MANY BODY INTERACTIONS AND LATTICE DYNAMICS OF ATOMIC CRYSTALS

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To my mother whose faith and
love has never failed
through hardship and sorrow.

ABSTRACT

The aim of this work is to establish whether the addition of three body interactions are by themselves sufficient to ensure mechanical stability of a particular crystal structure or whether higher multibody interactions are needed also.

The criteron chosen to establish such stability is namely the positive definiteness of the elastic energy, which can be calculated from the elastic constants. The elastic constants can in turn be calculated from values of the atomic force constants which are obtained by fitting theoretical dispersion curves to experimental data.

A summary of the general theory of lattice dynamics as well as atomic elasticity theory is presented with additional comments on the various types of elastic constants often found in the literature. A parallel account of elasticity theory by including a general three body potential function instead of the usual two body (central force) potential is given where most of the simplifications found in previous works vanished so that some of the consequential results such as the Cauchy relations where found not to be valid. A new set of three body parameters are developed and used to work out expressions for the elastic constants and also to test whether in a cubic lattice a three body potential confers stability.

We test the usefulness of such parameters when we use them to write down the elastic constants for the diamond crystal lattice. The expressions are then compared to those arrived at by the use of valence bond potentials. Calculations using general force constant

parameters to describe atomic interactions show that we need to go to fifth nearest neighbours (at least) before the crystal stability conditions are fulfilled. This problem of stability is readdressed here by the inclusion of possible three body interactions amongst atoms.

We also use an analytical expression based on a Morse potential function which describes the interactions amongst three carbon atoms. This potential comes from considering the spectroscopic data of the C_3 molecule. We use such a potential as an example of how the elastic constants of diamond might be calculated.

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1.1 LATTICE DYNAMICS

Since the pioneering work of Born and von Karman (Born and Th. von Karman 1912) the majority of the theoretical work done on vibrational properties of solids has been based on force constants models in which the values of the atomic force constants have been obtained by fitting theoretical dispersion curves to experimental data.

The dispersion curves of long wavelengths acoustic phonons can be fitted to the predictions of elasticity theory, while the frequencies of long wavelength optical phonons can be fitted to the results of infrared absorption or Raman scattering.

The phenomenological approaches to lattice dynamics suffer from two major deficiencies. The first is that they are not predictive: the values of the atomic force constants and of the resulting dispersion curves are inferred from experimental data rather than predicted by some more fundamental approach to their determination. The second is that they are not unique: often more than one model can reproduce the experimental curves equally well.

The general theory of lattice dynamics has been described in detail by several authors (Born and Huang 1954, Maradudin *et el* 1963, Horton and Maradudin 1974). The theory is based on two approximations. First the adiabatic approximation is used to postulate that the total energy of the solid is the sum of the kinetic energy of the atoms and a potential energy depending only on the instantaneous nuclear positions. This is tantamount to the assumption that the electrons are always able to adapt themselves completely to the instantaneous nuclear positions. Then the potential energy of the lattice may be written in a general Taylor series in terms of the displacements $u_\alpha\begin{pmatrix} l \\ k \end{pmatrix}$ of the kth atom in the lth unit cell as

$$\Phi = \Phi_0 + \sum_{lk\alpha} \Phi_\alpha\begin{pmatrix} l \\ k \end{pmatrix} u_\alpha\begin{pmatrix} l \\ k \end{pmatrix} + \frac{1}{2}\sum_{l\,k}\sum_{\substack{l'\,k'}}\!{}_{,\alpha\beta}\ \Phi_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} u_\alpha\begin{pmatrix} l \\ k \end{pmatrix} u_\beta\begin{pmatrix} l' \\ k' \end{pmatrix} + \ldots$$

[1.1.1]

For small displacements only the leading quadratic term is considered, i.e. the harmonic approximation. Though the other higher terms are small they are responsible for thermal resistance and thermal expansion. Thus we write

$$\Phi - \Phi_0 = \frac{1}{2}\sum_{l\,k}\sum_{\substack{l'\,k'}}\!{}_{,\alpha\beta}\ \Phi_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} u_\alpha\begin{pmatrix} l \\ k \end{pmatrix} u_\beta\begin{pmatrix} l' \\ k' \end{pmatrix}.$$

[1.1.2]

The parameters (coefficients of the Taylor expansion) of the potential function cannot be determined in a unique way from the macroscopic properties. From the equations of motion we have

$$\Omega W = C(q)W,$$

[1.1.3]

where $C(q)$ is the force constant matrix and W are its eigenvectors corresponding to the normal modes with associated frequencies Ω.

