta_\ell - i)\langle\beta_L(\underline{r}_1)\rangle = 0$$

where the average coefficients are defined in precisely the same way as previously and $p(\underline{r}_2|\underline{r}_1)$ is the pair distribution of atoms. If the quasi-crystalline approximation is invoked ;

$$\langle \beta_L(\underline{r}_2|\underline{r}_1)\rangle \simeq \langle \beta_L(\underline{r}_2)\rangle \tag{219}$$

then it is found that (218) does not admit a solution of the form

$$\langle \beta_L(\underline{r}_1)\rangle = \langle \beta_L\rangle e^{i\underline{K}\cdot\underline{r}_1} \tag{220}$$

if $\underline{K}$ is a purely real wave vector. On the other hand if $\underline{K}$ is allowed to be complex the integral in (218) diverges at the upper limit of integration. This must be contrasted with the behaviour for negative energies when only waves with real propagation vectors occur. This is also the case when equation (212) is averaged. However if the divergent upper limit to the integration over $\underline{r}_2$ is ignored the imaginary part of the wave vector can be extracted explicitly in the limit when the potential wells are weak scatterers, i.e. when $\sin\eta_\ell$ is small and this imaginary part or attenuation coefficient is proportional to the total cross section per unit volume for an assembly of scatterers. (Ziman 1966).

The explanation of why this apparently hazardous procedure gives extremely reasonable results lies in the earlier work of Lax (1951,1952) and Waterman and Truell (1961). The latter two authors considered the problem of a plane wave normally incident on a disordered system of potentials which are confined to a half space as depicted in Figure 7

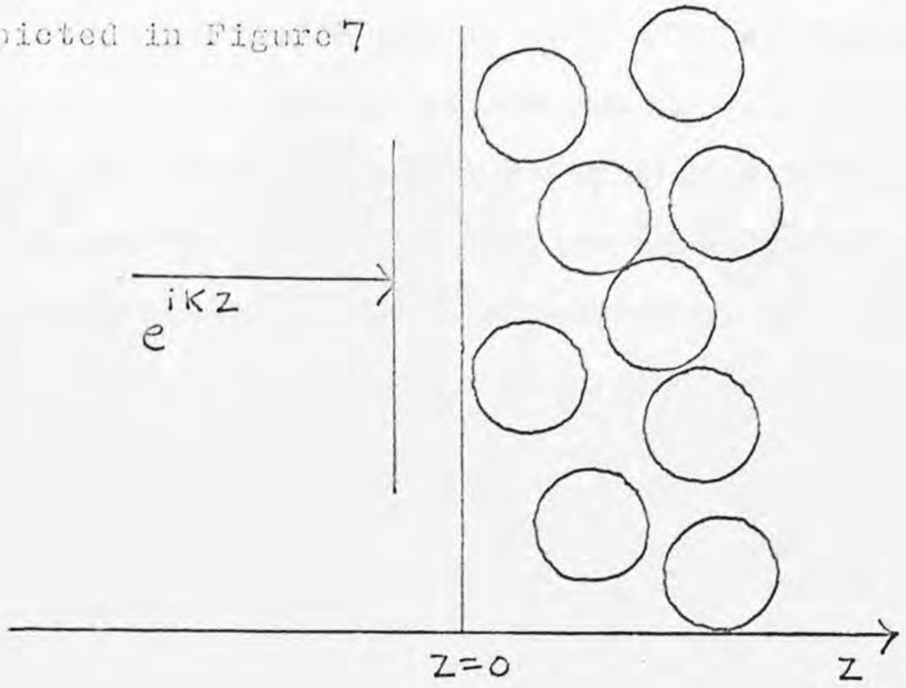


Figure 7

The energy of the incident electron is by definition greater or equal to zero and is equal to k^2. There is now a source of electrons present so that equation (205) is amended to read

$$\psi(\underline{r}) = e^{ikz} + \int G^+(\underline{r},\underline{r}') \sum_j u(\underline{r}'-\underline{r}_j)\, \psi(\underline{r}')\, d\underline{r}' . \qquad (221)$$

This scattering problem can also be formulated in terms of the amplitudes of the spherical solutions within each potential. Adapting Waterman and Truell's (1961) results to the notation of this chapter we have

$$\sum_{L'} \sum_{j' \neq j} B_{LL'}(k, \underline{r}_{jj'})\, \beta^{j'}_{L'} + k(\cot \eta_\ell - i)\beta^{j}_{L} = \frac{4\pi}{R_s^2} Y_L(0)\, e^{ikz_j} \qquad (222)$$

where the phase shifts are to be evaluated for an energy $E = K^2$ i.e. at the energy of the incident plane wave. Waterman and Truell showed that if this equation is averaged and the quasi-crystalline approximation made, the inhomogeneous terms are cancelled by the upper limit of the integral which occurs when the first term is averaged. This is interpreted as cancellation of the incident wave within the semi-infinite medium by waves produced at the interface.

The reason why solutions to the averaged equation of motion for a harmonic solid, and the averaged forms of equations (212) and (213), fail to give attenuated plane waves, was stated in 1·3·1, to be due to the fact that the equations do not contain any information about the boundary conditions. Equation (218) does contain this information but it is fair to say that this is a little fortuitous since it is derived starting from the "wrong" equation (217) instead of (222).

The question may be asked: why is it not possible to set up the same kind of problem for vibrational waves and electrons with negative energies? In the case of vibrational waves the answer is that we do not have a suitable representation analogous to free electron waves while for electrons in the negative energy region, plane waves will not propagate in the space $z < 0$

After this digression we turn to the problem of calculating the density of electronic states using the Greenian theory. It is convenient to write equations (212) and (213) as

$$\frac{1}{\lambda_\ell(\kappa)} \sum_{L'} \sum_{j' \neq j} \tilde{B}_{LL'}(\kappa, r_{jj'}) \beta^{j'}_{L'} + \kappa \, \beta^{j}_{L} = 0 \tag{223}$$

where

$$\begin{aligned} \tilde{B}_{LL'}(\kappa, r_{jj'}) &= B'_{LL'}(\kappa, r_{jj'}) \ (E>0) \ ; & \lambda_\ell(\kappa) &= \cot\eta_\ell \ (E>0) \ . \\ &= B_{LL'}(\kappa, r_{jj'}) \ (E<0) \ ; & &= \cot\eta_\ell - i \ (E<0) \ . \end{aligned} \tag{224}$$

We may formally define a Green function which is the solution to

$$\frac{1}{\lambda_\ell(\kappa)} \sum_{L'} \sum_{j' \neq j} \tilde{B}_{LL'}(\kappa, r_{jj'}) G^{j'j_0}_{L'L_0} + \kappa \, G^{jj_0}_{LL_0} = \delta_{LL_0} \delta_{jj_0} \tag{225}$$

and try to express the density of states in terms of this function. The standard procedure outlined in 1.3.2 is not directly applicable here for the following reason:

If $\beta^{s,j}_{L}$ denotes the s'th solution to equation (223) it may readily be shown by standard means (e.g. Friedman p. 199.) that it is not orthogonal to a solution $\beta^{s'j}_{L}$ corresponding to a different energy, namely

$$\sum_{L} \sum_{j} \beta^{*s'j}_{L} \beta^{sj}_{L} \neq \delta_{ss'} \ . \tag{226}$$

Different solutions corresponding to the same energy can be assumed orthogonal since in principle if they are not the Schmidt procedure can be used to construct a set of solutions which are orthogonal. This means that the Green function cannot be constructed out of the β^{sj}_L by means of the bilinear expansion (Lanczos p.291) and hence the method of Edwards (1961) cannot be used directly to derive the density of states in terms of the Green function.

This situation can be remedied however by means of a very simple device. Suppose we want the Green function for a particular energy $E_0 = \kappa_0^2$ we can write down a fictitious homogeneous equation

$$\frac{1}{\Lambda_\ell(\kappa_0)} \sum_{L'} \sum_{j' \neq j} \tilde{B}_{LL'}(\kappa_0, r_{jj'}) \alpha^{j'}_{L'} + \kappa \alpha^{j}_{L} = 0 \tag{227}$$

which differs from (223) because κ which occurs in the matrix in (223) is replaced by κ_0 We now assume that a set of solutions to (227) exist which will be called α^{sj}_L and these solutions are orthogonal to each other. The Green function may therefore be written as

$$G^{\pm jj_0}_{LL_0} = \sum_s \frac{\alpha^{*sj_0}_{L_0} \alpha^{sj}_{L}}{\kappa_0 - \kappa_s \pm \epsilon} \tag{228}$$

where ϵ is a positive infinitesimal to indicate how the integration around the pole should be carried out. The solutions α^{sj}_L will only be equal to the β^{sj}_L when they both correspond to an energy E_0

Using the theorem

$$\int \frac{f(x)}{x \pm \epsilon}\,dx \equiv P\int \frac{f(x)}{x}\,dx \mp i\pi \int \delta(x)\,f(x)\,dx \qquad (229)$$

we have

$$\text{Imaginary part} \sum_{L}\sum_{j} G^{\pm jj}_{LL} = \mp 2i\pi \sum_{s} \delta(E_0 - E_s)\,k_0 \qquad (230)$$

where the values of E_s change as E_0 is altered. But we know that when $E_s = E_0$ this corresponds to an energy level of the "correct" equation (223) so that the true density of states is given by

$$n(E) = \frac{1}{4\pi i k}\sum_{L}\sum_{j}\left\{G^{-jj}_{LL} - G^{+jj}_{LL}\right\}. \qquad (231)$$

because it is only when $E_s = E_0$ that the right hand side of (230) is non-zero. The methods discussed in 1.3.2. for constructing average Green functions can therefore also be used to calculate the average density of states using the Greenian equations.

Finally it should be pointed out that a qualitative understanding of the properties of electrons can be achieved by averaging Schroedinger's differential equation. It is however difficult to take into account the fact that the potential wells in a real solid are very deep by this means although for a hypothetical model with very weak potentials it is useful as an aid to understanding.

2.2. The Greenian and A.P.W. methods for calculating the electronic band structure of a perfect solid and the scattering of a Bloch wave from an impurity potential.

In the case of a perfect lattice of identical potentials Bloch's theorem may be invoked so that the coefficients β_L^j which occur in (212) and (213) may be written as

$$\beta_L^j = \beta_L e^{i\underline{K}\cdot\underline{r}_j} \tag{232}$$

where $\underline{K}$ is a real wave vector for the stationary states of an infinite system or when periodic boundary conditions are imposed. Despite the remarks made in 2.1.2. about the correct choice of the Green function in formulating the equations we will assume that the form

$$\sum_{L'}\sum_{j'\neq j} B_{LL'}(\kappa, r_{jj'})\,\beta_{L'}^{j'} + \kappa(\cot\eta_\ell - i)\,\beta_L^j = 0 \tag{233}$$

is correct for both negative and positive energies. It is a curious fact that for positive energies it does not matter whether we use $G^s(\underline{r},\underline{r}')$ or $G^+(\underline{r},\underline{r}')$ when considering a perfect lattice. The reason is that owing to the high symmetry in a lattice there is zero net current out of the system, the currents which arise from using $G^+(\underline{r},\underline{r}')$ cancel out exactly.

Substituting from (232) into (233) we then have to solve

$$\sum_{L'} \mathcal{B}_{LL'}(\kappa, \underline{k})\, \beta_{L'} + \kappa(\cot\eta_\ell - i)\,\beta_L = 0 \tag{234}$$

where

$$\mathcal{B}_{LL'}(\kappa, \underline{k}) = \sum_{j' \neq j} B_{LL'}(\kappa, r_{jj'})\, e^{-i\underline{k}\cdot\underline{r}_{jj'}} , \tag{235}$$

and is usually called a structure constant, the point being that it is independent of the nature of the potential wells which make up the solid. One of the chief merits of this method is that once the structure constants are calculated for a particular kind of lattice the numerical work involved in solving (234) is confined to the calculation of the phase shifts and the actual solving of the simultaneous equations.

The use of computers make it possible to calculate the most complicated band structure from (234) as shown for example by the calculations of Segall (1962) and recently by Ballinger and Marshall (1967) for copper. However it is often desirable to work with equations which show the physics of a situation in the clearest perspective. Thus for example equation (234) is particularly suitable for discussing the origin of tightly bound bands of electrons, where the structure constants can be estimated by including just a few values of j' close to j because the $B_{LL'}(\kappa, r_{jj'})$ diminish rapidly with increasing $|\underline{r}_j - \underline{r}_{j'}|$. In the case of the conduction band of a simple metal $\sin\eta_\ell$ can be small and $\cot\eta_\ell$ therefore becomes large which corresponds to the potentials being weak scattering centres. The energy levels are given by the condition

$$\det \left| B_{LL'}(\kappa, \underline{k}) + \kappa(\cot\eta_\ell - i)\,\delta_{LL'} \right| = 0 \tag{236}$$

and it was pointed out by Ziman (1965) that the singular behaviour of $\cot\eta_\ell$ makes it awkward to extract the essential properties of conduction electrons from this determinant if we wish to examine why the conduction electrons behave as they do, namely like electrons in a system of weak potentials.

Ziman showed that the determinantal equation (236) could be transformed to an equivalent reciprocal lattice representation

$$\det \left| \Gamma_{\underline{g}\underline{g}'} + \left(|\underline{k} + \underline{g}|^2 - \kappa^2\right) \delta_{\underline{g}\underline{g}'} \right| = 0 \tag{237}$$

where

$$\Gamma_{\underline{g}\underline{g}'} = -\frac{4\pi N}{\kappa} \sum_\ell (2\ell+1) \tan\eta'_\ell \, \frac{j_\ell(|\underline{k}+\underline{g}|R)\, j_\ell(|\underline{k}+\underline{g}'|R')}{j_\ell(\kappa R)\; j_\ell(\kappa R')}\, P_\ell(\cos\theta_{\underline{g}\underline{g}'}) . \tag{238}$$

In (237) $\underline{g}$ is a reciprocal lattice vector, N is the number of atoms per unit volume, R and R' lie with a unit cell of the lattice where the coordinate origin is at the centre of the cell but are otherwise arbitrary, $P_\ell(\cos\theta_{\underline{g}\underline{g}'})$

is a Legendre polynomial, $\theta_{\underline{g}\underline{g}'}$ is the angle between $\underline{g}$ and $\underline{g}'$ and

$$\cot \eta'_{\ell} = \cot \eta_{\ell} - \frac{n_{\ell}(\kappa R')}{j_{\ell}(\kappa R')} \tag{239}$$

where $n_{\ell}(\kappa R')$ is spherical Neumann function. The important point about this new form is that when $\sin \eta_{\ell}$ becomes small the matrix $\Gamma_{\underset{\sim}{g}\underset{\sim}{g}'}$ also becomes small rather than singular. This result will now be rederived by a less abstract method than that used by Ziman which indicates its significance more clearly. This derivation is however confined to the special choice $R = R' = R_s$.

First we consider the form of the structure constants, which can be defined by (Kohn and Rostoker 1954)

$$N \sum_{\underline{g}} \frac{e^{i(\underline{k}+\underline{g})\cdot(\underline{\rho}-\underline{\rho}')}}{|\underline{k}+\underline{g}|^{2} - \kappa^{2}} - \frac{1}{4\pi} \frac{e^{i\kappa|\underline{\rho}-\underline{\rho}'|}}{|\underline{\rho}-\underline{\rho}'|}$$

$$= - \sum_{L} \sum_{L'} i^{\ell-\ell'} \mathcal{B}_{LL'}(\kappa, \underline{k})\, j_{\ell}(\kappa\rho)\, j_{\ell'}(\kappa\rho')\, \mathcal{Y}_{L}(\underline{\rho})\, \mathcal{Y}_{L'}(\underline{\rho}') \tag{240}$$

where ρ and ρ' lie with a unit cell of the lattice, the coordinate origin being at the centre of the cell. For convenience we assume that $\rho < \rho'$, then using the standard formulae

$$-\frac{1}{4\pi}\frac{e^{i\kappa|\underline{\rho}-\underline{\rho}'|}}{|\underline{\rho}-\underline{\rho}'|} = -i\kappa\sum_{L} j_{\ell}(\kappa\rho)\, h_{\ell}(\kappa\rho')\, \mathcal{Y}_{L}(\underline{\rho})\, \mathcal{Y}_{L}(\underline{\rho}') , \qquad (241)$$

$$e^{i\underline{q}\cdot\underline{R}} = 4\pi\sum_{L} i^{\ell}\, j_{\ell}(qR)\, \mathcal{Y}_{L}(\underline{R})\, \mathcal{Y}_{L}(\underline{q}) , \qquad (242)$$

the left hand side of (240) may be arranged as

$$N\sum_{\underset{\sim}{g}} \frac{1}{|\underline{k}+\underline{g}|^{2}-\kappa^{2}} \sum_{L}\sum_{L'} (4\pi)^{2}\, i^{\ell-\ell'}\, j_{\ell}(|\underline{k}+\underline{g}|\rho)\, j_{\ell'}(|\underline{k}+\underline{g}|\rho')\, \mathcal{Y}_{L}(\underline{\rho})\, \mathcal{Y}_{L'}(\underline{\rho}')$$
$$\times\, \mathcal{Y}_{L}(\underline{k}+\underline{g})\, \mathcal{Y}_{L'}(\underline{k}+g) \qquad (243)$$
$$-i\kappa\sum_{L} j_{\ell}(\kappa\rho)\, h_{\ell}(\kappa\rho')\, \mathcal{Y}_{L}(\underline{\rho})\, \mathcal{Y}_{L}(\underline{\rho}') .$$

The $\mathcal{B}_{LL'}(\kappa,\underline{k})$ may now be written down using the orthogonality properties of the spherical harmonics if ρ and ρ' are less than or equal to the inscribed sphere radius, i.e. the radius of the largest sphere which lies completely within the unit cell. In practice this is the same as the radius of the spherical potentials R_{s} . For particular values of ρ and ρ' say R and R' we then have

$$\mathcal{B}_{LL'}(\kappa,\underline{k}) = -N\sum_{\underline{g}} \frac{(4\pi)^{2}}{|\underline{k}+\underline{g}|^{2}-\kappa^{2}}\; \frac{j_{\ell}(|\underline{k}+\underline{g}|R)\, j_{\ell'}(|\underline{k}+\underline{g}|R')}{j_{\ell}(\kappa R)\, j_{\ell'}(\kappa R')}\, \mathcal{Y}_{L}(\underline{k}+\underline{g})\, \mathcal{Y}_{L'}(\underline{k}+\underline{g})$$
$$+\, i\kappa\, \frac{h_{\ell}(\kappa R')}{j_{\ell}(\kappa R')}\, \delta_{LL'} . \qquad (244)$$

This formula breaks down if either $j_{\ell}(\kappa R)$ or $j_{\ell}(\kappa R')$ is zero making the matrix indeterminate, but a more general form is obtained by differentiating both sides of (240) with respect to ρ and ρ' an arbitrary number of times. This gives

$$\mathcal{B}_{LL'}(\kappa, \underline{k}) = -N \sum_{\underline{g}} \frac{(4\pi)^2}{|\underline{k}+\underline{g}|^2-\kappa^2} \frac{j^s_\ell(|\underline{k}+\underline{g}|R)\, j^{s'}_{\ell'}(|\underline{k}+\underline{g}|R')}{j^s_\ell(\kappa R)\, j^{s'}_{\ell'}(\kappa R')} \mathcal{Y}_L(\underline{k}+\underline{g})\mathcal{Y}_{L'}(\underline{k}+\underline{g}) + i\kappa \frac{h^{s'}_\ell(\kappa R')}{j^{s'}_\ell(\kappa R')} \delta_{LL'} \tag{245}$$

where

$$j^s_\ell(ax) = \frac{d}{dx} j_\ell(ax) \quad , \quad h^s_\ell(ax) = \frac{d}{dx} h_\ell(ax). \tag{246}$$

However for the present purpose it will be assumed that (244) presents no difficulties.

The next step is to expand the Bloch wave $\Psi_{\underline{k}}(\underline{\rho})$ in plane waves, namely

$$\Psi_{\underline{k}}(\underline{\rho}) = \sum_{\underline{g}} \alpha_{\underline{k}+\underline{g}}\, e^{i(\underline{k}+\underline{g})\cdot\underline{\rho}} \quad . \tag{247}$$

This expansion is valid for all values of $\underline{\rho}$ but here we only require this expansion to converge to the correct answer in a restricted region of space, namely the region where the potential is zero in between the muffin tin potentials. The coefficients are not unique for this reason, (Ham and Segall 1961). These authors have shown explicitly that only a few coefficients are necessary to represent $\Psi_{\underline{k}}(\underline{\rho})$. The $\beta_L(\underline{k})$ may be expressed in terms of the $\alpha_{\underline{k}+\underline{g}}$ by writing

$$\left\{ \sum_{\underline{g}} \alpha_{\underline{k}+\underline{g}} e^{i(\underline{k}+\underline{g})\cdot\underline{\rho}} \right\}_{\rho=R_s} = \left\{ \sum_{L} i^{l} \frac{\beta_L(\underline{k})}{[\mathcal{R}_l, j_l]} \mathcal{R}_l(\rho)\, \mathcal{Y}_L(\underline{\rho}) \right\}_{\rho=R_s} . \tag{248}$$

Assuming that the functions $\mathcal{R}_l(\rho)$ do not vanish at $\rho=R_s$ we find

$$\beta_L(\underline{k}) = \sum_{\underline{g}} \frac{4\pi\,[\mathcal{R}_l, j_l]\, \mathcal{Y}_L(\underline{k}+\underline{g})\, j_l(|\underline{k}+\underline{g}|R_s)}{\mathcal{R}_l(R_s)}\, \alpha_{\underline{k}+\underline{g}} = \sum_{\underline{g}} \beta_{L\underline{g}}\, \alpha_{\underline{k}+\underline{g}} . \tag{249}$$

Alternatively, if the denominator in (249) goes through a zero the procedure of differentiating both sides of (248) till a finite answer is obtained can be adopted but this consideration will again be set aside.

If we now take (249) and (244) in the special case when $R = R' = R_s$ and note that

$$[j_l, n_l] = \frac{1}{\kappa R_s^2} , \qquad \tan\eta'_l = \left\{ \cot\eta_l - \frac{n_l(\kappa R_s)}{j_l(\kappa R_s)} \right\}^{-1} = \kappa R_s^2\, [\mathcal{R}_l, j_l]\, \frac{j_l(\kappa R_s)}{\mathcal{R}_l(R_s)} , \tag{250}$$

substitution into (233) and a little rearrangement gives

$$\sum_{\underline{g}} F_{L\underline{g}} \left[\sum_{\underline{g}'} \alpha_{\underline{k}+\underline{g}'} \left\{ \sum_{L'} \frac{-\tan\eta'_{l'}\, F_{L'\underline{g}}}{\rho(\underline{g})\,\kappa} F_{L'\underline{g}'} + \delta_{\underline{g}\underline{g}'} \right\} \right] = 0 \tag{251}$$

where

$$F_{L\underline{g}} = 4\pi N^{\frac{1}{2}} \mathcal{Y}_L(\underline{k}+\underline{g})\, j_\ell(|\underline{k}+\underline{g}|R_s) / j_\ell(\kappa R_s), \tag{252}$$

$$\rho(\underline{g}) = |\underline{k}+\underline{g}|^2 - \kappa^2 . \tag{253}$$

Condition (251) can be satisfied for all values of L if

$$\sum_{\underline{g}'} \alpha_{\underline{k}+\underline{g}'} \left\{ \sum_{L'} -\frac{\tan\eta'_{\ell'}}{\kappa} F_{L'\underline{g}} F_{L'\underline{g}'} + \rho(\underline{g})\,\delta_{\underline{g}\underline{g}'} \right\} = 0 \tag{254}$$

and using the addition formula

$$\sum_{m=-\ell}^{\ell} \mathcal{Y}_L(\underline{k}+\underline{g})\,\mathcal{Y}_L(\underline{k}+\underline{g}') = P_\ell(\cos\theta_{\underline{g}\underline{g}'}) \tag{255}$$

we can make the identification

$$\left\{ \Gamma_{\underline{g}\underline{g}'} \right\}_{R=R'=R_s} = \sum_{L'} -\frac{\tan\eta'_{\ell'}}{\kappa} F_{L'\underline{g}} F_{L'\underline{g}'} . \tag{256}$$

The matrix $\Gamma_{\underline{g}\underline{g}'}$ can be called an "effective matrix element" for the following reason. Suppose we use the expansion (247) in plane wave to represent the Bloch function in all regions of space, i.e.

$$\psi_{\underline{k}}(\underline{\rho}) = \sum_{\underline{g}} \gamma_{\underline{k}+\underline{g}}\, e^{i(\underline{k}+\underline{g})\cdot\underline{\rho}} \tag{257}$$

then the coefficients $\gamma_{\underline{k}+\underline{g}}$ satisfy the equation

$$\sum_{\underline{g}'} \gamma_{\underline{k}+\underline{g}'} \left\{ V_{\underline{g}\underline{g}'} + \rho(\underline{g})\,\delta_{\underline{g}\underline{g}'} \right\} = 0 \tag{258}$$

where

$$V_{\underline{g}\underline{g}'} = N \int u(\rho)\, e^{i(\underline{g}-\underline{g}')\cdot\underline{\rho}}\, d\underline{\rho} , \tag{259}$$

$u(\rho)$ being a single spherical potential. This method of calculating band structures is hopeless in practice because so many of the $\gamma_{\underline{k}+\underline{g}}$ are needed to represent the wave function. The potential wells are so deep that the wave function oscillates rapidly near the centre of them. In contrast we expect that only a few of the $\alpha_{\underline{k}+\underline{g}}$ are needed in equation (254) i.e. $\Gamma_{\underline{g}\,\underline{g}'}$ seems to be something like the matrix element of a weak potential. This is borne out by considering a situation where $\kappa^2 \simeq |\underline{k}|^2$ and the coefficient $\alpha_{\underline{k}}$ is assumed to be large compared with the other coefficients (Ziman 1965) then

$$\kappa^2 \simeq |\underline{k}|^2 + \Gamma_{00} \tag{260}$$

where

$$\Gamma_{00} \simeq -\frac{4\pi N}{\kappa} \sum_{l} (2l+1) \tan \eta'_{l} \ . \tag{261}$$

The significance of this result is found by examining the exact transition probability for scattering of a plane wave with wave vector $\underline{k}$ to a state $\underline{k}'$, due to a single spherical potential. The standard result of phase shift analysis is

$$P_{\underline{k}}^{\underline{k}'} = \frac{2\pi}{\hbar}\, \delta\left(|\underline{k}|^2 - |\underline{k}'|^2\right) \left| -\frac{4\pi}{\kappa} \sum_{l} (2l+1) \sin \eta_l \, e^{i\eta_l} \, P_l(\cos \theta_{\underline{k}k'}) \right|^2 \tag{262}$$

and the quantity inside the modulus sign can be thought of an as effective matrix element of the potential for the scattering problem. It is properly called the T matrix element and will be denoted by $T_{\underline{k}\underline{k}'}$ In the limit when $\sin\eta_\ell$ is small (i.e. weak scattering) we have

$$\Gamma_{00} \simeq N\, T_{\underline{k}\underline{k}} \; . \tag{263}$$

This connection with scattering theory is important because it directs attention to the primary role played by the phase shifts in determining the band structure.

The more general form for the $\Gamma_{\underline{g}\underline{g}'}$ in (237) does not seem to be readily interpretable but the arbitrariness in the choice of R and R' is not of great moment. It is a general feature of the effective or pseudo matrix element argument that many different choices can be made which will give the correct eigen values of the Schroedinger equation (e.g. Lloyd 1965). Another example of this arbitrariness is that

$$\left\{\cot\eta_\ell - \frac{n_\ell(\kappa R_s)}{j_\ell(\kappa R_s)}\right\}^{-1} \frac{j_\ell(|\underline{k}+\underline{g}|R_s)\; j_\ell(|\underline{k}+\underline{g}'|R_s)}{j_\ell^2(\kappa R_s)} \tag{264}$$

occurring in $\Gamma_{\underline{g}\underline{g}'}$ can be replaced by

$$\left\{\cot\eta_\ell - \frac{n_\ell'(\kappa R_s)}{j_\ell'(\kappa R_s)}\right\}^{-1} \frac{j_\ell'(|\underline{k}+\underline{g}|R_s)\; j_\ell'(|\underline{k}+\underline{g}'|R_s)}{j_\ell'^2(\kappa R_s)} \tag{265}$$

whenever it is convenient to do so to avoid singularities.

This may easily be shown using (245) and the comments below equation (249). This singular kind of behaviour should not be serious in practice however since the equations (254) are closely related to those for another method of band calculation, namely the "augmented plane wave method" (Slater 1937, 1965) which has been used successfully many times.

The basis of the A.P.W. method is to expand a Bloch wave within a single unit cell in the form

$$\psi_{\underline{k}}(\underline{\rho}) = \sum_{\underline{g}} \alpha_{\underline{k}+\underline{g}} \, \phi_{\underline{k}+\underline{g}}(\underline{\rho}) \tag{266}$$

where the A.P.W's, $\phi_{\underline{k}+\underline{g}}(\underline{\rho})$ are defined by

$$\phi_{\underline{k}+\underline{g}}(\underline{\rho}) = H(\rho - R_s)\, e^{i(\underline{k}+\underline{g})\cdot\underline{\rho}} + H(R_s - \rho) \sum_{L} \frac{i^{l}\,\beta_{L\underline{g}}}{[\mathcal{R}_l, j_l]} \mathcal{R}_l(\rho)\, \mathcal{Y}_L(\underline{\rho}) \; ; \tag{267}$$

$H(x)$ being Heaviside's unit function and the $\beta_{L\underline{g}}$ are defined by equation (249). The A.P.W's are continuous but have a discontinuous derivative at $\rho = R_s$. The conventional equation for the $\alpha_{\underline{k}+\underline{g}}$ is obtained by substituting from (266) into the variational formula which gives the energy of a Bloch state namely

$$\delta[E] = \delta\left[\frac{\int \psi^{*}(\underline{r})\, H \;\; \psi(\underline{r})\, d\underline{r}}{\int \psi^{*}(\underline{r})\, \psi(\underline{r})\, d\underline{r}}\right] . \tag{268}$$

By this means the form

$$\sum_{\underline{g}'} \alpha_{\underline{k}+\underline{g}'} \left\{ \Gamma'_{\underline{g}\underline{g}'} + \rho(\underline{g})\,\delta_{\underline{g}\underline{g}'} \right\} = 0 \tag{269}$$

is obtained where

$$\Gamma'_{\underline{g}\underline{g}'} = 4\pi R_s^2 N \Big[- \frac{\left\{ (\underline{k}+\underline{g})\cdot(\underline{k}+\underline{g}') - \kappa^2 \right\} j_1(|\underline{g}-\underline{g}'|R_s)}{|\underline{g}-\underline{g}'|} + \sum_{\ell} (2\ell+1) \frac{\mathcal{R}'_\ell(R_s)\, j_\ell(|\underline{k}+\underline{g}|R_s)\, j_\ell(|\underline{k}+\underline{g}'|R_s)\, P_\ell(\cos\theta_{\underline{g}\underline{g}'})}{\mathcal{R}_\ell(R_s)} . \tag{270}$$

This form of the effective matrix element can be compared with (256) by using the relation

$$\frac{\mathcal{R}'_\ell(R_s)}{\mathcal{R}_\ell(R_s)} = \frac{j'_\ell(\kappa R_s)}{j_\ell(\kappa R_s)} - \frac{\tan\eta'_\ell}{\kappa R_s^2\, j_\ell^2(\kappa R_s)} \tag{271}$$

which is just the definition of $\tan\eta'_\ell$. It is found that

$$\Gamma'_{\underline{g}\underline{g}'} = \Gamma_{\underline{g}\underline{g}'} + \Gamma^0_{\underline{g}\underline{g}'} \tag{272}$$

where $\Gamma^0_{\underline{g}\underline{g}'}$ is the value of $\Gamma'_{\underline{g}\underline{g}'}$ for an empty lattice, namely when $\mathcal{R}_\ell(\rho) = j_\ell(\kappa\rho)$. In general $\Gamma^0_{\underline{g}\underline{g}'}$ is not zero for an empty lattice which is to be contrasted with the behaviour of $\Gamma_{\underline{g}\underline{g}'}$ which vanishes for all values of κ and $\underline{k}$ when the potential wells are absent.

The A.P.W. method and the reciprocal lattice representation of the Greenian equations have been compared by Johnson (1966) who is of the opinion that there is little to choose between the methods as regards efficiency in calculating energy bands using a computer. The simple form of $\Gamma_{\underline{g}\underline{g}'}$ is definitely an aid to thinking about how electron bands are formed, for example Ziman has given a discussion on the origin of d-bands (1965) in a qualitative way.

To conclude this chapter we consider the scattering of a Bloch wave from an "impurity" potential. The model used is highly simplified. Although a lattice of identical atoms may be represented very well by a muffin tin potential the introduction of an impurity spoils the picture unless it has the same valency as the host atoms.

In addition, the lattice around the impurity will usually be strained but we set all these points aside and consider a system of spherical potentials of radius R_s where the potentials are located at lattice sites. It would not be too difficult to calculate the errors introduced by the muffin tin approximation by standard perturbation methods, but the purpose here is to show that in the simplified case the transition probability for scattering of a Bloch wave is similar in form to $\Gamma_{\underline{g}\underline{g}'}$.

If $\Delta\mathcal{U}(\rho)$ denotes the difference between an impurity potential and a perfect lattice potential then the transition probability from a Bloch state $\psi_{\underline{k}}(\rho)$ to a state $\psi_{\underline{k}'}(\rho)$ may be written as

$$P_{\underline{k}}^{\underline{k}'} = \frac{2\pi}{\hbar} \left| T_{\underline{k}\underline{k}'} \right|^2 \delta\left(E(\underline{k}) - E(\underline{k}')\right) \tag{273}$$

where $T_{\underline{k}\underline{k}'}$ is the T-matrix defined by

$$T_{\underline{k}\underline{k}'} = \int \psi_{\underline{k}'}^{*}(\underline{\rho})\,\Delta\mathcal{U}(\underline{\rho})\,\psi(\underline{\rho})\,d\underline{\rho} \quad , \tag{274}$$

The energy $E(\underline{k}')$ of the state $\underline{k}'$ is the same as the initial state $\underline{k}$ and $\psi(\underline{\rho})$ is the solution to the time independent Schroedinger equation describing the scattering of the wave $\psi_{\underline{k}}(\underline{\rho})$. It has been assumed that the impurity potential has the same radius as the host potentials so that the integration in (274) is over a sphere with radius R_s centred on a perfect lattice site.

$T_{\underline{k}\underline{k}'}$ can be expressed as an integral over the surface of the sphere using the equations satisfied by $\psi_{\underline{k}'}(\underline{\rho})$ and $\psi(\underline{\rho})$

$$T_{\underline{k}\underline{k}'} = R_s^2 \int \left\{ \psi_{\underline{k}'}^{*}(\underline{\rho}) \frac{\partial}{\partial\rho} \psi(\underline{\rho}) - \psi(\underline{\rho}) \frac{\partial}{\partial\rho} \psi_{\underline{k}'}^{*}(\underline{\rho}) \right\}_{\rho = R_s} d\Omega(\underline{\rho}) \; . \tag{275}$$

The T-matrix will be expressed in terms of the Fourier coefficients of the Bloch waves in between the potential wells namely

$$T_{\underline{k}\underline{k}'} = \sum_{\underline{g}} \sum_{\underline{g}'} \alpha_{\underline{k}+\underline{g}}^{*} \; \alpha_{\underline{k}+\underline{g}} \; V_{eff}(\underline{k}+\underline{g}, \underline{k}'+\underline{g}') \tag{276}$$

and $V_{eff}(\underline{k}+\underline{g}, \underline{k}'+\underline{g}')$ will be termed an effective matrix element.