The force constants cannot be deduced from the frequencies alone. If a set of force constants agrees with the frequencies exactly there is no guarantee that the force constants are correct. A solid has many more force constants than frequencies so that the lattice frequencies can be satisfied by very different force constants. The knowledge of these frequencies is not sufficient for calculation of the force constants (Former and Lomer 1957, Cochran 1971, Leigh *et al* 1971) and the eigenvectors W must also be measured (Strauch *et al* 1990).

Restrictions on the atomic force constant come from the translational and rotational invariance of the potential energy. The translational invariance condition is (Born and Huang 1954) given by

$$\sum_{lk} \Phi_{\alpha}\begin{pmatrix} l \\ k \end{pmatrix} = 0, \qquad \sum_{lk} \Phi_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} = \sum_{l'k'} \Phi_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} = 0.$$

[1.1.4]

The rotational invariance condition is

$$\sum_{lk} \Phi_{\alpha}\begin{pmatrix} l \\ k \end{pmatrix} x_{\beta}\begin{pmatrix} l \\ k \end{pmatrix} = \sum_{lk} \Phi_{\beta}\begin{pmatrix} l \\ k \end{pmatrix} x_{\alpha}\begin{pmatrix} l \\ k \end{pmatrix},$$

$$\sum_{l'k'} \Phi_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} x_{\gamma}\begin{pmatrix} l' \\ k' \end{pmatrix} - \delta_{\alpha\beta}\Phi_{\gamma}\begin{pmatrix} l \\ k \end{pmatrix} = \sum_{l'k'} \Phi_{\alpha\gamma}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} x_{\beta}\begin{pmatrix} l' \\ k' \end{pmatrix} - \delta_{\alpha\gamma}\Phi_{\beta}\begin{pmatrix} l \\ k \end{pmatrix}.$$

[1.1.5]

Further restrictions are placed by the symmetry of the crystal structure also. If we write equation [1.1.3] explicitly we have

$$\omega^2 W_{\alpha}(k) = -\sum_{k'}\sum_{\beta} C_{\alpha\beta}\begin{pmatrix} & q & \\ k & & k' \end{pmatrix} W_{\beta}(k').$$

[1.1.6]

where $C_{\alpha\beta}(q:kk')$ is the dynamical matrix in reciprocal space (the Fourier transform of $\Phi_{\alpha\beta}(ll':kk')$. The vibrational frequencies ω are the roots of the secular equation

$$| C(q) - \omega^2 I | = 0, \qquad [1.1.7]$$

where I is the unit matrix of order 3s×3s. For a particular wave vector q, the characteristic equation [1.1.7] has 3s roots ω_j where s is the number of atoms in the unit cell. These roots (the acoustic modes) tend to zero as $q \longrightarrow 0$ while the remaining 3s-3 roots (the optical modes) tend to finite values as $q \longrightarrow 0$. These 3s-3 limiting frequencies may contibute to the first-order Raman spectrum of the lattice.

When the wave vector q lies along one of the symmetry directions of a particular crystal structure then the secular equation [1.1.7] factorises and may therefore be solved directly. The physical interpretation of this is that along a symmetry direction the wave propagating corresponds to the vibrations of complete planes of atoms so that the mathematical problem becomes one of a linear chain of particles, each connected to its neighbour by harmonic forces and where each particle represents a plane of atoms.

The solution of the secular equation for a particular value of q gives rise to dispersion relations that is the frequency given as a function of the wave vector q. These dispersion curves can be determined experimentally (Cochran 1973) by the use of radiation comparable with the interatomic distances. The most powerful method of studying lattice vibrations uses a beam of mono-energetic neutrons. The changes in wavelengths of the scattered neutrons lead directly to the dispersion relations between the frequencies and wave vectors of normal modes of vibrations of the crystal.

1.2 PARAMETRIC THEORY OF ELASTICITY

The microscopic theory of elasticity is built on the concept of interatomic forces. These are derived from an atomic potential energy usually taken in the adiabatic approximation. The second derivatives of the potential are the force constants. Huang (1950) and Born and Huang (1954) have derived a relation between the force constants and the elastic constants by comparing the microscopic equations for long waves with the equation for homogeneous deformation.

It is usual in standard treatments of lattice theory of crystals to assume some specific types of atomic interactions, such as central forces, interactions between oriented molecules, etc. In view of the great diversity of binding forces which are known to occur in different types of solids, then no such assumption will prove generally valid. Much that is basic in the lattice theory is, however common to all types of crystalline solids independent of the particular nature of the binding forces. The work of Born and Huang (1954) on lattice dynamics as given in previous section 1.1 can be thought of in two ways: the first describes the existence of a potential energy function Φ which is assumed but not specified. The crystal properties are expressed in terms of the Taylor expansion coefficients of Φ and these coefficients are regarded as parameters in the theory. In the second a function is assumed for the potential energy so that the crystal properties are now expressed in terms of the parameters of the potential itself. We usually assume that the potential is a two body (central force) potential which Born and his co workers follow through in their analysis. If we focus on the first assumption it was found (Born 1954) that complications arise when we try to write down expressions for the elastic coefficients. Elastic properties are macroscopic and the corresponding theory is expressed in terms of the energy density (i.e. energy per unit volume) and its expansion are in terms of small displacements from equilibrium. The relationships of this to the Taylor expansion of the potential energy is not simple and the method of long waves discussed later in the chapter, was introduced to deal with this problem. The resulting expressions for the stresses and the elastic constants in terms of the potential energy coefficients are complicated and also it is actually not possible to express the hydrostatic pressure in these terms.