On the surface of and just outside the perturbation $\Delta\mathcal{U}(\underline{\rho})$ the function $\psi_{\underline{k}}(\underline{\rho})$ may be expanded as

$$\psi_{\underline{k}}(\underline{\rho}) = \sum_{L} i^{l} a_{L}(\underline{k}) \{ j_{l}(\kappa\rho) + i \sin\eta_{l} e^{i\eta_{l}} h_{l}(\kappa\rho) \} \mathcal{Y}_{L}(\underline{\rho}) \tag{277}$$

where the coefficients $a_L(\underline{k})$ are presumed known from the solution of the Greenian equations for a perfect lattice. They can easily be obtained from the β_L which occur in equation (234). Inside the perturbation the wave function $\psi(\underline{\rho})$ will be of the general form

$$\psi(\underline{\rho}) = \sum_{L} i^{l} C_{L}(\underline{k}) \mathcal{R}^{i}_{l}(\rho) \mathcal{Y}_{L}(\underline{\rho}) \tag{278}$$

where $\mathcal{R}^{i}_{l}(\rho)$ is a solution of the radial Schroedinger equation for the impurity potential and the $C_L(\underline{k})$ are to be determined.

The picture of wave function $\psi(\underline{\rho})$ is that it is composed of an "incident" wave $\psi_{\underline{k}}(\underline{\rho})$ which is scattered by the impurity. The scattered wave can be broken down into two parts: outgoing spherical waves diverging from the impurity just as in the scattering of a plane wave from a single potential, and secondary waves produced by the initial outgoing waves being scattered by the surrounding lattice. Thus just outside $\Delta\mathcal{U}(\underline{\rho})$ the scattered wave can be written as

$$\psi_{s}(\underline{\rho}) = \sum_{L} i^{l} \{ b_{L}(\underline{k}) h_{l}(\kappa\rho) + \sum_{L'} T_{LL'} b_{L'}(\underline{k}) j_{l}(\kappa\rho) \} \mathcal{Y}_{L}(\underline{\rho}). \tag{279}$$

The significance of the matrix $T_{LL'}$ is that an outgoing wave $b_{L'}(\underline{k})\, h_{\ell'}(\kappa\rho)\, \mathcal{Y}_{L'}(\underline{\rho})$ diverging from the impurity is scattered by the surrounding lattice causing a wave $T_{LL'}\, b_{L'}(\underline{k})\, j_{\ell}(\kappa\rho)\, \mathcal{Y}_{L}(\underline{\rho})$ back on the surface of the impurity. The impurity potential is not itself counted as a scattering centre in calculating $T_{LL'}$.

The requirement that the wave function and its radial derivative must be continuous on the surface of the impurity potential means that

$$\left\{ \Psi_{\underline{k}}(\underline{\rho}) + \Psi_{s}(\underline{\rho}) \right\}_{\rho=R_s} = \left\{ \Psi(\underline{\rho}) \right\}_{\rho=R_s} , \qquad (280)$$

$$\left\{ \frac{\partial}{\partial\rho} \Psi_{\underline{k}}(\underline{\rho}) + \frac{\partial}{\partial\rho} \Psi_{s}(\underline{\rho}) \right\}_{\rho=R_s} = \left\{ \frac{\partial}{\partial\rho} \Psi(\underline{\rho}) \right\}_{\rho=R_s} .$$

On substitution from equations (277), (278) and (279) it is found that the coefficients $b_L(\underline{k})$ satisfy the equation

$$b_L - i\sin\eta^i_\ell\, e^{i\eta^i_\ell} \sum_{L'} T_{LL'}\, b_{L'} = a_L \left\{ i\sin\eta^i_\ell\, e^{i\eta^i_\ell} - i\sin\eta_\ell\, e^{i\eta_\ell} \right\} \qquad (281)$$

where η^i_ℓ is the ℓ'th phase shift for the impurity potential. The coefficients C_L are defined in terms of the b_L by

$$C_L = \frac{i\, a_L \left\{ 1 + \sum_{L} T_{LL'}\, b_{L'}/a_L \right\}}{\kappa\, R_s^2 \left[R^i_\ell , h_\ell \right]} , \qquad (282)$$

The T-matrix may now be written as

$$T_{\underline{k}\underline{k}'} = k^{-1} \sum_{L} a^{*}_{L}(\underline{k}')\, a_{L}(\underline{k})\, e^{i2\eta^{i}_{\ell}} \left\{ 1 + \sum_{L'} T_{LL'} b_{L'} / a_{L}(\underline{k}) \right\} \times \left\{ \sin\eta_{\ell}\, e^{-i\eta_{\ell}} - \sin\eta^{i}_{\ell}\, e^{-i\eta^{i}_{\ell}} \right\} \tag{283}$$

by substituting from (277) and (278) into equation (275). If the product $a^{*}_{L}(\underline{k}')\, a_{L}(\underline{k})$ is expressed in terms of the Fourier coefficients of $\psi^{*}_{\underline{k}'}(\rho)$ and $\psi_{\underline{k}}(\rho)$ as shown in equation (248), then

$$V_{eff.}(\underline{k}+\underline{g}, \underline{k}'+\underline{g}') =$$

$$\frac{(4\pi)^2}{k} \sum_{L} \frac{\tan^2\eta'_{\ell}}{\sin^2\eta_{\ell}} e^{2i\eta^{i}_{\ell}} \left\{ \sin\eta_{\ell}\, e^{-i\eta_{\ell}} - \sin\eta^{i}_{\ell}\, e^{-i\eta^{i}_{\ell}} \right\} \times \left\{ 1 + \sum_{L'} T_{LL'} b_{L'} / a_{L}(\underline{k}) \right\} \frac{\mathcal{Y}_{L}(\underline{k}+\underline{g})\, \mathcal{Y}_{L}(\underline{k}'+\underline{g}')\, j_{\ell}(|\underline{k}+\underline{g}|R_s)\, j_{\ell}(|\underline{k}'+\underline{g}'|R_s)}{j^{2}_{\ell}(k R_s)} \tag{284}$$

which however still contains the unknown coefficients b_L, so this is just a formal expression.

It is useful to compare the procedure given here with another approach to the same problem given by Dupree (1961) and applied to the residual resistance produced by alkali metal impurities in other alkali metals. Dupree's formulation required the knowledge of the Green function for a perfect lattice which is analogous to the matrix $T_{LL'}$ which occurs in equation (281). They are both difficult quantities to calculate but it is felt that it is rather easier to envisage simple approximations to $T_{LL'}$ rather than the Green function. Both methods however require the solution of equations like (281) which can become quite involved if it is necessary to use a large number of L's to obtain an accurate solution.

Fortunately in the case of simple metals where the conduction electrons behave as if the potentials are weak, a reasonable answer can be obtained straight away. A free electron wave travelling through a perfect metal, with an energy lying in the conduction band, can be scattered very little by a single potential well if the $\sin \eta_l$ are small and strong reflection occurs only when the electron is Bragg reflected. The same type of behaviour is to be expected for a spherical wave spreading out from a lattice point. If the reflected waves are ignored, i.e. if $T_{LL'}$ is put equal to zero it is found from (284) that

$$V_{eff}(\underline{k}+\underline{g}, \underline{k}'+\underline{g}') \simeq$$

$$\frac{4\pi}{\kappa} \sum_l (2l+1) \frac{\tan^2 \eta'_l}{\sin^2 \eta_l} e^{2i\eta^i_l} \left\{ \sin \eta_l e^{-i\eta_l} - \sin \eta^i_l e^{-i\eta^i_l} \right\}$$

$$\times \frac{j_l(|\underline{k}+\underline{g}|R_s)\, j_l(|\underline{k}'+\underline{g}'|R_s)}{j_l^2(\kappa R_s)} P_l(\cos \theta_{\underline{k}+\underline{g},\underline{k}'+\underline{g}'}) \tag{285}$$

where $\theta_{\underline{k}+\underline{g},\underline{k}'+\underline{g}'}$ is the angle between $\underline{k}+\underline{g}$ and $\underline{k}'+\underline{g}'$. The above approximation is especially good when the outgoing waves are weak, because in (284) the product $T_{LL'}b_{L'}$ is small. This result is clearly very similar in form to the expression (238) for $\Gamma_{\underline{g}\underline{g}'}$.

It is interesting to compare (285) with the effective matrix element suggested by Ziman (1964) in the situation when the plane wave amplitude $\alpha_{\underline{k}}$ is much larger than all the others. Ziman's conjectured matrix element was (albeit for the much more general case of overlapping potentials)

$$V_{eff.}(\underline{k},\underline{k}')$$

$$\simeq \frac{4\pi}{\kappa}\sum_{\ell}(2\ell+1)\left\{\sin\eta_\ell e^{i\eta_\ell}-\sin\eta_\ell^i e^{i\eta_\ell^i}\right\}P_\ell(\cos\theta_{\underline{k},\underline{k}'}) \tag{286}$$

and (285) reduces to this when $\sin\eta_\ell$ and $\sin\eta_\ell^i$ are small and $\kappa^2\simeq|\underline{k}|^2$.

It is tantalising to know that there must be much more general results than (285), which however should be of similar form, applying to the case of overlapping potential wells. In addition a general method is needed for calculating the transport properties of structurally disordered solids, which goes beyond the nearly free electron approach, and it is possible that this may be achieved by working along the lines described for vibrating solids.

Appendix A. Continuum elasticity theory.

The Lame constants λ and μ which specify an isotropic elastic continuum cannot take just any values but are subject to restrictions obtained from the requirement that there should be a positive change in the potential energy of a solid when it is deformed from the equilibrium state. This leads to the conditions (Landau and Lifshitz, p. 11)

$$\mu \geqslant 0 , \qquad K = \lambda + \tfrac{2}{3}\mu \geqslant 0 \tag{A1}$$

where K is the modulus of compression. In addition the fact that Young's modulus E and Poisson's ratio σ are always positive means that (Sokolnikoff p.69) we must have

$$\mu \geqslant 0 , \qquad \lambda \geqslant 0 . \tag{A2}$$

These conditions are violated by taking $\lambda = -\mu$ as has been done for the loaded continuum model. This unphysical choice of the elastic constants will not lead to misleading results for the simple arguments of this thesis and has many precedents in simplified descriptions of the properties of vibrating lattices.

The full elastic wave equation for an isotropic medium of uniform elasticity and density is

$$\mu \nabla^2 \underline{U}(\underline{\rho}) + (\lambda-\mu)\,\mathrm{grad.div.}\,\underline{U}(\underline{\rho}) + \rho\,\omega^2\, \underline{U}(\underline{\rho}) = 0 \quad , \qquad (A3)$$

The special choice $\lambda=-\mu\ (\mu\geqslant 0)$ reduces this complicated vector equation to

$$\mu \nabla^2 \underline{U}(\underline{\rho}) + \rho\,\omega^2\, \underline{U}(\underline{\rho}) = 0 \qquad (A4)$$

which is equivalent to three independent scalar equations for the components of the displacement field $\underline{U}(\underline{\rho})$. The solutions of this equation for an infinite medium may be expressed as transverse and longitudinal running waves which have equal velocities $\sqrt{\frac{\mu}{\rho}}$. The unphysical nature of the elastic constants is unimportant if we wish to obtain an outline of the way in which elastic waves are scattered by variations in density and elasticity. The trouble occurs when we consider, say, the response to an isotropic pressure.

An apparent contradiction of the conditions (A2) is found by considering a lattice model which is often used as an introduction to the way vibrating solids behave, (e.g. Maradudin, Montroll and Weiss 1963, Montroll 1956). The model consists of a monatomic simple cubic lattice (a structure which does not occur in nature) where the harmonic potential energy is assumed to be

$$
\begin{aligned}
\frac{1}{2}\sum_{\ell}\sum_{m}\sum_{n}\Big(g\Big[&\{U_x(\ell,m,n) - U_x(\ell+1,m,n)\}^2 + \{U_x(\ell,m,n) - U_x(\ell-1,m,n)\}^2 \\
&+ \{U_y(\ell,m,n) - U_y(\ell,m+1,n)\}^2 + \{U_y(\ell,m,n) - U_y(\ell,m-1,n)\}^2 \\
&+ \{U_z(\ell,m,n) - U_z(\ell,m,n+1)\}^2 + \{U_z(\ell,m,n) - U_z(\ell,m,n-1)\}^2 \Big] \\
+ h\Big[&\{U_x(\ell,m,n) - U_x(\ell,m+1,n)\}^2 + \{U_x(\ell,m,n) - U_x(\ell,m-1,n)\}^2 \\
&+ \{U_x(\ell,m,n) - U_x(\ell,m,n+1)\}^2 + \{U_x(\ell,m,n) - U_x(\ell,m,n-1)\}^2 \\
&+ \{U_y(\ell,m,n) - U_y(\ell+1,m,n)\}^2 + \{U_y(\ell,m,n) - U_y(\ell-1,m,n)\}^2 \\
&+ \{U_y(\ell,m,n) - U_y(\ell,m,n+1)\}^2 + \{U_y(\ell,m,n) - U_y(\ell,m,n-1)\}^2 \\
&+ \{U_z(\ell,m,n) - U_z(\ell+1,m,n)\}^2 + \{U_z(\ell,m,n) - U_z(\ell-1,m,n)\}^2 \\
&+ \{U_z(\ell,m,n) - U_z(\ell,m+1,n)\}^2 + \{U_z(\ell,m,n) - U_z(\ell,m-1,n)\}^2 \Big).
\end{aligned}
\tag{A5}
$$

U_x.U_y and U_z denote the cartesian components of the displacement of the atom at

$$l a\hat{x} + m a\hat{y} + n a\hat{z} \tag{A6}$$

where a is the lattice spacing and l, m and n are integers. The attractiveness of this form is that the equation of motion again separates into three scalar ones, for example for the x-component of the displacement we have

$$\begin{aligned} & g\left\{u_x(l+1,m,n) + u_x(l-1,m,n) - 2\,u_x(l,m\,n)\right\} \\ & + h\left\{u_x(l,m+1,n) + u_x(l,m-1,n) - 2\,u_x(l,m,n)\right. \\ & \left. + u_x(l,m,n+1) + u_x(l,m,n-1) - 2\,u_x(l,m,n)\right\} \\ & + M\omega^2 u_x(l,m,n) = 0 \end{aligned} \tag{A7}$$

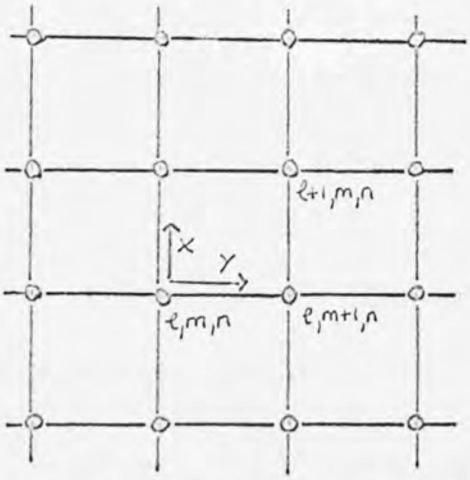
where M is the mass of the atoms.

When the wavelength of a disturbance passing through the solid is large compared with a this difference equation can be replaced by the differential equation

$$\frac{g}{a}\,\frac{d^2}{dx^2}u_x(\underline{r}) + \frac{h}{a}\left\{\frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right\}u_x(\underline{r}) + \rho\,\omega^2 u_x(\underline{r}) = 0 \tag{A8}$$

If we now set $g = h$ then (A7) is equivalent to (A4) if the identification $\frac{g}{a} = \mu$ is made. The paradox is that the change in potential energy on deformation of the lattice is positive definite if g is positive.

The flaw in the argument is that the form (A5) is not invariant with respect to rotations of the solid (Lax, 1963) and is therefore unacceptable as a realistic description of atomic interactions. The unrealistic part of the potential is that part multiplied by the "non-central" force constant h. Let us consider a covalently bound solid as depicted in Figure 8



(A9)

Figure 8

where the bonds are represented by the lines joining nearest neighbours. The potential energy (A5) means that when the atom $(\ell, m+1, n)$ is displaced in the X direction the force exerted on the atom (ℓ, m, n) is in the same direction irrespective of the positions of any other atoms. In reality the non-central forces between the atoms in covalent solids arise from bending of the angles between the bonds and therefore involves the displacements of other atoms. These points were realised long ago by Born (1914) when constructing a model for diamond.

However, it often happens that in working out the modes of vibration of a lattice an "incorrect" potential can give the same results as a "correct" potential which is rotationally invariant. (De Launey 1956). This is due to the high degree of symmetry present in a lattice. In a disordered system it is rather more dangerous to use a potential like (A5) but providing the results are not taken too seriously it remains a useful means of testing ideas about the disorder problem.

In 1.2.2. the force acting on a rigid sphere was calculated using the formula (Morse and Feshbach, p. 1808) for the stress dyadic

$$S = \mu\left(\nabla \underline{U}(\underline{r}) + \underline{U}(\underline{r})\nabla\right) - \mu \,\mathrm{div}\, U(\underline{r})\, I \qquad \text{(A10)}$$

where λ has been set equal to $-\mu$ and I denotes the unit dyadic. The corresponding form for the model described by (A5) is

$$S = \frac{g}{a}\, \underline{U}(\underline{r})\, \nabla \qquad \text{(A11)}$$

where g has been set equal to h and the long wavelength limit has been taken.

These two forms for the stress dyadic both give the same value of the γ_ℓ defined by equation (11) so that if desired the material filling the spaces between the rigid spheres in the loaded continuum model can be looked on as being an elastic continuum whose microscopic properties are defined by (A5).

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PROC. PHYS. SOC., 1967, VOL. 91. PRINTED IN GREAT BRITAIN

Wave propagation through an assembly of spheres
V. The vibrations of a loaded elastic continuum

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MS. received 7th February 1967, *in revised form* 22nd *March* 1967

Abstract. The properties of a 'loaded continuum'—an assembly of rigid spheres embedded in an elastic medium of zero density—are investigated. When the spheres are arranged in a perfect lattice the model shows the characteristic dynamical properties of a harmonic solid. Some of the qualitative effects of structural disorder have been investigated by means of this model.

1. Introduction

The system to be studied in this paper consists of rigid spheres of mass M and radius R_s embedded in an elastic medium of zero density. This model is not intended as a substitute for the usual 'spring' model of a solid, nor is it necessarily a realistic description of the restoring forces acting on atoms in a real solid. The merit of the model is that it provides a simple and convenient way of investigating the general properties of a system of masses bound by harmonic forces. The model is described by the elastic wave equation for which modern methods of treating the propagation of waves in ordered and disordered systems can be used.

The prime motivation for this work was the fact that at the present time a theory of wave propagation and thermal conductivity in disordered solids hardly exists, except when a solid can be described as a perturbation of a perfect lattice or when continuum theory can be used. Vitreous, polycrystalline and dislocated solids cannot be described as perturbed lattices except by rather artificial means (i.e. introducing atoms of zero mass), and it was hoped that the loaded continuum would provide a guide to the effects of these kinds of structural disorder. The origin of the difficulty is the impossibility of using perfect lattice states as a basis for the representation of dynamical excitations. In the problem of electrons in liquid metals one may fall back from a representation in perfect lattice states (i.e. Bloch functions) to a description in terms of free-electron plane waves. There is no natural analogue of free-electron waves for disordered solids.

Recent developments in the theory of electrons in disordered systems (e.g. Edwards 1965, Waterman and Truell 1961) appear to by-pass the introduction of a set of basic states and the construction of a transport equation. In particular, the averaging methods introduced by Foldy (1945) and reviewed recently by Ziman (1966) offer new possibilities for investigating the loaded continuum. These methods involve looking for a complex propagation constant for waves in a disordered medium. For example, the imaginary part of the propagation constant, in the case of electrons in liquid metals, is related to the electrical resistivity (Edwards 1965).

In this paper this approach is used to treat a disordered loaded continuum. It turns out, however, that within the approximations of the method the propagation constant is purely real and the thermal resistivity of the system apparently zero, which of course is nonsense. The application of averaging methods to a conventional spring model of a solid similarly fails to produce a complex propagation constant and the reasons for this are discussed.

This paper is basically an account of the theory of a loaded continuum in its own right. The insight gained from this investigation has helped in constructing a new approach to the thermal conductivity of disordered solids which will be given in a later publication.

2. The loaded continuum

Our view is that the mechanical properties of a harmonic solid ought to be similar to those of a system of rigid spheres, embedded in an elastic medium of zero density, and that

The γ_l can be obtained from the boundary conditions on the surface of the rigid spheres. This information is contained in the equation of motion for the jth sphere:

$$-M\omega^2\mathbf{U}_j(\mathbf{S}) = \int \mu\{\nabla\mathbf{U}_j(\mathbf{S})+\mathbf{U}_j(\mathbf{S})\nabla - \operatorname{div}\mathbf{U}_j(\mathbf{S})\} \,.\, d\mathbf{S} \tag{6}$$

where $\mathbf{S}$ lies on the surface of the sphere, M is the mass of a sphere, ω is the vibrational frequency and the right-hand side of (6) is simply the total force due to the stress field round the sphere (Morse and Feshbach 1953, p. 1808). Substitution of (5) into (6) gives

$$\begin{aligned} \gamma_0 &= \frac{4\pi\mu}{M\omega^2} - \frac{1}{R_s} \\ \gamma_l &= -\frac{1}{R_s^{\,2l+1}} \qquad (l > 0). \end{aligned} \tag{7}$$

The main problem is to obtain an expansion of $\mathrm{G}(\boldsymbol{\rho}-\boldsymbol{\rho}'-\mathbf{r}_{j'j})$ in spherical harmonic functions of $\boldsymbol{\rho}$ and $\boldsymbol{\rho}'$. When $|\mathbf{r}_{j'j}| = 0$ and $\rho' > \rho$, then

$$\mathrm{G}(\boldsymbol{\rho}-\boldsymbol{\rho}') = -\sum_L \frac{1}{2l+1}\rho^l\rho'^{-l-1}\mathscr{Y}_L(\boldsymbol{\rho})\mathscr{Y}_L(\boldsymbol{\rho}') \tag{8}$$

and when $|\mathbf{R}| = |\boldsymbol{\rho}-\boldsymbol{\rho}'|$ is less than $|\mathbf{r}_{j'j}|$

$$\mathrm{G}(\mathbf{R}-\mathbf{r}_{j'j}) = -\sum_L \frac{1}{2l+1} R^l r_{j'j}^{-l-1}\mathscr{Y}_L(\mathbf{R})\mathscr{Y}_L(\mathbf{r}_{j'j}). \tag{9}$$

The function $R^l\mathscr{Y}_L(\mathbf{R})$ can be obtained in terms of $\mathscr{Y}_L(\boldsymbol{\rho})$ and $\mathscr{Y}_L(\boldsymbol{\rho}')$ by using the expansion of $\mathrm{j}_l(\eta R)\mathscr{Y}_L(\mathbf{R})$ given by Kohn and Rostoker (1954), in the limit as η tends to zero. By this means the following form is obtained:

$$R^l\mathscr{Y}_L(\mathbf{R}) = 4\pi\sum_{L'}\sum_{L''}\frac{i^{l'-l-l''}\delta_{l'+l'',l}(2l+1)!!C^L_{L'L''}\rho^{l'}\rho^{l''}\mathscr{Y}_{L'}(\boldsymbol{\rho})\mathscr{Y}_{L''}(\boldsymbol{\rho}')}{(2l'+1)!!(2l''+1)!!} \tag{10}$$

where

$$C^L_{L'L''} = \int \mathscr{Y}_L(\boldsymbol{\rho})\mathscr{Y}_{L'}(\boldsymbol{\rho})\mathscr{Y}_{L''}(\boldsymbol{\rho})\, d\Omega(\boldsymbol{\rho}). \tag{11}$$

$\mathrm{G}(\mathbf{R}-\mathbf{r}_{j'j})$ can now be expanded as

$$\begin{aligned} \mathrm{G}(\mathbf{R}-\mathbf{r}_{j'j}) = {} & -\delta_{jj'}\sum_L\frac{1}{2l+1}\rho^l\rho'^{-l-1}\mathscr{Y}_L(\boldsymbol{\rho})\mathscr{Y}_L(\boldsymbol{\rho}') \\ & -(1-\delta_{jj'})\sum_{L'}\sum_{L''}B_{L'L''}(\mathbf{r}_{jj'})\rho^{l'}\rho'^{l''}\mathscr{Y}_{L'}(\boldsymbol{\rho})\mathscr{Y}_{L''}(\boldsymbol{\rho}') \end{aligned} \tag{12}$$

where

$$B_{L'L''}(\mathbf{r}_{jj'}) = 4\pi\sum_L\frac{i^{l'-l''-l}\delta_{l'+l'',l}(2l+1)!!C^L_{L'L''}\mathscr{Y}_L(\mathbf{r}_{j'j})}{(2l+1)(2l'+1)!!(2l''+1)!!r_{j'j}^{l+1}}. \tag{13}$$

Substitution of the expansion for $U_j(\boldsymbol{\rho})$ and (12) into the matching condition (4) gives the equation satisfied by the $\beta_L{}^j$:

$$(2l+1)^{-1}\gamma_l\beta_L{}^j = \sum_{L'}\sum_{j'\neq j} B_{LL'}(\mathbf{r}_{jj'})\beta_{L'}{}^{j'}. \tag{14}$$

Equation (14) is very similar in form to the equations derived by Phariseau and Ziman (1963) for electrons in liquid metals. In their notation the wave function within the jth potential is of the general form

$$\psi_j(\boldsymbol{\rho}) = \sum_L \frac{i^l\beta_L{}^j}{[\mathscr{R}_l,\mathrm{j}_l]}\mathscr{R}_l(\rho)\mathscr{Y}_L(\boldsymbol{\rho}). \tag{15}$$

the qualitative effects of structural disorder can be investigated by means of this model. In some senses this model is akin to the continuum theory of lattice defects. For example, in the continuum theory the scattering of long-wave lattice vibrations from impurity atoms is held to be equivalent to the scattering of sound waves from a sphere whose density and elastic constants differ from the continuum in which it is embedded. However, the model is *not* supposed to simulate the actual forces between atoms in any real solid. It is a 'physical toy' (Ziman 1965 a) which is highly convenient for testing out methods and ideas about the properties of non-crystalline systems.

In view of the complicated vector algebra of the solutions of the elastic wave equation, the problem has again been simplified by assuming that the Lamé constants of the elastic medium μ and λ are related by $\lambda = -\mu$. This again lacks physical reality since in practice we must have $\lambda > -\frac{2}{3}\mu$ and $\mu > 0$ (Landau and Lifshitz 1959, p. 11), but the general features of the loaded continuum can be obtained by this means and that is sufficient for the present purpose. This simplification is equivalent to the common assumption that central and non-central forces are of equal strength in a conventional model of a solid.

The special choice $\lambda = -\mu$ allows the elastic wave equation to be separated into three scalar equations. If $U(r)$ denotes a Cartesian component of the ~~strain~~ displacement field, then

$$\nabla^2 U(\mathbf{r}) - V(\mathbf{r})U(\mathbf{r}) = 0 \tag{1}$$

where $V(\mathbf{r})$ is an operator symbolizing the departure of the system from a structureless elastic medium of zero density, i.e. in our case the presence of the spheres. Equation (1) differs from, say, the Schrödinger equation for an electron in a system of spherical non-overlapping potentials, where plane waves can propagate in between the potentials, whereas the elastic medium in between the spheres in our model will not propagate plane waves with a finite velocity. This difference has important consequences when we attempt to find a complex propagation constant for a disordered loaded continuum.

One of the most successful methods for solving the Schrödinger equation for a lattice of spherical potentials is that originally proposed by Korringa (1947) and by Kohn and Rostoker (1954). This method was generalized to arbitrary arrangements of potentials by Phariseau and Ziman (1963). An analogue to the generalized theory will be used here.

Equation (1) can be changed to the integral form

$$U(\mathbf{r}) = \int \mathrm{G}(\mathbf{r}-\mathbf{r}')V(\mathbf{r}')U(\mathbf{r}')\,d\mathbf{r}' \tag{2}$$

where $\mathrm{G}(\mathbf{r}-\mathbf{r}')$ is the Green function for the Laplace operator, i.e.

$$\mathrm{G}(\mathbf{r}-\mathbf{r}') = -\frac{1}{4\pi|\mathbf{r}-\mathbf{r}'|}. \tag{3}$$

Fortunately, it is not necessary to inquire into the precise form of the operator $V(\mathbf{r})$ because this problem can be reformulated in terms of the ~~strain~~ displacement field on the surface of the spheres. A convenient way to do this is by using the condition (Ziman 1965 b, 1966)

$$\sum_{j'} \int \left\{ \mathrm{G}(\boldsymbol{\rho}-\boldsymbol{\rho}'-\mathbf{r}_{j'j}) \frac{\partial}{\partial \rho'} U_{j'}(\boldsymbol{\rho}') - U_{j'}(\boldsymbol{\rho}') \frac{\partial}{\partial \rho'} \mathrm{G}(\boldsymbol{\rho}-\boldsymbol{\rho}'-\mathbf{r}_{j'j}) \right\}_{\rho' = R_s+\epsilon} d\Omega(\boldsymbol{\rho}') = 0 \tag{4}$$

where $\mathbf{r}_{j'j} = \mathbf{r}_{j'} - \mathbf{r}_j$, $\boldsymbol{\rho} = \mathbf{r} - \mathbf{r}_j$, $\boldsymbol{\rho}' = \mathbf{r}' - \mathbf{r}_{j'}$, ϵ is a positive infinitesimal,

$$R_{\mathrm{s}} < \rho < R_{\mathrm{s}} + \epsilon$$

R_{s} is the sphere radius and $U_j(\boldsymbol{\rho})$ is the ~~strain~~ displacement component around the jth sphere located at $\mathbf{r}_j$. The ~~strain~~ displacement component $U_j(\boldsymbol{\rho})$ can be expanded in terms of the spherical solutions of Laplace's equation:

$$U_j(\boldsymbol{\rho}) = \sum_L \frac{\beta_{l,m}{}^j}{2l+1} (\rho^{-l-1} + \gamma_l \rho^l) \mathscr{Y}_{l,m}(\boldsymbol{\rho}) \tag{5}$$

where L denotes collectively the angular label l and the azimuthal label m, $\mathscr{Y}_L(\boldsymbol{\rho})$ denotes a real normalized spherical harmonic (Segall and Ham 1961), and the coefficients $\beta_L{}^j$ are to be determined.

where

$$
\begin{aligned}
B_{00,00}(\mathbf{k}) &= 4\pi C^{00}_{00.00} \sum_{j' \neq j} \frac{\exp(-i\mathbf{k}\,.\,\mathbf{r}_{jj'})}{r_{j'j}} \mathscr{Y}_{00}(\mathbf{r}_{j'j}) \\
B_{10,00}(\mathbf{k}) &= -B_{00,10}(\mathbf{k}) = \frac{4\pi}{3} C^{10}_{10.00} \sum_{j' \neq j} \frac{\exp(-i\mathbf{k}\,.\,\mathbf{r}_{jj'})}{{r_{j'j}}^2} \mathscr{Y}_{10}(\mathbf{r}_{j'j}) \qquad (25) \\
B_{10,10}(\mathbf{k}) &= -\frac{4\pi}{3} C^{20}_{10.10} \sum_{j' \neq j} \frac{\exp(-i\mathbf{k}\,.\,\mathbf{r}_{jj'})}{{r_{j'j}}^3} \mathscr{Y}_{20}(\mathbf{r}_{j'j}).
\end{aligned}
$$

These structure constants have been estimated by replacing the sums by integrals, whence

$$B_{00,00}(\mathbf{k}) \simeq \frac{4\pi}{\Delta|\mathbf{k}|^2}, \qquad B_{10,00}(\mathbf{k}) = -B_{00,10}(\mathbf{k}) \simeq \frac{4\pi i}{3^{1/2}\Delta|\mathbf{k}|}, \qquad B_{10,10}(\mathbf{k}) \simeq \frac{8\pi}{9\Delta}. \qquad (26)$$

In the limit of small $|\mathbf{k}|$

$$\omega^2(\mathbf{k}) \simeq \frac{\mu}{D}\frac{1+2\nu/\Delta}{1-\nu/\Delta}|\mathbf{k}|^2 \qquad (27)$$

where ν is the volume of a sphere and D is the mean density. The model, therefore, behaves like a continuum with an effective elastic constant

$$\mu_{\text{eff}} = \mu\frac{1+2\nu/\Delta}{1-\nu/\Delta}. \qquad (28)$$

The value of ω at the band edge may also be obtained in a simple way. If the wave vector $\mathbf{k}$ is written as

$$\mathbf{k} = \frac{\pi}{a}(\hat{\mathbf{k}}_x + \hat{\mathbf{k}}_y + \hat{\mathbf{k}}_z) - \mathbf{k}' \qquad (29)$$

then

$$B_{LL'}(\mathbf{k}) \propto |\mathbf{k}'|^{l+l'}. \qquad (30)$$

This conclusion is arrived at splitting the summation in (19) into negative and positive parts using (29), and replacing the summations by integrals. Only the $l = 0$ harmonic need be retained to determine the band-edge frequency. The zero-order structure constant at the zone boundary is simply

$$B_{00,00} = -\frac{\zeta}{a} \simeq -\frac{1{\cdot}75}{a} \qquad (31)$$

where ζ is the Madelung constant for an Na–Cl type lattice. The band-edge frequency ω_L is therefore given by

$$\omega_L{}^2 = \frac{4\pi\mu R_s}{M}\left(1 - \frac{\zeta R_s}{a}\right)^{-1}. \qquad (32)$$

These limiting formulae for $\omega(\mathbf{k})$ indicate that the loaded continuum behaves like a lattice of point masses coupled by harmonic springs. For example, the ratio of ω_L to the frequency $\omega_L{}'$, which would be obtained using (27) without dispersion, is

$$\frac{\omega_L}{\omega_L{}'} = \left\{\frac{4R_s(1-\nu/\Delta)}{3\pi a(1+2\nu/\Delta)(1-\zeta R_s/a)}\right\}^{1/2}. \qquad (33)$$

The parameter R_s can be adjusted to give a value of this ratio typical of the values found for more conventional systems. It is interesting to consider the formulation of the perfect lattice problem in terms of a plane-wave representation. This is discussed in the appendix where some modifications of the corresponding procedure for electrons are also derived.

The coefficients $\beta_L{}^j$ then satisfy the equation

$$\kappa(1-\cot\eta_l)\beta_L{}^j = \sum_{L'}\sum_{j'\neq j} B_{LL'}(\kappa, \mathbf{r}_{jj'})\beta_{L'}{}^{j'}. \tag{16}$$

The similarity between (14) and (16) makes clearer the motive for studying the loaded continuum. There is, however, an important difference between these two equations. The loaded continuum equations are simpler because the frequency does not occur in the matrix on the right-hand side. This means that the frequencies can be found explicitly. In the electron case the energy $E = \kappa^2$ occurs in the matrix and the energy levels come out as the solution of an implicit equation.

3. The perfect lattice

The solution of equation (14) will now be considered for spheres arranged on perfect lattice sites. The problem is enormously simplified for a perfect lattice of spheres. The Bloch theorem can be invoked whereby there exists a real wave vector **k** such that

$$\beta_L{}^j = \beta_L \exp(i\mathbf{k}\,.\,\mathbf{r}_j) \tag{17}$$

and the equation is reduced to

$$(2l+1)^{-1}\gamma_l\beta_L = \sum_{L'} B_{LL'}(\mathbf{k})\beta_{L'} \tag{18}$$

where

$$B_{LL'}(\mathbf{k}) = \sum_{j'\neq j} B_{LL'}(\mathbf{r}_{jj'})\exp(-i\mathbf{k}\,.\,\mathbf{r}_{jj'}). \tag{19}$$

The axis of the spherical harmonics is taken in the direction of **k**. The amplitude of motion of the jth sphere, A_j, is obtained from (5):

$$A_j = (4\pi)^{-1/2}\left(\frac{4\pi\mu}{M\omega^2}\right)\beta_{0,0}\exp(i\mathbf{k}\,.\,\mathbf{r}_j). \tag{20}$$

It is clear from the form of the structure constants $B_{LL'}(\mathbf{k})$ that equation (18) will give a periodic dispersion law for $\omega(\mathbf{k})$. This is because the structure constants are unaltered by adding a reciprocal lattice vector to **k**.