Since in this thesis we pay most attention to the elastic properties it is useful to recognise that parametric form of lattice theory is possible, which unlike the Born approach begins with the assumption of an energy density function and examines the possibility of expressing the results in terms of the coefficients in an appropriate expansion. We can identify those results which are general and which do not depend on the form of the potential assumed. The potential energy density is denoted by Ψ and we go on to find expressions for the change in value of this function when departures from the initial atomic configurations are made. Any generalized displacement will be composed of changes in the Cartesian coordinates of the atoms $u_{\alpha}\begin{pmatrix} l \\ k \end{pmatrix}$ i.e. the same coordinates as used in the last section.

The displacements are restricted as in the homogeneous deformations to small displacements. Homogeneous here is equivalent to the macroscopic sense that is that there is no departure from uniform density. At the atomic level this can be taken to be equivalent to the requirement that the initial unit cell remains a unit cell of the deformed lattice. In this way the atomic displacements in a homogeneous deformation can be written as

$$u_\alpha\begin{pmatrix} l \\ k \end{pmatrix} = u_\alpha(k) + \sum_\beta u_{\alpha\beta}\text{æ}_\beta\begin{pmatrix} l \\ k \end{pmatrix} \qquad [1.2.1]$$

The coefficients $u_{\alpha\beta}$ are constants which may be identified with components of the strain in elasticity theory (strain is described in more detail in section 1.5). The strain coefficients specify the change in shape of the unit cell. The symbol $\text{æ}_\beta\begin{pmatrix} l \\ k \end{pmatrix}$ represents the coordinates of the atom with respect to some crystal fixed origin. The shape and size of the unit cell is not sufficient to determine the atomic positions completely. Changes in atomic position may take place within the cell as a result of the deformation and these changes are represented by $u_\alpha(k)$ and called internal strains (Cousins 1978). The unit cell index l does not appear since the displacement is clearly the same for all unit cells. It is recognised at this point that the unit cell shape changes and the atomic displacements are not totally independent. In the extreme case of one atom per unit cell, the atomic coordinates determine the size and shape of the unit cell.

Elasticity theory focuses on the strains and the changes in atomic position $u_\alpha(k)$ would be taken as zero. When we generalise this idea we can see that only relative changes in atomic positions contribute to [1.2.1].

A formal expansion for the change in energy density in terms of the coefficients in [1.2.1] is written down as

$$\Delta\Psi = \sum_{k\alpha} \left\{ \begin{matrix} k \\ \alpha \end{matrix} \right\} u_\alpha(k) + \sum_{\alpha\beta} \{\alpha\beta\} u_{\alpha\beta} + \tfrac{1}{2} \sum_{k\alpha} \sum_{k'\beta} \left\{ \begin{matrix} k & k' \\ \alpha & \beta \end{matrix} \right\} u_\alpha(k) u_\beta(k')$$

$$+ \sum_{k\alpha} \sum_{\beta\gamma} \left\{ \begin{matrix} k & \\ \alpha & \beta\gamma \end{matrix} \right\} u_\alpha(k) u_{\beta\gamma} + \tfrac{1}{2} \sum_{\alpha\beta} \sum_{\gamma\lambda} \left\{ \alpha\beta\gamma\lambda \right\} u_{\alpha\beta} u_{\gamma\lambda}.$$

[1.2.2]

The linear coefficients of $u_{\alpha\beta}$ may be identified with the elastic stresses in the initial configuration. If we require that the system is initially stress free then the linear coefficients must vanish

$$\{\alpha\beta\} = 0.$$

[1.2.3]

Correspondingly the linear coefficients of $u_\alpha(k)$ represent the force acting on the atom must also be zero if the system is initially in equilibrium then

$$\left\{ \begin{matrix} k \\ \alpha \end{matrix} \right\} = 0.$$

[1.2.4]

Born has discussed this in detail and points out that for an infinite crystal system, both conditions are necessary for equilibrium.