In order to obtain some idea of how the loaded continuum depends on the parameter R_s, the limiting behaviour of $\omega(\mathbf{k})$ will be obtained near $|\mathbf{k}| = 0$ and at the zone boundary for a simple cubic lattice with **k** in the (111) direction. The vibrational frequencies of the loaded continuum are given by the usual determinantal condition for a non-trivial solution to a set of simultaneous equations, i.e.

$$\det|B_{LL'}-(2l+1)^{-1}\gamma_l\delta_{LL'}| = 0. \tag{21}$$

Near $|\mathbf{k}| = 0$ the structure constants may be estimated by replacing the summation by an integral, i.e.

$$B_{LL'}(\mathbf{k}) \simeq \Delta^{-1}\int B_{LL'}(\mathbf{r})\exp(-i\mathbf{k}\,.\,\mathbf{r})\,d\mathbf{r} \tag{22}$$

where $\Delta = a^3$ and a is the lattice spacing. For small values of $|\mathbf{k}|$

$$B_{LL'}(\mathbf{k}) \propto |\mathbf{k}|^{l+l'-2}. \tag{23}$$

Using (23) it can readily be ascertained that for small $|\mathbf{k}|$ the only important spherical harmonics in determining $\omega(\mathbf{k})$ are those with $l = 0$ and $l = 1$. Along the (111) direction, symmetry arguments can be used to show that only spherical harmonics with

$$m = 0,\ +3,\ +6,\ \ldots$$

need be retained in the expansion (5) (Segall and Ham 1961). The determinantal condition then gives

$$\omega^2(\mathbf{k}) = \frac{4\pi\mu R_s}{M}\left(1+R_s B_{00,00}-\frac{3R_s{}^4 B_{10,00}B_{00,10}}{1+3R_s{}^3 B_{10,10}}\right)^{-1} \tag{24}$$

Hence equation (37) is simplified to

$$(2l+1)^{-1}\langle\beta_L(\mathbf{r})\rangle = (N-1)\sum_{L'}\int d\mathbf{r}'\; p(\mathbf{r}'|\mathbf{r})B_{LL'}(\mathbf{r}-\mathbf{r}')\langle\beta_{L'}(\mathbf{r}')\rangle. \tag{40}$$

In an isotropic homogeneous medium when $p(\mathbf{r}'|\mathbf{r}) = p(|\mathbf{r}'-\mathbf{r}|)$ the spatial dependence of $\langle\beta_L(\mathbf{r})\rangle$ can be removed by writing

$$\langle\beta_L(\mathbf{r})\rangle = \langle\beta_L\rangle\exp(i\mathbf{k}\,.\,\mathbf{r}) \tag{41}$$

providing $\langle\beta_L\rangle$ satisfies

$$(2l+1)^{-1}\gamma_l\langle\beta_L\rangle = \sum_{L'} B^{\mathrm{d}}_{LL'}(\mathbf{k})\langle\beta_{L'}\rangle. \tag{42}$$

The matrix $B^{\mathrm{d}}_{LL'}(\mathbf{k})$ is defined by

$$B^{\mathrm{d}}_{LL'}(\mathbf{k}) = (N-1)\int d\mathbf{R}\; p(|\mathbf{R}|)B_{LL'}(\mathbf{R})\exp(-i\mathbf{k}\,.\,\mathbf{R}) \tag{43}$$

and $B^{\mathrm{d}}_{LL'}(\mathbf{k})$ is purely real. This means that the solution of (43) will yield a purely real relation between the frequency ω and the wave vector $\mathbf{k}$, in contrast with the electron case.

This is not a peculiarity of the loaded continuum, as can be demonstrated by averaging the equations of motion for a 'spring' model of a disordered solid. Let us assume that the Hamiltonian of a disordered solid can be written in the form

$$H = \sum_{\alpha}\sum_{j}\left[\frac{p_\alpha{}^2(j)}{2M} + \tfrac{1}{2}\sum_{\alpha'}\sum_{j'\neq j}\mathscr{B}_{\alpha\alpha'}(\mathbf{r}_j-\mathbf{r}_{j'})\{u_\alpha(j)-u_\alpha(j')\}\{u_{\alpha'}(j)-u_{\alpha'}(j')\}\right] \tag{44}$$

where $p_\alpha(j)$ and $u_\alpha(j)$ are Cartesian components of the momentum and displacement of the jth atom located at $\mathbf{r}_j$. $\mathscr{B}(\mathbf{r}_j-\mathbf{r}_{j'})$ is a harmonic force constant which depends only on the separation of the atoms at $\mathbf{r}_j$ and $\mathbf{r}_{j'}$ and M is the mass of an atom. From (44) the time-independent equation of motion is

$$M\omega^2 u_\alpha(j) = 2\sum_{\alpha'}\sum_{j'\neq j}\mathscr{B}_{\alpha\alpha'}(\mathbf{r}_j-\mathbf{r}_{j'})\{u_{\alpha'}(j)-u_{\alpha'}(j')\} \tag{45}$$

and this equation can be averaged in precisely the same way as before. Let us set $j = 1$ in (45), multiply by $p(\mathbf{r}_2\ldots\mathbf{r}_N|\mathbf{r}_1)$ and integrate over $\mathbf{r}_2\ldots\mathbf{r}_N$. The equation analogous to (37) is

$$M\omega^2\langle u_\alpha(\mathbf{r}_1)\rangle = \overset{(N-1)}{\underset{\wedge}{2}}\sum_{\alpha'}\int d\mathbf{r}_2\, p(|\mathbf{r}_2-\mathbf{r}_1|)\mathscr{B}_{\alpha\alpha'}(\mathbf{r}_1-\mathbf{r}_2)(\langle u_{\alpha'}(\mathbf{r}_1|\mathbf{r}_2)\rangle - \langle u_{\alpha'}(\mathbf{r}_2|\mathbf{r}_1)\rangle). \tag{46}$$

Using the approximations

$$\begin{aligned}\langle u_\alpha(\mathbf{r}_1|\mathbf{r}_2)\rangle &\simeq \langle u_\alpha(\mathbf{r}_1)\rangle\\ \langle u_\alpha(\mathbf{r}_2|\mathbf{r}_1)\rangle &\simeq \langle u_\alpha(\mathbf{r}_2)\rangle\end{aligned} \tag{47}$$

and writing

$$\langle u_\alpha(\mathbf{r})\rangle = \langle u_\alpha\rangle\exp(i\mathbf{k}\,.\,\mathbf{r}) \tag{48}$$

then

$$M\omega^2\langle u_\alpha\rangle = 2\sum_{\alpha'}\mathscr{B}_{\alpha\alpha'}(\mathbf{k})\langle u_{\alpha'}\rangle \tag{49}$$

where

$$\mathscr{B}_{\alpha\alpha'}(\mathbf{k}) = (N-1)\int d\mathbf{R}\; p(|\mathbf{R}|)\mathscr{B}_{\alpha\alpha'}(\mathbf{R})\{1-\exp(-i\mathbf{k}\,.\,\mathbf{R})\}. \tag{50}$$

It is obvious that equations (49) and (50) will also yield a purely real relation between ω and $\mathbf{k}$.

Before we go on to discuss the reason for the absence of attenuation in the average wave amplitude, the sort of dispersion law generated from (42) will be briefly considered. Because of the spherical symmetry of the disordered system it is unnecessary to use

4. The disordered loaded continuum

Having obtained a general idea of the properties of the perfect loaded continuum, we shall now consider the disordered case.

The similarity between the angular momentum representation of the Schrödinger equation (16) and the equations for the loaded continuum (14) suggests that averaging methods which have been applied successfully to (16) might also provide useful information here. The properties of an amorphous loaded continuum will be considered, perhaps something like a 'monatomic glass'.

The basic idea behind averaging methods is that, although the fine details of waves in disordered systems depend on the microscopic nature of the medium in which the waves travel, there exist grosser features of the waves which are insensitive to the precise microscopic structure. It is convenient to consider an ensemble of disordered systems each of unit volume, containing a large number (N) of rigid spheres. Using the conventional notation (Lax 1951, Ziman 1966), $p(\mathbf{r}_1\mathbf{r}_2 \ldots \mathbf{r}_N)$ will denote the probability of finding the first particle in $d\mathbf{r}_1$, the second in $d\mathbf{r}_2$ and so on. The conditional probability $p(\mathbf{r}_{S+1} \ldots \mathbf{r}_N|\mathbf{r}_1 \ldots \mathbf{r}_S)$ will denote the probability of finding the $(S+1)$th particle in $d\mathbf{r}_{S+1}$, etc., when particles $1 \ldots S$ are definitely at $\mathbf{r}_1 \ldots \mathbf{r}_S$. A useful relation between the conditional probabilities is

$$p(\mathbf{r}_{S+1} \ldots \mathbf{r}_N|\mathbf{r}_1 \ldots \mathbf{r}_S) = p(\mathbf{r}_{S+1}|\mathbf{r}_1 \ldots \mathbf{r}_S)p(\mathbf{r}_{S+2} \ldots \mathbf{r}_N|\mathbf{r}_1 \ldots \mathbf{r}_{S+1}). \tag{34}$$

A hierarchy of equations can be constructed in the usual way for various averages of the coefficients which occur in equation (14). The $\beta_L{}^j$ for a particular disordered system depend on the positions of all the other rigid spheres. The simplest type of average coefficient will be denoted by $\langle\beta_L(\mathbf{r}_j)\rangle$ and is defined by

$$\langle\beta_L(\mathbf{r}_j)\rangle = \int p(\mathbf{r}_1 \ldots' \mathbf{r}_N|\mathbf{r}_j)\beta_L{}^j \, d\mathbf{r}_1 \ldots' d\mathbf{r}_N \tag{35}$$

where the prime denotes omission of a position coordinate. A general type of average is defined by

$$\langle\beta_L(\mathbf{r}_j|\mathbf{r}_{j'} \ldots)\rangle = \int p(\mathbf{r}_1 \ldots''^{\cdots} |\mathbf{r}_j\mathbf{r}_{j'} \ldots)\beta_L{}^j \, d\mathbf{r}_1 \ldots''^{\cdots} d\mathbf{r}_N. \tag{36}$$

The series of equations for these functions is generated by multiplying equation (14) by a probability function and integrating over all positions not held fixed. For example, setting $j = 1$ in (14), multiplying by $p(\mathbf{r}_2 \ldots \mathbf{r}_N|\mathbf{r}_1)$ and integrating over $\mathbf{r}_2 \ldots \mathbf{r}_N$ gives

$$(2l+1)^{-1}\gamma_l\langle\beta_L(\mathbf{r}_1)\rangle = (N-1)\sum_{L'}\int d\mathbf{r}_2\, p(\mathbf{r}_2|\mathbf{r}_1)B_{LL'}(\mathbf{r}_1-\mathbf{r}_2)\langle\beta_{L'}(\mathbf{r}_2|\mathbf{r}_1)\rangle. \tag{37}$$

This equation is linked to a second equation containing $\langle\beta_L(\mathbf{r}_1|\mathbf{r}_2)\rangle$ and $\langle\beta_L(\mathbf{r}_1|\mathbf{r}_2\mathbf{r}_3)\rangle$, obtained by setting $j = 1$ in (14), multiplying by $p(\mathbf{r}_3 \ldots \mathbf{r}_N|\mathbf{r}_1\mathbf{r}_2)$ and integrating over $\mathbf{r}_3 \ldots \mathbf{r}_N$. By this means it is found that

$$\begin{aligned}(2l+1)^{-1}\gamma_l\langle\beta_L(\mathbf{r}_1|\mathbf{r}_2)\rangle = {}& \sum_{L'} B_{LL'}(\mathbf{r}_1-\mathbf{r}_2)\langle\beta_{L'}(\mathbf{r}_2|\mathbf{r}_1)\rangle \\ & + (N-2)\sum_{L'}\int d\mathbf{r}_3\, p(\mathbf{r}_3|\mathbf{r}_1\mathbf{r}_2)B_{LL'}(\mathbf{r}_1-\mathbf{r}_3)\langle\beta_{L'}(\mathbf{r}_3|\mathbf{r}_1\mathbf{r}_2)\rangle.\end{aligned} \tag{38}$$

Each successive equation contains more and more information about the precise details of the vibrations of the rigid spheres. The final equation in the series is (14), i.e. the equation for a particular configuration of rigid spheres. Only the simplest equation (37) will be considered here.

In a recent paper by Ziman (1966) it was shown that the equivalent equation to (37) for electrons in liquid metals could be solved using the quasi-crystalline approximation of Lax (1951). This is equivalent to the assumption that

$$\langle\beta_L(\mathbf{r}_2|\mathbf{r}_1)\rangle \simeq \langle\beta_L(\mathbf{r}_2)\rangle. \tag{39}$$

The spatial dependence may be removed by writing

$$\langle \beta_L(\mathbf{r}) \rangle = \langle \beta_L \rangle \exp(i\mathbf{k} \,.\, \mathbf{r}) \tag{55}$$

which reduces equation (54) to

$$\kappa(i - \cot \eta_l) \langle \beta_L \rangle = \sum_{L'} B_{LL'}(\kappa, \mathbf{k}) \langle \beta_{L'} \rangle \tag{56}$$

where

$$B_{LL'}(\kappa, \mathbf{k}) = (N-1) \int d\mathbf{R}\, p(|\mathbf{R}|) B_{LL'}(\kappa, \mathbf{R}) \exp(-i\mathbf{k} \,.\, \mathbf{R}). \tag{57}$$

It is not possible to satisfy equation (56) for real values of **k** (except when $E < 0$); but, on the other hand, the integral in (57) diverges for complex values of **k**. Equation (54) is in fact not appropriate for the average standing-wave solutions of the Schrödinger equation. It is the equation for a plane wave with energy $E = \kappa^2$ which is scattered by a system of potential wells, but with the inhomogeneous terms representing the incident plane wave omitted. Lax (1951) and Waterman and Truell (1961) have shown that it is legitimate to ignore the inhomogeneous terms providing the contributions from the upper limits of the integral in (57) are also ignored. This is a case of the extinction theorem whereby waves produced at the boundary of the system of scatterers cancel the incident wave within the system.

The reason why the loaded continuum and the spring models do not produce a complex propagation constant is that the equations are appropriate to 'standing-wave' boundary conditions. Apart from localized modes (which this theory is not sensitive enough to show), there is no reason to suppose that the standing waves should not be spread throughout the system, in view of the assumption of homogeneous disorder. Because the propagator (3) in the empty space between the spheres satisfies the Laplace equation rather than the wave equation it is not possible to set up the scattering type of boundary condition in this case. We should have to modify the model by considering waves travelling through a continuum of finite density before they impinge upon the loaded continuum. If this is attempted the simplicity of the equations (14) is lost. It is possible that attenuation effects might be calculated by using higher-order approximations to the hierarchy of averaged equations. The renormalization procedure used by Lloyd (1967) may be applicable to this problem.

The conclusion of this work is that, although the work of Phariseau and Ziman (1963) and Ziman (1966) seems to be a way of circumventing the need for introducing a set of basic states, their work implicitly involves the use of free-electron waves as a basic set. The use of averaging methods might provide interesting information about the vibrations of disordered systems if investigated in greater detail, but the route seems paved with difficulties, for example, the need to know higher particle-correlation functions. One approach which might prove useful is a direct attempt to calculate a Green function for the loaded continuum or spring model by averaging the inhomogeneous form of (14) or the equations of motion (45). In the electron problem Edwards (1958) showed that the Green function was of the form $\exp(i\lambda|\mathbf{R}|)/|\mathbf{R}|$, where λ is complex. Surely it must be possible to obtain a similar result for vibrating harmonic solids without using a perturbation method which starts from unperturbed lattice waves. There seems to be a real need for a set of basic states suitable for describing the vibrations and transport properties of a disordered solid. It is this problem which will be broached and partially answered in a later paper.

Appendix. The plane-wave representation

The ~~strain~~ displacement-field in the elastic medium can be expanded in plane waves in the usual way

$$U(\boldsymbol{\rho}) = \sum_{\mathbf{g}} \alpha_{\mathbf{k}+\mathbf{g}} \exp\{i(\mathbf{k}+\mathbf{g}) \,.\, \boldsymbol{\rho}\} \tag{A1}$$

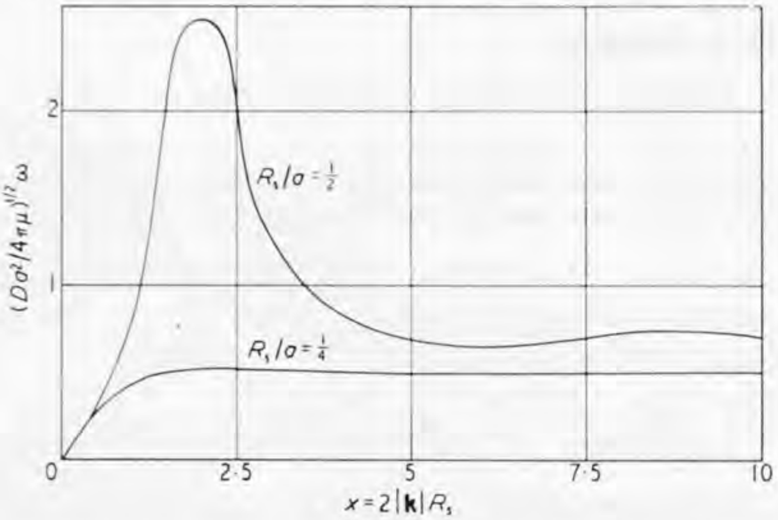
where **g** denotes a reciprocal lattice vector. Once the coefficients β_L are known, the Fourier coefficients can be determined using the procedure given by Ham and Segall (1961). The spherical harmonics with $m > 0$ if the axis of the harmonics is taken to be in the direction of $\mathbf{k}$ (Phariseau and Ziman 1963). If just the $l = 0$ term is retained, then

$$\omega^2(\mathbf{k}) \simeq \frac{4\pi\mu R_s}{M}\{1 + R_s B^{\mathrm{d}}_{00,00}(\mathbf{k})\}^{-1} \tag{51}$$

where

$$B^{\mathrm{d}}_{00,00}(\mathbf{k}) = (N-1)\int \frac{d\mathbf{R}\, p(|\mathbf{R}|)\exp(-i\mathbf{k}\,.\,\mathbf{R})}{|\mathbf{R}|}. \tag{52}$$

The 'dispersion law' obtained from (42) when $p(|\mathbf{R}|) = 1$ for $|\mathbf{R}| \geqslant 2R_s$ and $p(|\mathbf{R}|) = 0$ for $|\mathbf{R}| < 2R_s$ is sketched in the figure using just the $l = 0$ and $l = 1$ harmonics.



Sketch of $(Da^2/4\pi\mu)^{1/2}\omega$ against $x = 2|\mathbf{k}|R_s$, where a^3 is the volume per sphere.

In the figure it is noticeable that for high densities the 'dispersion law' echoes the perfectly repeating structure of a perfect lattice. The long-wavelength region corresponds to acoustic waves, but the significance of the short-wavelength oscillations is not clear. Although one might be tempted to impose periodic boundary conditions on the plane waves, the counting of modes loses its significance because of the averaging process. This presumably occurs because an infinite number of atoms are introduced by taking an ensemble average, turning the discrete structure of a single system into a smeared continuum.

The reason why unattenuated plane-wave solutions are found for the loaded continuum can be found by examining the corresponding electron theory. Equation (16) constitutes a precise formulation of the Schrödinger equation for an electron with $E = \kappa^2$ moving through a system of spherical potential wells. However, if we had used 'standing wave boundary conditions', (16) would have been replaced by the equally valid pair of equations (Ziman 1965 b)

$$-\kappa \cot \eta_l\, \beta_L{}^j = \sum_{L'} \sum_{j' \neq j} B_{LL'}{}'(\kappa, \mathbf{r}_{jj'})\beta_{L'}{}^{j'} \qquad (E > 0) \tag{53a}$$

$$\kappa(i - \cot \eta_l)\beta_L{}^j = \sum_{L'} \sum_{j' \neq j} B_{LL'}(\kappa, \mathbf{r}_{jj'})\beta_{L'}{}^{j'} \qquad (E < 0) \tag{53b}$$

where $B_{LL'}{}'$ denotes the real part of the $B_{LL'}$.

In this form the Greenian theory for electrons also seems to have purely real solutions. The question that must be answered is: why does the average form of (16) (for $E > 0$) have an attenuated plane-wave solution while (53*a*) yields an unattenuated solution after averaging? The answer to this paradox lies in the work of Lax (1951) and Waterman and Truell (1961).

After making the quasi-crystalline approximation the averaged form of (16) is

$$\kappa(i - \cot \eta_l)\langle \beta_L(\mathbf{r})\rangle = (N-1)\sum_{L'}\int d\mathbf{r}'\, p(|\mathbf{r}' - \mathbf{r}|)B_{LL'}(\kappa, \mathbf{r} - \mathbf{r}')\langle \beta_{L'}(\mathbf{r}')\rangle. \tag{54}$$

in the electron problem (Ziman 1965 b) by using

$$\begin{aligned}\Delta^{-1}\sum_{\mathbf{g}}\frac{\exp\{i(\mathbf{k}+\mathbf{g}).(\boldsymbol{\rho}-\boldsymbol{\rho}')\}}{|\mathbf{k}+\mathbf{g}|^2}-\frac{1}{4\pi}\frac{1}{|\boldsymbol{\rho}-\boldsymbol{\rho}'|}\\ =\sum_{L}\sum_{L'}B_{LL'}(\mathbf{k})\boldsymbol{\rho}^{l}\boldsymbol{\rho}'^{l'}\mathscr{Y}_L(\boldsymbol{\rho})\mathscr{Y}_{L'}(\boldsymbol{\rho}')\\ =N\sum_{\mathbf{g}}\frac{1}{|\mathbf{k}+\mathbf{g}|^2}\sum_{L}\sum_{L'}(4\pi)^2 i^{l-l'}\mathscr{Y}_L(\mathbf{k}+\mathbf{g})\mathscr{Y}_{L'}(\mathbf{k}+\mathbf{g})\mathrm{j}_l(|\mathbf{k}+\mathbf{g}|\rho)\mathrm{j}_{l'}(|\mathbf{k}+\mathbf{g}|\rho')\\ \times\mathscr{Y}_L(\boldsymbol{\rho})\mathscr{Y}_{L'}(\boldsymbol{\rho}')-\sum_{L}\frac{1}{2l+1}\rho^{l}\rho'^{-l-1}\mathscr{Y}_L(\boldsymbol{\rho})\mathscr{Y}_L(\boldsymbol{\rho}'). \qquad \text{(A11)}\end{aligned}$$

The structure constants can be obtained from (A11) as it stands, setting $\rho = \rho' = R_s$ or by taking the derivative of both sides with respect to ρ and ρ' and then taking $\rho = \rho' = R_s$. The best form for the present purpose is obtained by taking the derivative of (A11) with respect to ρ or ρ' for terms with l or l' greater than zero. The structure constants may then be written as

$$B_{LL'}(\mathbf{k})=\sum_{\mathbf{g}}\frac{F_{L\mathbf{g}}F_{L'\mathbf{g}}}{|\mathbf{k}+\mathbf{g}|^2}+S_l\delta_{LL'} \qquad \text{(A12)}$$

where

$$\left.\begin{aligned}F_{00,\mathbf{g}}&=4\pi N^{1/2}\mathrm{j}_0(|\mathbf{k}+\mathbf{g}|R_s)\mathscr{Y}_{00}(\mathbf{k}+\mathbf{g})\\ F_{L\mathbf{g}}&=\frac{4\pi N^{1/2}i^{l}\mathrm{j}_l'(|\mathbf{k}+\mathbf{g}|R_s)\mathscr{Y}_L(\mathbf{k}+\mathbf{g})}{lR_s^{\,l-1}} \qquad (l>0)\end{aligned}\right\} \qquad \text{(A13)}$$

and

$$\left.\begin{aligned}S_0&=-R_s^{\,-1}\\ S_l&=\frac{(l+1)R_s^{\,-2l-1}}{l(2l+1)} \qquad (l>0).\end{aligned}\right\} \qquad \text{(A14)}$$

Substitution for the β_L from equation (A14) and use of (A12) finally gives

$$\sum_{\mathbf{g}}\alpha_{\mathbf{k}+\mathbf{g}}(\Gamma_{\mathbf{g}\mathbf{g}'}-|\mathbf{k}+\mathbf{g}|^2\delta_{\mathbf{g}\mathbf{g}'})=0 \qquad \text{(A15)}$$

where

$$\Gamma_{\mathbf{g}\mathbf{g}'}=\sum_{L}N^{1/2}t_l F_{L\mathbf{g}}{}^{*}F_{L\mathbf{g}'} \qquad \text{(A16)}$$

and

$$\left.\begin{aligned}t_0&=\frac{M\omega^2}{4\pi\mu N^{1/2}}\\ t_l&=-\frac{lR_s^{\,2l+1}}{N^{1/2}} \qquad (l>0).\end{aligned}\right\} \qquad \text{(A17)}$$

This is the required result, an equation which looks as if the rigid spheres can be treated as weak perturbation to the elastic medium of zero density.

The procedure used here for deriving (A15) may be of interest in the corresponding problem of electrons in a periodic lattice. In Ziman's (1965 b) original derivation of a reciprocal representation of equation (16) effective matrix elements of the lattice potential were obtained in the form

$$\Gamma_{\mathbf{g}\mathbf{g}'}=-\frac{4\pi N}{\kappa}\sum_{l}(2l+1)\tan\eta_l{}'\frac{\mathrm{j}_l(|\mathbf{k}+\mathbf{g}|R_s)\mathrm{j}_l(|\mathbf{k}+\mathbf{g}'|R_s)\mathrm{P}_l{}^0(\cos\theta_{\mathbf{g}\mathbf{g}'})}{\mathrm{j}_l{}^2(\kappa R_s)} \qquad \text{(A18)}$$

with

$$\tan\eta_l{}'=\left\{\cot\eta_i-\frac{\mathrm{n}_l(\kappa R_s)}{\mathrm{j}_l(\kappa R_s)}\right\}^{-1} \qquad \text{(A19)}$$

and with the usual meaning for the other symbols. This effective matrix element can become infinite, at the zeros of $\mathrm{j}_l(\kappa R_s)$ or at the zeros of $\mathscr{R}_l(R_s)$, where $\mathscr{R}_l(\rho)$ is a radial strain field outside the spheres is given by

$$U(\boldsymbol{\rho}) = R_s^2 \int \left\{ \mathscr{G}(\boldsymbol{\rho}-\boldsymbol{\rho}') \frac{\partial}{\partial \rho'} U(\boldsymbol{\rho}') - U(\boldsymbol{\rho}') \frac{\partial}{\partial \rho'} \mathscr{G}(\boldsymbol{\rho}-\boldsymbol{\rho}') \right\}_{\rho'=R_s} d\Omega(\boldsymbol{\rho}') \tag{A2}$$

where $\mathscr{G}(\boldsymbol{\rho}-\boldsymbol{\rho}')$ is the Greenian (Ziman 1965 b)

$$\mathscr{G}(\boldsymbol{\rho}-\boldsymbol{\rho}') = -\frac{1}{4\pi} \sum_{l} \frac{\exp(i\mathbf{k} \cdot \mathbf{r}_{l'l})}{|\boldsymbol{\rho}-\boldsymbol{\rho}'-\mathbf{r}_{l'l}|} = -\frac{1}{\Delta} \sum_{\mathbf{g}} \frac{\exp\{i(\mathbf{k}+\mathbf{g}) \cdot (\boldsymbol{\rho}-\boldsymbol{\rho}')\}}{|\mathbf{k}+\mathbf{g}|^2}. \tag{A3}$$

Adopting the procedure of Ham and Segall, we can expand the Greenian (for $\rho > \rho'$) in the form

$$\mathscr{G}(\boldsymbol{\rho}-\boldsymbol{\rho}') = \sum_{L} D_L(\boldsymbol{\rho}) \rho'^{l} \mathscr{Y}_L(\boldsymbol{\rho}') \tag{A4}$$

where

$$D_L(\boldsymbol{\rho}) = -\frac{4\pi}{\Delta} i^{-l} R_s^{-l} \sum_{\mathbf{g}} \frac{\exp\{i(\mathbf{k}+\mathbf{g}) \cdot \boldsymbol{\rho}\}}{|\mathbf{k}+\mathbf{g}|^2} \mathrm{j}_l(|\mathbf{k}+\mathbf{g}|R_s) \mathscr{Y}_L(\mathbf{k}+\mathbf{g}). \tag{A5}$$

Using (A4) and (A5) in (A1), then

$$\alpha_{\mathbf{k}+\mathbf{g}} = \sum_{L} \frac{4\pi i^{-l} R_s^{-l}}{|\mathbf{k}+\mathbf{g}|^2} \beta_L \mathrm{j}_l(|\mathbf{k}+\mathbf{g}|R_s) \mathscr{Y}_L(\mathbf{k}+\mathbf{g}). \tag{A6}$$

At low frequencies it has been shown that only the $l = 0$ and the $l = 1$ harmonics are important, so that β_{00} and β_{10} will be assumed to be the only non-zero coefficients. Using equation (18) and the approximate values of the structure constants (26), then

$$\beta_{10} \simeq \frac{3^{1/2} i}{\Delta|\mathbf{k}|} \left(\frac{\mu-\mu_{\mathrm{eff}}}{\mu\mu_{\mathrm{eff}}} \right) \beta_{00}. \tag{A7}$$

From equation (A6) it can be seen that $\alpha_{\mathbf{k}}$ is larger than any of the other coefficients by a factor $|\mathbf{k}|^{-1}$.

This suggests that a reciprocal lattice representation (Ziman 1965 b, Morgan 1966) might be a useful means of investigating the loaded continuum. This approach turns out to be of limited usefulness, however, but the derivation of the equations illustrates a number of points which can arise in the corresponding electron theory, and so the opportunity to set them out will be taken here.

A simple way of obtaining the equations satisfied by the $\alpha_{\mathbf{k}+\mathbf{g}}$ is straightforward substitution for the β_L in (18) in terms of the $\alpha_{\mathbf{k}+\mathbf{g}}$. On the surface of a sphere the expansion (5) must be matched to the expansion in plane waves (A1). To obtain the β_L in terms of the Fourier coefficients it is necessary in this case to consider the matching of both the amplitude and radial derivative. This is because the terms with $l > 0$ in equation (5) vanish for $\rho = R_s$. By this means it is found that

$$\beta_L = \sum_{\mathbf{g}} \beta_{L\mathbf{g}} \alpha_{\mathbf{k}+\mathbf{g}} \tag{A8}$$

where

$$\beta_{00,\mathbf{g}} = \frac{M\omega^2}{\mu} \mathrm{j}_0(|\mathbf{k}+\mathbf{g}|R_s) \mathscr{Y}_{00}(\mathbf{k}+\mathbf{g})$$

$$\beta_{L\mathbf{g}} = -4\pi i^l R_s^{l+2} \mathrm{j}_l'(|\mathbf{k}+\mathbf{g}|R_s) \mathscr{Y}_L(\mathbf{k}+\mathbf{g}) \qquad (l > 0) \tag{A9}$$

and

$$\mathrm{j}_l'(|\mathbf{k}+\mathbf{g}|R_s) = \frac{d}{dR_s} \mathrm{j}_l(|\mathbf{k}+\mathbf{g}|R_s). \tag{A10}$$

The next step is to obtain a suitable expression for the structure constants in terms of a summation over reciprocal lattice vectors. This can be done in precisely the same way as

Reprinted from
Proceedings of the Physical Society, Vol. 89, Part 2, No. 564, pp. 476–478
1966
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Variational estimates of the scattering of phonons from static lattice imperfections

Abstract. A comparison is made between the results of a calculation using the Schwinger variational method (Lippmann and Schwinger 1950) and an exact calculation of the single mode relaxation time for phonons scattered by pairs of isotopes. The aim is to provide a guide to the accuracy which can be expected for more complicated defects.

The calculation of the scattering of phonons from small lattice imperfections is simple in principle. The isotope problem can be solved easily enough (Lifshitz 1956, Takeno 1963) but, once changes in force constants are introduced, the labour required to obtain an exact solution increases rapidly. The merit of using an approximate method is that more complicated models can be used and the effect of changes in the details of a model investigated more easily. A pair of isotopes is the only lattice defect (apart from a single isotope) for which an exact solution of the scattering problem has been given (Takeno 1963).

solution of Schrödinger's equation for a spherical potential well. The procedure used for the loaded continuum to avoid such singularities may be employed to show that

$$\left\{\cot\eta_l - \frac{\mathrm{n}_l(\kappa R_s)}{\mathrm{j}_l(\kappa R_s)}\right\}^{-1} \frac{\mathrm{j}_l(|\mathbf{k}+\mathbf{g}|R_s)\mathrm{j}_l(|\mathbf{k}+\mathbf{g}'|R_s)}{\mathrm{j}_l^2(\kappa R_s)} \tag{A20}$$

in (A18) can be replaced by

$$\left\{\cot\eta_l - \frac{\mathrm{n}_l'(\kappa R_s)}{\mathrm{j}_l'(\kappa R_s)}\right\}^{-1} \frac{\mathrm{j}_l'(|\mathbf{k}+\mathbf{g}|R_s)\mathrm{j}_l'(|\mathbf{k}+\mathbf{g}'|R_s)}{\mathrm{j}_l'^2(\kappa R_s)} \tag{A21}$$

whenever it is convenient.

Returning to the loaded continuum equations (A15), if all the coefficients except $\alpha_{\mathbf{k}}$ are assumed to be zero, then we find that the long-wavelength form for $\omega^2(\mathbf{k})$ is

$$\omega^2(\mathbf{k}) = \frac{\mu}{D}\left(1+\frac{\nu}{\Delta}\right)|\mathbf{k}|^2. \tag{A22}$$

This result contradicts equation (27). The reason is that it is not possible to ignore higher Fourier coefficients, even for long waves, despite the fact that $\alpha_{\mathbf{k}}$ is much larger than the other terms. This can be seen by setting $\mathbf{g} = 0$ in (A15) and writing

$$\Gamma_{00} - |\mathbf{k}|^2 = \frac{1}{\alpha_{\mathbf{k}}} \sum_{\mathbf{g}'\neq 0} \alpha_{\mathbf{k}+\mathbf{g}'}\Gamma_{0\mathbf{g}'}. \tag{A23}$$

If the right-hand side of (A23) can be neglected then (A22) is obtained, but, in fact, $\alpha_{\mathbf{k}-\mathbf{g}}/\alpha_{\mathbf{k}}$ is of the order $|\mathbf{k}|$ from (A6), and $\Gamma_{0\mathbf{g}}$ is of the order $|\mathbf{k}|$. This means that the right-hand side of (A23) is of the order $|\mathbf{k}|^2$ and cannot be neglected. This seems to be a peculiarity of the elastic wave equation and not a defect of the method.