As with the potential energy parametric theory, $\Delta\Psi$ must be rotationally invariant. At the level of the homogeneous deformation [1.2.1], this implies that the antisymmetric part of $u_{\alpha\beta}$ which is wholly rotational gives no change in the energy density. In consequence all coefficients are symmetric to interchange of α and β.

$$\{\alpha\beta\} = \{\beta\alpha\}, \tag{1.2.5}$$

$$\{\alpha\beta,\gamma\lambda\} = \{\beta\alpha,\gamma\lambda\} = \{\alpha\beta,\lambda\gamma\}, \tag{1.2.6}$$

$$\left\{\begin{matrix} k \\ \alpha \end{matrix}\ \beta\gamma\right\} = \left\{\begin{matrix} k \\ \alpha \end{matrix}\ \gamma\beta\right\}. \tag{1.2.7}$$

For a system initially at equilibrium the linear terms in [1.2.2] vanish. The quadratic terms now lead the expansion. They involve not only the macroscopic but also the internal strains which do not appear directly in the macroscopic theory. It would be expected that the atomic displacements within the unit cell would be such as to minimise the rise in energy density. In this way

$$\frac{\partial\Delta\Psi}{\partial u_\alpha(k)} = \sum_{k'\beta}\left\{\begin{matrix} k & k' \\ \alpha & \beta \end{matrix}\right\}u_\beta(k') + \sum_{\beta\gamma}\left\{\begin{matrix} k \\ \alpha \end{matrix}\ \beta\gamma\right\}u_{\beta\gamma} = 0, \tag{1.2.8}$$

so that the internal strains and external strains are related. Since only relative atomic displacements contribute (this can be thought of as a consequence of translational invariance), the matrix of coefficients of internal strain is of rank (3n-3). A convenient procedure is to fix $u_\alpha(1)=0$ and to invert the square matrix of order (3n-3). This leads to

$$u_\alpha(k) = -\sum_{k'\beta}\sum_{\gamma\lambda}\left\{\begin{matrix} k & k' \\ \alpha & \beta \end{matrix}\right\}^{\dagger}\left\{\begin{matrix} k' & \gamma\lambda \\ \beta & \end{matrix}\right\}u_{\gamma\lambda}. \qquad [1.2.9]$$

Where k,k'= 2,3...n and $\{k\alpha:k'\beta\}^{\dagger}$ is the inverse matrix. Substituting back into [1.2.2] leads to a term quadratic only in $u_{\alpha\beta}$. The corresponding coefficients can be identified with the elastic moduli of conventional elasticity theory

$$\Delta\Psi = \frac{1}{2}\sum_{\alpha\beta}\sum_{\lambda\gamma} c_{\alpha\beta\gamma\lambda}u_{\alpha\beta}u_{\gamma\lambda}, \qquad [1.2.10]$$

in which

$$c_{\alpha\beta,\gamma\lambda} = \{\alpha\beta,\gamma\lambda\} - \sum_{kk'}\sum_{\mu\nu}\left\{\begin{matrix} k & k' \\ \mu & \nu \end{matrix}\right\}^{\dagger}\left\{\begin{matrix} k & \alpha\beta \\ \mu & \end{matrix}\right\}\left\{\begin{matrix} k' & \gamma\lambda \\ \nu & \end{matrix}\right\}. \qquad [1.2.11]$$

The coefficients $\{k\alpha:k'\beta\}$ may be discussed in terms of lattice vibrations. It has been stated that Ψ is the potential energy density and Φ (in section 1.1) is the potential energy. The two may be related

$$\Phi = Nv_a\Psi, \tag{1.2.12}$$

in which v_a is the volume of the unit cell and N the number of unit crystals. In the development of Ψ described in this section, attention is confined to displacements in which the unit cell is preserved i.e. a homogeneous deformation. The quadratic terms in the expansion of the potential energy are from [1.1.1]

$$\frac{1}{2}\sum_{\substack{lk\\ l'k'}}\sum_{\alpha\beta} \Phi_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} u_\alpha\begin{pmatrix} l \\ k \end{pmatrix} u_\beta\begin{pmatrix} l' \\ k' \end{pmatrix}, \tag{1.2.13}$$

which becomes (if attention is restricted to homogeneous deformations and account taken of lattice translational invariance of the force constants)

$$\frac{1}{2}\sum_{k\alpha}\sum_{k'\beta}\left[N\sum_{l}\Phi_{\alpha\beta}\begin{pmatrix} l & 0 \\ k & k' \end{pmatrix}\right]u_\alpha(k)u_\beta(k'). \tag{1.2.14}$$

Comparing [1.2.12] and [1.2.2]

$$\begin{Bmatrix} k & k' \\ \alpha & \beta \end{Bmatrix} = v_a^{-1}\sum_{l}\Phi_{\alpha\beta}\begin{pmatrix} l & 0 \\ k & k' \end{pmatrix}. \tag{1.2.15}$$