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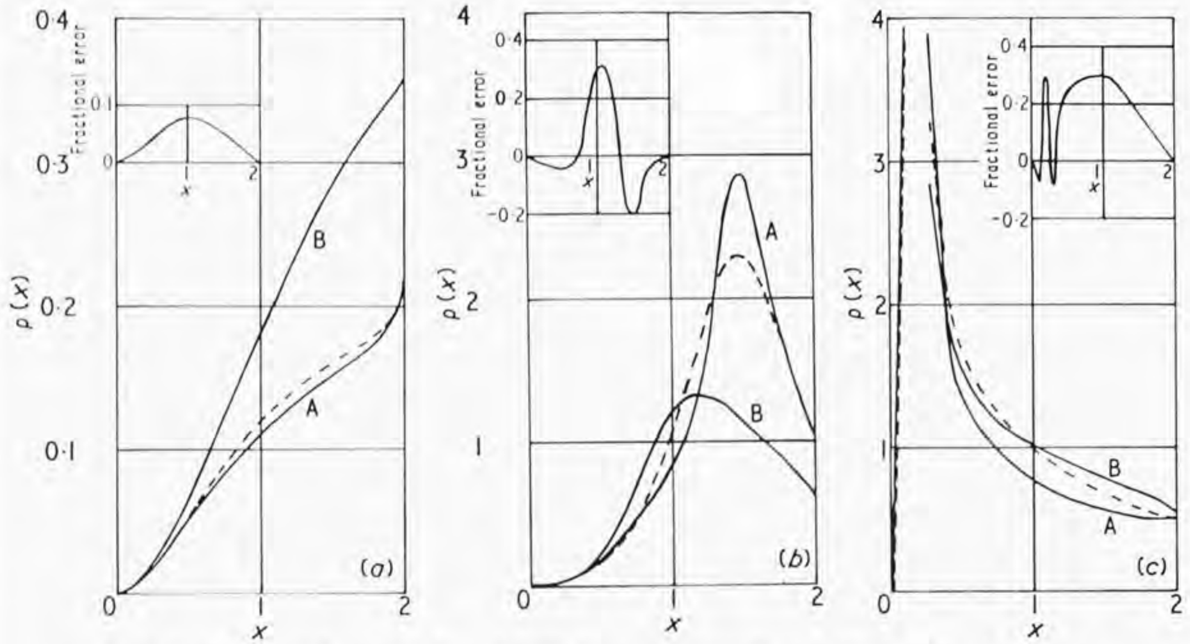

Variation of ρ with x: (*a*) $\underset{\sim}{Q} = 1$; (*b*) $\underset{\sim}{Q} = -1$; (*c*) $\underset{\sim}{Q} = -10$; broken lines correspond to the approximate solutions, and full lines correspond to the exact solutions.

Two directions of the incident wave are considered: A, when **k** is the same direction as the line joining the two isotopes and B, when **k** is normal to this line. For case B the variational answer is exact. The exact solutions given by Takeno (1963) are also plotted and a sketch of the fractional error is given. For $\underset{\sim}{Q} = 1$ the maximum fractional error is about 0·1, while for $\underset{\sim}{Q} = -1$ and $\underset{\sim}{Q} = -10$ where resonance occurs the error rises to about 0·3.

The variational approximation, therefore, gives quite reasonable accuracy using the unperturbed solutions as trial functions even when resonant scattering occurs. It is suggested that the errors involved in a variational calculation of the scattering from other localized defects will not be very different from those found for a pair of isotopes.

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8th August 1966

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The equation of motion for a perfect lattice can be written symbolically as (Takeno 1963)

$$(\omega^2 - L)\mathbf{u}(l) = 0$$

where $\mathbf{u}(l)$ is the displacement of the lth atom. The scattering of a perfect lattice wave $\mathbf{u}_{\mathbf{k}j}{}^0(l)$ of frequency ω is described by the equation

$$\mathbf{u}_{\mathbf{k}j}(l) = \mathbf{u}_{\mathbf{k}j}{}^0(l) + \sum_{l'} \mathbf{G}_\omega(l, l') \,.\, V\mathbf{u}_{\mathbf{k}j}(l')$$

where V is an operator symbolizing a perturbation to the perfect lattice and $\mathbf{G}_\omega(l, l')$ is a Green dyadic. The important quantity to determine is

$$M(\mathbf{k}j, \mathbf{k}'j') = \sum_{l} \mathbf{u}_{\mathbf{k}'j'}{}^{0*}(l) \,.\, V\mathbf{u}_{\mathbf{k}j}(l)$$

where $\mathbf{u}_{\mathbf{k}'j'}{}^0(l)$ is a perfect lattice wave having the same frequency as $\mathbf{u}_{\mathbf{k}j}{}^0(l)$. The quantum-mechanical T-matrix element can be written as

$$T(\mathbf{k}j, \mathbf{k}'j') = \frac{\hbar}{2\omega} M(\mathbf{k}j, \mathbf{k}'j')$$

and using the optical theorem the single-mode relaxation time of a system containing n defects per unit volume can be expressed in terms of the imaginary part of M, i.e.

$$\tau_s{}^{-1} = -\frac{n}{\omega} \mathscr{I} M(\mathbf{k}j, \mathbf{k}\, j\ ).$$

Let $\mathbf{u}_{\mathbf{k}'j'}(l)$ denote the solution to

$$\mathbf{u}_{\mathbf{k}'j'}(l) = \mathbf{u}_{\mathbf{k}'j'}{}^0(l) + \sum_{l'} \mathbf{G}_\omega(l, l') \,.\, V\mathbf{u}_{\mathbf{k}'j'}(l').$$

Schwinger's variational method states that

$$\mathscr{M}[\mathbf{u}_{T\mathbf{k}j}, \mathbf{u}_{T\mathbf{k}'j'}] = \frac{\Sigma_l \mathbf{u}_{\mathbf{k}'j'}{}^{0*}(l) \,.\, V\mathbf{u}_{T\mathbf{k}j}(l) \Sigma_{l'} \mathbf{u}_{T\mathbf{k}'j'}{}^*(l') \,.\, V\mathbf{u}_{\mathbf{k}j}{}^0(l')}{\Sigma_l \mathbf{u}_{T\mathbf{k}'j'}{}^*(l) \,.\, V\mathbf{u}_{T\mathbf{k}j}(l) - \Sigma_l \Sigma_{l'} \mathbf{u}_{T\mathbf{k}'j'}{}^*(l) \,.\, V\mathbf{G}_\omega(l, l') \,.\, V\mathbf{u}_{T\mathbf{k}j}(l')}$$

reduces to $M(\mathbf{k}j, \mathbf{k}'j')$ and is stationary when the trial functions $\mathbf{u}_{T\mathbf{k}j}$ and $\mathbf{u}_{T\mathbf{k}'j'}$ are equal to $\mathbf{u}_{\mathbf{k}j}$ and $\mathbf{u}_{\mathbf{k}'j'}$. Furthermore, an error $O(\eta)$ in $\mathbf{u}_{T\mathbf{k}j}$ and $\mathbf{u}_{T\mathbf{k}'j'}$ leads to an error $O(\eta^2)$ in M. Using Schwinger's method M has been calculated for a pair of isotopes in a monatomic simple cubic lattice using a nearest-neighbour model with equal non-central and central spring constants (denoted by γ). This is the only model for which tables of the Green dyadic are available (Yussouff and Mahanty 1965). The only trial functions which have been considered are $\mathbf{u}_{T\mathbf{k}j} = \mathbf{u}_{\mathbf{k}j}{}^0$ and $\mathbf{u}_{T\mathbf{k}'j'} = \mathbf{u}_{\mathbf{k}'j'}{}^0$. It is found that M is given correctly in the limits of very long and very short waves using these trial functions. It is convenient to write $\tau_s{}^{-1}$ in the form

$$\tau_s{}^{-1} = \frac{2n}{N}\left(\frac{2\gamma}{m}\right)^{1/2} \rho(x)$$

where $x = m\omega^2/2\gamma$ and N is the number of atoms per unit volume. Let

$$Q = (m - m')/m$$

where m is the mass of a host atom and m' is the isotope mass. In the figure $\rho(x)$ is plotted for $Q = 1$, -1 and -10, when the isotopes occupy nearest-neighbour sites.

Reprinted from

Proceedings of the Physical Society

The Institute of Physics and the Physical Society
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PROC. PHYS. SOC., 1966, VOL. 89

Bloch waves and scattering by impurities

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MS. received 9th June 1966

Abstract. The reciprocal lattice representation of the Green function method used by Ziman in 1965 for calculating band structures is derived. It is shown that the coefficients $\nu_{\mathbf{g}}$ introduced by Ziman are the Fourier coefficients of the wave function outside the potential wells of a 'muffin tin' lattice. The relationship between the method and the augmented plane wave approach is discussed.

An exact formulation of the problem of Bloch wave scattering from an impurity potential is given. Simple approximations are suggested for tightly bound electrons for nearly free electrons and for d-band electrons.

1. The Green function method

The Green function method for electronic band structure has been developed by various authors (Korringa 1947, Kohn and Rostoker 1954, Ham and Segall 1961). It is assumed there that the potential wells of a lattice can be considered as spherically symmetric and that the potential in between the wells is zero. Let R_s denote the cut-off radius of the spherical wells. The wave function $\psi(\boldsymbol{\rho})$ must satisfy a condition

$$\int\left\{\mathrm{G}(\boldsymbol{\rho},\boldsymbol{\rho}')\frac{\partial}{\partial\rho'}\psi(\boldsymbol{\rho}')-\psi(\boldsymbol{\rho}')\frac{\partial}{\partial\rho'}\mathrm{G}(\boldsymbol{\rho},\boldsymbol{\rho}')\right\}_{\rho'=R_s-\epsilon}d\Omega(\boldsymbol{\rho}')=0 \tag{1}$$

where $\mathrm{G}(\boldsymbol{\rho},\boldsymbol{\rho}')$ is the Greenian (Ziman 1965), ϵ is an infinitesimal positive quantity and $\rho < R_s-\epsilon$. Let $\mathscr{R}_l(\rho)$ denote a solution to the radial Schrödinger equation for a single potential well, with energy $E = \kappa^2$ and $\mathscr{Y}_L(\theta,\phi)$ denote a real normalized spherical harmonic. It may be assumed that

$$\begin{aligned}\psi(\boldsymbol{\rho}) &= \sum_L i^l\alpha_L\mathscr{R}_l(\rho)\mathscr{Y}_L(\theta,\phi) \qquad (\rho\leqslant R_s)\\ &= \sum_L \frac{i^l\beta_L\mathscr{R}_l(\rho)\mathscr{Y}_L(\theta,\phi)}{[\mathscr{R}_l,\mathrm{j}_l]}\end{aligned} \tag{2}$$

with the usual notation for the spherical Bessel functions and with

$$[g,f]=g(R_s)\frac{d}{dR_s}f(R_s)-f(R_s)\frac{d}{dR_s}g(R_s). \tag{3}$$

Kohn and Rostoker (1954) have shown that the coefficients satisfy the equation

$$\sum_{L'}\beta_{L'}\{B_{LL'}+\kappa(\cot\eta_l-i)\delta_{LL'}\}=0. \tag{4}$$

η_l is the lth phase shift for a potential well and the $B_{LL'}$ are structure constants. It has recently been shown (Ziman 1965) that the equation for the β_L can be transformed to a reciprocal lattice representation and effective matrix elements of the lattice potentials can be defined. This will now be derived in a less abstract manner but with less generality.

The wave function outside the spherical wells can be expanded in terms of plane waves, i.e.

$$\psi_{\mathbf{k}}(\boldsymbol{\rho}) = \sum_{\mathbf{g}} \alpha_{\mathbf{k}+\mathbf{g}} \exp\{i(\mathbf{k}+\mathbf{g}) \cdot \boldsymbol{\rho}\}. \tag{5}$$

The coefficients in this Fourier expansion are not unique because the sum is required to converge to the correct answer only in a restricted region of space (Ham and Segall 1961). The expansion (5) must be matched to the expansion (2) which is valid for $\rho \leqslant R_s$. Therefore

$$\left\{\sum_{\mathbf{g}} \alpha_{\mathbf{k}+\mathbf{g}} \exp\{i(\mathbf{k}+\mathbf{g}) \cdot \boldsymbol{\rho}\} = \sum_{L} \frac{i^l \beta_L \mathscr{R}_l(\rho) \mathscr{Y}_L(\theta, \phi)}{[\mathscr{R}_l, \mathrm{j}_l]}\right\}_{\rho = R_s}. \tag{6}$$

Using the orthogonality of the spherical harmonics and the usual expansion of a plane wave in spherical Bessel functions it is found that

$$\begin{aligned} \beta_L &= \sum_{\mathbf{g}} \frac{4\pi[\mathscr{R}_l, \mathrm{j}_l]\, \mathscr{Y}_L(\mathbf{k}+\mathbf{g})\mathrm{j}_l(|\mathbf{k}+\mathbf{g}|R_s)\alpha_{\mathbf{k}+\mathbf{g}}}{\mathscr{R}_l(R_s)} \\ &= \sum_{\mathbf{g}} \beta_{L\mathbf{g}}\alpha_{\mathbf{k}+\mathbf{g}}. \end{aligned} \tag{7}$$

The structure constants $B_{LL'}$ may be expressed as (Ziman 1965)

$$B_{LL'} = -\sum_{\mathbf{g}} \frac{F_{L\mathbf{g}}F_{L'\mathbf{g}}}{\rho(\mathbf{g})} + \frac{\delta_{LL'} i\kappa \mathrm{h}_l(\kappa R_s)}{\mathrm{j}_l(\kappa R_s)} \tag{8}$$

where

$$F_{L\mathbf{g}} = \frac{4\pi N^{1/2} \mathscr{Y}_L(\mathbf{k}+\mathbf{g})\mathrm{j}_l(|\mathbf{k}+\mathbf{g}|R_s)}{\mathrm{j}_l(\kappa R_s)} \tag{9}$$

and

$$\rho(\mathbf{g}) = |\mathbf{k}+\mathbf{g}|^2 - \kappa^2. \tag{10}$$

N is the number of atoms in the lattice. If we substitute for the coefficients β_L in terms of the plane wave amplitudes in the Kohn–Rostoker equation (4), it is found that

$$\sum_{\mathbf{g}} F_{L\mathbf{g}}\left[\sum_{\mathbf{g}'} \alpha_{\mathbf{k}+\mathbf{g}'}\left\{\sum_{L'} \frac{-\tan \eta_l' F_{L'\mathbf{g}}F_{L'\mathbf{g}'}}{\rho(\mathbf{g})\kappa} + \delta_{\mathbf{g}\mathbf{g}'}\right\}\right] = 0. \tag{11}$$

This form is obtained by using (Morse and Feshbach 1953)

$$[\mathrm{j}_l, \mathrm{n}_l] = \frac{1}{\kappa {R_s}^2} \tag{12}$$

and by defining

$$\tan \eta_l' = \left\{\cot \eta_l - \frac{\mathrm{n}_l(\kappa R_s)}{\mathrm{j}_l(\kappa R_s)}\right\}^{-1} = \kappa {R_s}^2[\mathrm{j}_l, \mathrm{n}_l]\frac{\mathrm{j}_l(\kappa R_s)}{\mathscr{R}_l(R_s)}. \tag{13}$$

Condition (11) will be satisfied for all values of L if

$$\sum_{\mathbf{g}'} \alpha_{\mathbf{k}+\mathbf{g}'}\{\Gamma_{\mathbf{g}\mathbf{g}'} + \rho(\mathbf{g})\delta_{\mathbf{g}\mathbf{g}'}\} = 0 \tag{14}$$

where

$$\Gamma_{\mathbf{g}\mathbf{g}'} = -\frac{4\pi N}{\kappa}\sum_{l} (2l+1)\tan \eta_l' \frac{\mathrm{j}_l(|\mathbf{k}+\mathbf{g}|R_s)\mathrm{j}_l(|\mathbf{k}+\mathbf{g}'|R_s)}{\mathrm{j}_l^2(\kappa R_s)} \mathrm{P}_l^0(\cos \theta_{\mathbf{g}\mathbf{g}'}) \tag{15}$$

and $\theta_{\mathbf{g}\mathbf{g}'}$ is the angle between $\mathbf{k}+\mathbf{g}$ and $\mathbf{k}+\mathbf{g}'$. $\mathrm{P}_l^0(\cos \theta_{\mathbf{g}\mathbf{g}'})$ is a Legendre polynomial.

Equation (14) is similar to the equation

$$\sum_{\mathbf{g}'} \gamma_{\mathbf{k}+\mathbf{g}'}\{V_{\mathbf{g}\mathbf{g}'} + \rho(\mathbf{g})\delta_{\mathbf{g}\mathbf{g}'}\} = 0 \tag{16}$$

which can be obtained by expanding a Bloch wave in plane waves. $V_{\mathbf{g}\mathbf{g}'}$ is a matrix element of the lattice potential between the states $\mathbf{k}+\mathbf{g}$ and $\mathbf{k}+\mathbf{g}'$. Therefore $\Gamma_{\mathbf{g}\mathbf{g}'}$ can be thought of as an effective matrix element. Equation (14) and the definition of $\Gamma_{\mathbf{g}\mathbf{g}'}$ are identical with the results obtained by Ziman (1965) when the arbitrary radii R and R' occurring in his equation (52) are taken to be R_s.

The significance of replacing R_s by a smaller radius is not apparent, nor is the meaning of taking $R \neq R'$ in Ziman's equation (52) readily interpretable. R_s can, of course, be replaced by any radius between R_s and the inscribed sphere radius.