In this way, the internal strain coefficients can be identified with a block of force constants in the lattice vibration problem. Furthermore in terms of translation symmetry, the force constants block corresponds to zero wave vector. The corresponding vibrations are potentially allowed in optical transitions and hence information about the internal strain parameters is in principle obtainable from spectroscopic measurements. The vibrations corresponding to the force constant block [1.2.15] always include three zero frequencies representing lattice translation. This is in line with the general result from solid state physics that for there to be optical branches in the lattice vibration dispersion curves at least two atoms per unit cell are required. In a favourable case such as diamond, there is only one non-vanishing force constant, the value of which may be deduced from the Raman spectrum.

In the expression for the elastic constant [1.2.11], it is the inverse of the force constant matrix which appears, an element of which is known as a compliance constant.

1.3 CENTRAL FORCES AND THE METHOD OF LONG WAVES

When a specific assumption is made about the form of the potential function Φ, it becomes possible to write down the energy density Ψ and hence determine explicitly expressions for the coefficients in the homogeneous deformation expansion. The most usual choice has been the two atom (central) interaction (Epstein 1946, Zener 1947).

In this case, the potential energy has the form

$$\Phi = \frac{1}{2}\sum_{lk}\sum_{l'k'}\Psi\begin{pmatrix} l & l' \\ k & k' \end{pmatrix},$$

[1.3.1]

where Ψ(lk:l'k') is the pair potential for the two atoms indicated. The factor one half appears because each pair is counted twice. If attention is restricted to homogeneous deformations, the value of the sum over l for a fixed value of l' is independent of the value of l'. Hence in the case of a homogeneous deformation

$$\Phi = \frac{1}{2}N\sum_{lk}\sum_{k'}\Psi\begin{pmatrix} l & 0 \\ k & k' \end{pmatrix},$$

[1.3.2]

and the energy density from [1.2.12] is

$$\Psi = \frac{1}{2v_a}\sum_{lk}\sum_{k'}\Psi\begin{pmatrix} l & 0 \\ k & k' \end{pmatrix}.$$

[1.3.3]

As described in the last section, in a homogeneous deformation each atom is displaced by an amount depending on both the internal and external strain. Each pair potential depends on only one independent variable which will be taken as the square of the distance separating the two atoms. Expansions will be written in terms of derivatives with respect to this variable with the dependence on atomic Cartesian coordinates being written explicitly. In this way, the first two terms in an expansion describing atomic displacements for a single pair potential term may be written

$$\Psi'(|x|^2)\left[2\sum_{\alpha}\text{æ}_{\alpha}\,\Delta\text{æ}_{\alpha} + \sum_{\alpha}(\Delta\text{æ}_{\alpha})^2\right] + 2\Psi''(|x|^2)\left[\sum_{\alpha}\text{æ}_{\alpha}\Delta\text{æ}_{\alpha}\right]^2,$$

[1.3.4]

and by extension, the total energy change per unit cell to the same degree of approximation has the form

$$\frac{1}{2}\sum_{k}\sum_{l'k'}\left\{\Psi'_{kk'}\left(\left|x\begin{pmatrix} l' \\ k' \end{pmatrix} - x\begin{pmatrix} 0 \\ k \end{pmatrix}\right|^2\right) \times\right.$$

$$\left[2\sum_{\alpha}\left(\text{æ}_{\alpha}\begin{pmatrix} l' \\ k' \end{pmatrix} - \text{æ}_{\alpha}\begin{pmatrix} 0 \\ k \end{pmatrix}\right)\left(u_{\alpha}\begin{pmatrix} l' \\ k' \end{pmatrix} - u_{\alpha}\begin{pmatrix} 0 \\ k \end{pmatrix}\right) + \sum_{\alpha}\left(u_{\alpha}\begin{pmatrix} l' \\ k' \end{pmatrix} - u_{\alpha}\begin{pmatrix} 0 \\ k \end{pmatrix}\right)^2\right]$$

$$+\, 2\Psi''_{kk'}\left(\left|x\begin{pmatrix} l' \\ k' \end{pmatrix} - x\begin{pmatrix} 0 \\ k \end{pmatrix}\right|^2\right) \times$$

$$\left.\times\left[\sum_{\alpha}\left(\text{æ}_{\alpha}\begin{pmatrix} l' \\ k' \end{pmatrix} - \text{æ}_{\alpha}\begin{pmatrix} 0 \\ k \end{pmatrix}\right)\left(u_{\alpha}\begin{pmatrix} l' \\ k' \end{pmatrix} - u_{\alpha}\begin{pmatrix} 0 \\ k \end{pmatrix}\right)\right]^2\right\},$$

[1.3.5]

where $\Psi_{kk'}$ refers to the potential function between particles of the type k and k'. For a homogeneous deformation, the substitution

$$\left(u_{\alpha}\begin{pmatrix} l' \\ k' \end{pmatrix} - u_{\alpha}\begin{pmatrix} 0 \\ k \end{pmatrix}\right) = u_{\alpha}(k') - u_{\alpha}(k) + \sum_{\beta} u_{\alpha\beta}\text{æ}_{\beta}\begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix},$$

[1.3.6]

leads to an expression for the energy density given below

$$
\begin{aligned}
u = \frac{1}{v_a} \Bigg\{ & -2 \sum_{k\alpha} \left(u_\alpha(k) + \sum_{\beta} u_\beta(k) u_{\beta\alpha} \right) \sum_{l'k'} \left[\Psi' \text{æ}_\alpha \right]_x \begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix} + \\
& + \sum_{\alpha\beta} \left(u_{\alpha\beta} + \frac{1}{2} \sum_{\gamma} u_{\gamma\alpha} u_{\gamma\beta} \right) \sum_{l'k'k} \left[\Psi' \text{æ}_\alpha \text{æ}_\beta \right]_x \begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix} + \\
& \sum_{k\alpha} \sum_{k'\beta} u_\alpha(k) u_\beta(k') \Bigg(\delta_{kk'} \delta_{\alpha\beta} \sum_{l'k''} \left[\Psi' \right]_x \begin{pmatrix} l' & 0 \\ k'' & k \end{pmatrix} - \delta_{\alpha\beta} \sum_{l'} \left[\Psi' \right]_x \begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix} + \\
& + 2\delta_{kk'} \sum_{l'k''} \left[\Psi'' \text{æ}_\alpha \text{æ}_\beta \right]_x \begin{pmatrix} l' & 0 \\ k'' & k \end{pmatrix} - 2 \sum_{l'} \left[\Psi'' \text{æ}_\alpha \text{æ}_\beta \right]_x \begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix} \Bigg) - \\
& -4 \sum_{k\alpha} \sum_{\beta\gamma} u_\alpha(k) u_{\beta\gamma} \sum_{l'k'} \left[\Psi'' \text{æ}_\alpha \text{æ}_\beta \text{æ}_\gamma \right]_x \begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix} + \\
& + \sum_{\alpha\beta\gamma\lambda} u_{\alpha\gamma} u_{\beta\lambda} \sum_{l'k'k} \left[\Psi'' \text{æ}_\alpha \text{æ}_\gamma \text{æ}_\beta \text{æ}_\lambda \right]_x \begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix} \Bigg\}.
\end{aligned}
\qquad [1.3.7]
$$

To shorten this very complicated expression, the convention is adopted that all items within square brackets refer to the atom pair specified immediately after the brackets

The equilibrium conditions (corresponding to [1.2.3] and [1.2.4]) have the explicit form

$$\sum_{l'k'} \left[\Psi' \text{æ}_{\alpha} \right]_x \begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix} = 0, \qquad \sum_{l'k'k} \left[\Psi' \text{æ}_{\alpha} \text{æ}_{\beta} \right]_x \begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix} = 0.$$

[1.3.8]

By comparison with [1.2.2], expressions for the various elastic coefficients can be deduced. In particular, it is noticed that for the particular case of central interactions, the coefficients have additional symmetry properties. They are in fact symmetric to exchange of all Greek indices in contrast to [1.2.5] to [1.2.7].

It has already been mentioned that the Born theory starts from the potential energy function Φ and expresses crystal properties as far as possible in terms of the Taylor expansion coefficients. A connection is made with elasticity theory by noting that acoustic branch lattice vibrations and elastic waves become identical in the limit of long wavelength. For a particular direction of wave vector, the elastic dispersion curve is a straight line to be identified with the limiting slope of the corresponding acoustic branch. The theory is set as a perturbation expansion and known as the method of long waves.

The equation of motion is written as

$$m\ddot{u}_{\alpha}\begin{pmatrix} l \\ k \end{pmatrix} = -\sum_{l'k'\beta} \Phi_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} u_{\beta}\begin{pmatrix} l' \\ k' \end{pmatrix},$$

[1.3.9]

and becomes after taking the Fourier transform of the above equation

$$\omega^2 W_\alpha(k) = -\sum_{k'}\sum_{\beta} C_{\alpha\beta}\begin{pmatrix} q \\ k\;k' \end{pmatrix} W_\beta(k').$$

[1.3.10]