2. The relationship between the Green function method and the augmented plane wave approach

Within a single unit cell a Bloch wave can be constructed from a set of basis functions called augmented plane waves (Slater 1937). These are of the form

$$\Phi_{\mathbf{k}+\mathbf{g}}(\boldsymbol{\rho}) = H(\rho - R_s)\exp\{i(\mathbf{k}+\mathbf{g})\cdot\boldsymbol{\rho}\} + H(R_s - \rho)\sum_L \frac{i^l \beta_{L\mathbf{g}} \mathscr{R}_l(\rho)\mathscr{Y}_L(\theta,\phi)}{[\mathscr{R}_l, \mathrm{j}_l]} \tag{17}$$

where $H(x)$ is Heaviside's unit function and the $\beta_{L\mathbf{g}}$ are defined by equation (7). At $\rho = R_s$ the augmented plane waves are continuous but have a discontinuous normal derivative. A Bloch wave can be expanded in the form

$$\psi_{\mathbf{k}}(\boldsymbol{\rho}) = \sum_{\mathbf{g}'} \alpha_{\mathbf{k}+\mathbf{g}'}\Phi_{\mathbf{k}+\mathbf{g}'}(\boldsymbol{\rho}). \tag{18}$$

Usual augmented plane wave theory involves calculating the matrix elements of the Hamiltonian between two augmented plane waves. The Green function method, however, is only concerned with that part of an augmented plane wave which lies within a spherical well. If the expansion (18) is substituted into the matching condition (1), ρ' is less than R_s and the plane wave part of the augmented plane wave is irrelevant. This substitution gives

$$\sum_{\mathbf{g}'} \alpha_{\mathbf{k}+\mathbf{g}'}\{\sum_{L'} \beta_{L'\mathbf{g}'}B_{LL'} + \kappa(\cot\eta_l - i)\beta_{L\mathbf{g}'}\} = 0. \tag{19}$$

From the definition (7) of the $\beta_{L\mathbf{g}}$,

$$\beta_{L\mathbf{g}} = \frac{\tan\eta_l{}' F_{L\mathbf{g}}}{\kappa R_s{}^2 N^{1/2}}. \tag{20}$$

Using the Wronskian (12), equation (19) can be reduced to

$$\sum_{\mathbf{g}} F_{L\mathbf{g}}\left[\sum_{\mathbf{g}'} \alpha_{\mathbf{k}+\mathbf{g}'}\left\{\sum_{L'} - \frac{\tan\eta_l{}' F_{L'\mathbf{g}}F_{L'\mathbf{g}'}}{\rho(\mathbf{g})\kappa} + \delta_{\mathbf{g}\mathbf{g}'}\right\}\right] = 0 \tag{21}$$

which is precisely the same as equation (13). This illustrates that there is no fundamental difference between an expansion in augmented plane waves and the usual Green function method. Every plane wave can be associated with a set of interior functions which are matched at $\rho = R_s$, or each interior function can be matched to a set of plane waves.

The conventional augmented plane wave formulae can be derived by putting the sum (18) into a variational formula which gives the energy of a Bloch state (Slater 1937). By this method the form

$$\sum_{\mathbf{g}'} \alpha_{\mathbf{k}+\mathbf{g}'}\{\Gamma_{\mathbf{g}\mathbf{g}'}{}' + \rho(\mathbf{g})\delta_{\mathbf{g}\mathbf{g}'}\} = 0 \tag{22}$$

can be obtained. $\Gamma_{\mathbf{g}\mathbf{g}'}{}'$ is defined by

$$\Gamma_{\mathbf{g}\mathbf{g}'}{}' = 4\pi R_s{}^2 N\left[-\frac{\{(\mathbf{k}+\mathbf{g})\cdot(\mathbf{k}+\mathbf{g}')-\kappa^2\}\mathrm{j}_1(|\mathbf{g}-\mathbf{g}'|R_s)}{|\mathbf{g}-\mathbf{g}'|} + \sum_l \frac{(2l+1)\mathscr{R}_l{}'(R_s)\mathrm{j}_l(|\mathbf{k}+\mathbf{g}|R_s)\mathrm{j}_l(|\mathbf{k}+\mathbf{g}'|R_s)\mathrm{P}_l{}^0(\cos\theta_{\mathbf{g}\mathbf{g}'})}{\mathscr{R}_l(R_s)}\right] \tag{23}$$

where

$$\mathscr{R}_l{}'(R_s) = \frac{d}{dR_s}\mathscr{R}_l(R_s). \tag{24}$$

This definition of the effective matrix element can be compared with that obtained from the Kohn–Rostoker equations by using the relation

$$\frac{\mathscr{R}_l{}'(R_s)}{\mathscr{R}_l(R_s)} = \frac{\mathrm{j}_l{}'(\kappa R_s)}{\mathrm{j}_l(\kappa R_s)} - \frac{\tan\eta_l{}'}{\kappa R_s{}^2\mathrm{j}_l{}^2(\kappa R_s)} \tag{25}$$

which is just the definition of $\tan\eta_l{}'$, equation (11). It is found that

$$\Gamma_{\mathbf{g}\mathbf{g}'}{}' = \Gamma_{\mathbf{g}\mathbf{g}'} + \Gamma_{\mathbf{g}\mathbf{g}'}{}^0 \tag{26}$$

where $\Gamma_{\mathbf{g}\mathbf{g}'}{}^0$ is the value of $\Gamma_{\mathbf{g}\mathbf{g}'}{}'$ when $\mathscr{R}_l(\rho) = \mathrm{j}_l(\kappa\rho)$, i.e. it is the value of $\Gamma_{\mathbf{g}\mathbf{g}}{}'$ for an empty lattice. In general $\Gamma_{\mathbf{g}\mathbf{g}'}{}^0$ is not zero unless $\kappa^2 = |\mathbf{k}|^2$. This is an example of how different effective matrix elements can yield the same final result if the equations are solved exactly. In contrast with the behaviour of $\Gamma_{\mathbf{g}\mathbf{g}'}{}'$, $\Gamma_{\mathbf{g}\mathbf{g}'}$ vanishes for all values of κ and $\mathbf{k}$ for an empty lattice.

3. The scattering of Bloch waves by an impurity

The scattering of a Bloch wave $\psi_{\mathbf{k}}(\boldsymbol{\rho})$ by a perturbation $V(\boldsymbol{\rho})$ centred on a perfect lattice site will be considered, where $V(\boldsymbol{\rho})$ is the difference between an impurity potential and the perfect lattice potential. The transition probability per unit time from $\mathbf{k}$ to $\mathbf{k}'$ is given by

$$P_{\mathbf{k},\mathbf{k}'} = \frac{2\pi}{\hbar}|T_{\mathbf{k},\mathbf{k}'}|^2\delta\{E(\mathbf{k})-E(\mathbf{k}')\} \tag{27}$$

where $T_{\mathbf{k},\mathbf{k}'}$ is the T-matrix element, defined by

$$T_{\mathbf{k},\mathbf{k}'} = \int \psi_{\mathbf{k}'}{}^*(\boldsymbol{\rho})V(\boldsymbol{\rho})\psi(\boldsymbol{\rho})d\boldsymbol{\rho}. \tag{28}$$

$\psi_{\mathbf{k}'}(\boldsymbol{\rho})$ is a Bloch state having the same energy as the initial state $\psi_{\mathbf{k}}(\boldsymbol{\rho})$. $\psi(\boldsymbol{\rho})$ is the solution to the time-independent Schrödinger equation when a wave $\psi_{\mathbf{k}}(\rho)$ is scattered by $V(\boldsymbol{\rho})$. It will be assumed that the perturbation is spherically symmetric with the same radius R_s as the host atoms. The perfect lattice potentials themselves will be slightly altered owing to screening and other effects. A Bloch state will now mean a state calculated for the 'perfect perturbed' lattice. $T_{\mathbf{k},\mathbf{k}'}$ can be expressed as a surface integral over the volume of the perturbation by using standard methods, i.e.

$$T_{\mathbf{k},\mathbf{k}'} = R_s^2 \int \left\{ \psi_{\mathbf{k}'}^*(\boldsymbol{\rho}) \frac{\partial}{\partial \rho} \psi(\boldsymbol{\rho}) - \psi(\boldsymbol{\rho}) \frac{\partial}{\partial \rho} \psi_{\mathbf{k}'}^*(\rho) \right\}_{\rho = R_s} d\Omega(\boldsymbol{\rho}). \tag{29}$$

$T_{\mathbf{k},\mathbf{k}'}$ will be expressed in terms of the Fourier coefficients of the initial and final Bloch states in the form

$$T_{\mathbf{k},\mathbf{k}'} = \sum_{\mathbf{g}\mathbf{g}'} \alpha_{\mathbf{k}'+\mathbf{g}'}^* \alpha_{\mathbf{k}+\mathbf{g}} V_{\text{eff}}(\mathbf{k}+\mathbf{g}, \mathbf{k}'+\mathbf{g}') \tag{30}$$

and $V_{\text{eff}}(\mathbf{k}+\mathbf{g}, \mathbf{k}'+\mathbf{g}')$ will be defined as an effective matrix element between the states $\mathbf{k}+\mathbf{g}$ and $\mathbf{k}'+\mathbf{g}'$.

On the surface of, and just outside, the perturbation $\psi_{\mathbf{k}}(\boldsymbol{\rho})$ can be expanded as

$$\psi_{\mathbf{k}}(\boldsymbol{\rho}) = \sum_L i^l a_L(\mathbf{k}) \{ \mathrm{j}_l(\kappa\rho) + i \sin \eta_l \exp(i\eta_l) \mathrm{h}_l(\kappa\rho) \} \mathscr{Y}_L(\theta, \phi) \tag{31}$$

where the coefficients $a_L(\mathbf{k})$ are assumed known, say by a Kohn–Rostoker calculation. Inside the perturbation the wave function will be of the general form

$$\psi(\boldsymbol{\rho}) = \sum_L i^l c_L(\mathbf{k}) \mathscr{R}_l^1(\rho) \mathscr{Y}_L(\theta, \phi) \qquad (\rho \leqslant R_s) \tag{32}$$

where $\mathscr{R}_l^1(\rho)$ is a solution of the radial Schrödinger equation for the impurity potential and the c_L are to be determined. The scattered wave can be written as

$$\psi_s(\boldsymbol{\rho}) = \sum_L i^l \{ b_L(\mathbf{k}) \mathrm{h}_l(\kappa\rho) + \sum_{L'} T_{LL'} b_{L'}(\mathbf{k}) \mathrm{j}_l(\kappa\rho) \} \mathscr{Y}_L(\theta, \phi) \tag{33}$$

for ρ just greater than, or equal to, R_s. The significance of the matrix $T_{LL'}$ is that an outgoing wave $b_{L'}(\mathbf{k}) \mathrm{h}_{l'}(\kappa\rho) \mathscr{Y}_{L'}(\theta, \phi)$ diverging from the impurity is scattered by the surrounding lattice and produces a wave $T_{LL'} b_{L'}(\mathbf{k}) \mathrm{j}_l(\kappa\rho) \mathscr{Y}_L(\theta, \phi)$ at the origin. The impurity potential itself is not counted as a scattering centre. The wave function and its normal derivative must be continuous at $\rho = R_s$. This gives

$$[a_L \{ \mathrm{j}_l(\kappa\rho) + i \sin \eta_l \exp(i\eta_l) \mathrm{h}_l(\kappa\rho) \} + b_L \mathrm{h}_l(\kappa\rho) + \sum_{L'} T_{LL'} b_{L'} \mathrm{j}_l(\kappa\rho) = c_L \mathscr{R}_l^1(\rho)]_{\rho = R_s} \tag{34}$$

and

$$\left[\frac{d}{d\rho} [a_L \{ \mathrm{j}_l(\kappa\rho) + i \sin \eta_l \exp(i\eta_l) \mathrm{h}_l(\kappa\rho) \} + b_L \mathrm{h}_l(\kappa\rho) + \sum_{L'} T_{LL'} b_{L'} \mathrm{j}_l(\kappa\rho) = c_L \mathscr{R}_l^1(\rho)] \right]_{\rho = R_s}. \tag{35}$$

From (34) and (35) it is found that the coefficients $b_L(\mathbf{k})$ satisfy the equation

$$b_L - i \sin \eta_l^1 \exp(i\eta_l^1) \sum_{L'} T_{LL'} b_{L'} = a_L \{ i \sin \eta_l^1 \exp(i\eta_l^1) - i \sin \eta_l \exp(i\eta_l) \} \tag{36}$$

where η_l^1 is the lth phase shift for the impurity potential. The coefficients c_L are given in terms of the b_L by

$$c_L = \frac{i a_L \{ 1 + \sum_{L'} T_{LL'} b_{L'} / a_L \}}{\kappa R_s^2 [\mathscr{R}_l^1, \mathrm{h}_l]}. \tag{37}$$

Using an expression of the form (31) for $\psi_{\mathbf{k}'}(\boldsymbol{\rho})$ and expansion (32) for $\psi(\boldsymbol{\rho})$ it is found that

$$T_{\mathbf{k},\mathbf{k}'} = \kappa^{-1} \sum_{L} a_L^*(\mathbf{k}')a_L(\mathbf{k})\exp(i2\eta_l^1)\left\{1+\frac{\sum\limits_{L'} T_{LL'}b_{L'}}{a_L(\mathbf{k})}\right\}$$
$$\times\{\sin\eta_l\exp(-i\eta_l)-\sin\eta_l^1\exp(-i\eta_l^1)\}. \tag{38}$$

If the product $a_L^*(\mathbf{k}')a_L(\mathbf{k})$ is expressed in terms of the Fourier coefficients of $\psi_{\mathbf{k}'}^*$ and $\psi_{\mathbf{k}}$, then

$$V_{\text{eff}}(\mathbf{k}+\mathbf{g},\mathbf{k}'+\mathbf{g}')$$
$$=\frac{(4\pi)^2}{\kappa}\sum_{L}\frac{\tan^2\eta_l'}{\sin^2\eta_l}\exp(i2\eta_l^1)\{\sin\eta_l\exp(-i\eta_l)-\sin\eta_l^1\exp(-i\eta_l^1)\}\left\{1+\frac{\sum\limits_{L'} T_{LL'}b_{L'}}{a_L(\mathbf{k})}\right\}$$
$$\times\frac{\mathscr{Y}_L(\mathbf{k}+\mathbf{g})\mathscr{Y}_L(\mathbf{k}'+\mathbf{g}')\mathrm{j}_l(|\mathbf{k}+\mathbf{g}|R_s)\mathrm{j}_l(|\mathbf{k}'+\mathbf{g}'|R_s)}{\mathrm{j}_l^2(\kappa R_s)}. \tag{39}$$

There are two main difficulties in calculating the scattering of Bloch states. Firstly, knowledge of the matrix $T_{LL'}$ is required. Other formulations of the problem involve calculating the lattice Green function (Dupree 1961) which requires the evaluation of rather difficult integrals over the Brillouin zone. This difficulty has not been evaded, but phrasing the problem in terms of $T_{LL'}$ gives more insight into the scattering process, and simple approximations to $T_{LL'}$ can be envisaged more easily. The problem of calculating the Green function is replaced by the problem of determining the scattering by the surrounding lattice of a wave diverging from a lattice point. The second difficulty is solving equations like (36). If a large number of phase shifts are required to describe the scattering, this becomes rather difficult. Some situations will now be considered where simplifications can be introduced.

3.1. *Nearly free electrons*

A free electron travelling through a metal, with an energy lying in the conduction band, can be scattered very little by a single potential well, and strong reflection occurs only when the electron is Bragg reflected. The same type of behaviour is to be expected for a spherical wave spreading out from a lattice point. If the reflected waves are ignored, i.e. if $T_{LL'}$ is put equal to zero, it is found from equation (39) that

$$V_{\text{eff}}(\mathbf{k}+\mathbf{g},\mathbf{k}'+\mathbf{g}')$$
$$\simeq\frac{4\pi}{\kappa}\sum_{l}(2l+1)\frac{\tan^2\eta_l'}{\sin^2\eta_l}\exp(i2\eta_l^1)\{\sin\eta_l\exp(-i\eta_l)-\sin\eta_l^1\exp(-i\eta_l^1)\}$$
$$\times\frac{\mathrm{j}_l(|\mathbf{k}+\mathbf{g}|R_s)\mathrm{j}_l(|\mathbf{k}'+\mathbf{g}'|R_s)}{\mathrm{j}_l^2(\kappa R_s)}\mathrm{P}_l^0(\cos\theta_{\mathbf{k}+\mathbf{g},\mathbf{k}'+\mathbf{g}'}) \tag{40}$$

where $\theta_{\mathbf{k}+\mathbf{g},\mathbf{k}'+\mathbf{g}'}$ is the angle between $\mathbf{k}+\mathbf{g}$ and $\mathbf{k}'+\mathbf{g}'$. The above approximation is especially good when the outgoing waves are weak, because in equation (39) the product $T_{LL'}b_{L'}$ is then small. In other words $\psi(\boldsymbol{\rho})$ can be very nearly matched to the incoming wave alone. It is interesting to compare (40) with the form for $V_{\text{eff}}(\mathbf{k},\mathbf{k}')$ suggested by Ziman (1964). This was

$$V_{\text{eff}}(\mathbf{k},\mathbf{k}')\simeq\frac{4\pi}{\kappa}\sum_{l}(2l+1)\{\sin\eta_l\exp(i\eta_l)-\sin\eta_l^1\exp(i\eta_l^1)\}\mathrm{P}_l^0(\cos\theta_{\mathbf{k},\mathbf{k}'}). \tag{41}$$

Equation (40) reduces to this when sin η_l and sin η_l^1 are small and $\kappa^2 \simeq |\mathbf{k}|^2$. For an outgoing wave with an energy close to the band edge, coherent reflection will occur. This effect should be of secondary importance if the outgoing wave is weak. $T_{LL'}$ could be calculated approximately by ignoring multiple scattering effects, but even this simplification would involve quite a considerable amount of computation.

3.2. *Tightly bound electrons*

The transition probability from **k** to **k**′ for tightly bound electrons is not as important a problem as for electrons which can participate in electrical conduction. However, it is interesting to note that equation (40) is also a good approximation in this situation. This is because the energy of these states is negative. The outgoing waves now decay rapidly, and in consequence barely reach the surrounding lattice. This conclusion can also be obtained by using the tight-binding approximation for the lattice Green function given by Beeby and Edwards (1963).

3.3. *d-band electrons*

The most interesting and apparently most difficult situation is when an electron band crosses a resonant d level as in the noble metals. A free electron introduced into the lattice with these energies can be scattered strongly by a single potential well. However, if an impurity potential is introduced which has phase shifts η_l^1 close to the unperturbed η_l then the scattered wave must be weak and the remarks made in § 3.1 will be valid. Even in this extreme case, (40) should provide a reasonable estimate of the scattering.

When the outgoing waves are not weak and the lattice reflects strongly it is difficult to construct a simple approximation. It is suggested that $T_{LL'}$ might be calculated approximately by considering only the scattering from the nearest neighbours of the impurity. The outgoing wave may be 'trapped' in the region of the impurity if the scattering from the surrounding atoms is large.

Acknowledgments

I am grateful to Professor J. M. Ziman for suggesting this problem and for generous advice.

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