Where the coefficients are defined as

$$C_{\alpha\beta}\begin{pmatrix} q \\ k\;k' \end{pmatrix} = (m_k m_{k'})^{-1/2}\sum_{l'} \Phi_{\alpha\beta}\begin{pmatrix} l-l' \\ k\;k' \end{pmatrix}\exp\left\{-2\pi i q.\left(\text{æ}\begin{pmatrix} l \\ k \end{pmatrix} - \text{æ}\begin{pmatrix} l' \\ k' \end{pmatrix}\right)\right\}.$$

[1.3.11]

The coefficient $C_{\alpha\beta}(q{:}kk')$ is expanded in powers of the magnitude of q for a particular direction of the wave vector. A perturbation parameter λ is introduced by writing λq in place of the wave vector. The perturbation expansion is

$$C_{\alpha\beta}\begin{pmatrix} q \\ k\;k' \end{pmatrix} = C^{(0)}_{\alpha\beta}(kk') + i\lambda C^{(1)}_{\alpha\beta,\gamma}(kk')q_\gamma + \lambda^2 C^{(2)}_{\alpha\beta,\gamma\lambda}(kk')q_\gamma q_\lambda + \ldots,$$

[1.3.12]

in which the coefficients are

$$C^{(0)}_{\alpha\beta}(kk') = \frac{1}{(m_k m_{k'})^{1/2}}\sum_{l} \Phi_{\alpha\beta}\begin{pmatrix} l \\ k\;k' \end{pmatrix} = C^{(0)}_{\beta\alpha}(k'k),$$

$$C^{(1)}_{\alpha\beta,\gamma}(kk') = \frac{-2\pi}{(m_k m_{k'})^{1/2}}\sum_{l} \Phi_{\alpha\beta}\begin{pmatrix} l \\ k\;k' \end{pmatrix}\text{æ}_\gamma\begin{pmatrix} l \\ k\;k' \end{pmatrix} = -C^{(1)}_{\beta\alpha,\gamma}(k'k),$$

$$C^{(2)}_{\alpha\beta,\gamma\lambda}(kk') = \frac{-4\pi^2}{(m_k m_{k'})^{1/2}}\sum_{l} \Phi_{\alpha\beta}\begin{pmatrix} l \\ k\;k' \end{pmatrix}\text{æ}_\gamma\begin{pmatrix} l \\ k\;k' \end{pmatrix}\text{æ}_\lambda\begin{pmatrix} l \\ k\;k' \end{pmatrix} =$$

$$= C^{(2)}_{\alpha\beta,\lambda\gamma}(kk') = C^{(2)}_{\beta\alpha,\gamma\lambda}(k'k).$$

[1.3.13]

From the above equations the zero, first and second order equations are obtained. The zero order equations are satisfied by making an arbitrary choice for the three independent polarization vectors of the plane waves. The first order equations give the relative displacements of the various atoms in any unit cell; these are known as the inner strains which occur when the crystal is deformed homogeneously. The second order equations provide the characteristic determinant from which the vibration frequencies and the corresponding directions of particle polarisation can be deduced (Huntington 1958).

The macroscopic equation describing elastic waves is given as

$$\rho \ddot{u}_\alpha = \sum_{\beta\gamma\lambda} c_{\alpha\gamma,\beta\lambda} \frac{\partial^2 u_\beta}{\partial x_\gamma \partial x_\lambda},$$

[1.3.14]

where ρ is the mass density. If we consider an elastic wave

$$u(x,t) = \bar{u} \exp\{2\pi i q.r - i\omega t\},$$

[1.3.15]

and we substitute the expression back into [1.3.14] then we have

$$\rho\omega^2 \bar{u}_\alpha = 4\pi^2 \sum_\beta \left\{ \sum_{\gamma\lambda} c_{\alpha\gamma,\beta\lambda} q_\gamma q_\lambda \right\} \bar{u}_\beta .$$

[1.3.16]

We can compare this equation to that obtained by the method of long waves which is given as

$$\left(\frac{\sum_k m_k}{v_a}\right)\left[\omega^{(1)}\begin{pmatrix} q \\ j \end{pmatrix}\right]^2 u_\alpha(j) =$$

$$= 4\pi^2 \sum_\beta \left\{ \sum_{\gamma\lambda} [\alpha\beta,\gamma\lambda] q_\gamma q_\lambda + \sum_{\gamma\lambda} (\alpha\gamma,\beta\lambda) q_\gamma q_\lambda \right\} u_\beta(j).$$

[1.3.17]

in which

$$[\alpha\beta,\gamma\lambda] = (8\pi^2 v_a)^{-1} \sum_{kk'} \surd(m_k m_{k'}) C^{(2)}_{\alpha\beta,\gamma\lambda}(kk')$$

[1.3.18]

and

$$(\alpha\gamma,\beta\lambda) = -(4\pi^2 v_a)^{-1} \sum_{kk'}\sum_{\mu\nu} \Gamma_{\mu\nu}(kk')\left\{\sum_s C^{(1)}_{\mu\alpha,\gamma}(ks)\surd m_s\right\}\left\{\sum_t C^{(1)}_{\nu\beta,\lambda}(k't)\surd m_t\right\}$$

[1.3.19]

Where s=k'' and t=k'''. Matrix $\Gamma_{\mu\nu}$ (kk') in Born's notation is identical with the compliance matrix $\{k\mu:k'\nu\}^\dagger$ in [1.2.11].

The brackets satisfy the the symmetry relations

$$[\alpha\beta,\gamma\lambda] = [\beta\alpha,\gamma\lambda] = [\alpha\beta,\lambda\gamma],$$

$$(\alpha\beta,\gamma\lambda) = (\beta\alpha,\gamma\lambda) = (\gamma\lambda,\alpha\beta),$$

[1.3.20]

For the two expressions [1.3.16] and [1.3.17] to be identical we must have

$$\sum_{\gamma\lambda} c_{\alpha\gamma,\beta\lambda} q_\gamma q_\lambda = \sum_{\gamma\lambda} \left\{ [\alpha\beta,\gamma\lambda] + (\alpha\gamma,\beta\lambda) \right\} q_\gamma q_\lambda .$$

[1.3.21]

The solution to the equation above is

$$c_{\alpha\gamma,\beta\lambda} = [\alpha\beta,\gamma\lambda] + [\gamma\beta,\alpha\lambda] - [\gamma\alpha,\beta\lambda] + (\alpha\gamma,\beta\lambda),$$

[1.3.22]

where the solution holds subject to the following conditions

$$[\alpha\beta,\gamma\lambda] = [\gamma\lambda,\alpha\beta].$$

[1.3.23]

The treatment given by Born and Huang does not yield an explicit expression for the pressure, since it cannot be expressed in terms of the derivatives of the total crystal potential energy. Hence the second equilibrium condition for a crystal (that the equilibrium configuration correspond to vanishing stress) cannot be incorporated into the general theory of lattice dynamics, in which only the derivatives of the crystal potential energy appear. A specific lattice model, e.g. one in which the atoms interact through central forces, is required before an expression for the pressure can be obtained.

1.4 CRYSTAL STABILITY

A structure cannot exist unless it is mechanically stable, (Born 1940) that is, unless any small distortion raises its energy. There may be more than one structure which is mechanically stable for a given force law, and one of these is the structure of lowest energy. The usual method of investigating such stability of a crystal lattice consists of comparing its lattice energy with that of other possible lattices built from the same particles. This method is not very reliable because of the small energy differences between the different lattice configurations.

Monatomic lattices are generally face centered cubic or hexagonally close packed, there occur only a few body centered ones while simple cubic lattices seem not to exist. There is another stability criterion in which we can distinguish between absolute and relative stable configurations namely the positive definiteness of the elastic energy. From our expression for the homogeneous deformation the energy density [1.2.10] depends only on the symmetrised parameters

$$u_{\alpha\beta}+u_{\beta\alpha}. \qquad [1.4.1]$$

By making a Voigt cotraction we use instead of $u_{\alpha\beta}$:

$$\begin{aligned} s_\rho &= u_{\alpha\beta}+u_{\beta\alpha} && \beta\neq\alpha \\ &= u_{\alpha\beta} && \beta=\alpha \end{aligned} \qquad [1.4.2]$$

where the indicies where $\rho=1,2,\ldots,6$ are related to the tensor indices α,β as follows:

ρ	1	2	3	4	5	6
(α,β)	11	22	33	23(32)	31(13)	12(21)

[1.4.3]

Hence the energy density becomes a quadratic expression in s_ρ, which we may write as

$$\Psi = \frac{1}{2} \sum_{\rho\sigma} c_{\rho\sigma} s_\rho s_\sigma , \qquad [1.4.4]$$

where $\rho=\alpha\beta$ and $\sigma=\gamma\lambda$. The coefficient of the above equation are the elastic constants which can be written into a matrix form

$$\begin{bmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\ c_{21} & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\ c_{31} & c_{32} & c_{33} & c_{34} & c_{35} & c_{36} \\ c_{41} & c_{42} & c_{43} & c_{44} & c_{45} & c_{46} \\ c_{51} & c_{52} & c_{53} & c_{54} & c_{55} & c_{56} \\ c_{61} & c_{62} & c_{63} & c_{64} & c_{65} & c_{66} \end{bmatrix} . \qquad [1.4.5]$$

Then the above quadratic form is positive definite if the determinants of the matrices of successive orders (principle minors) are all positive. Cubic symmetry leads to three independent elastic constants which are taken as c_{11}, c_{12} and c_{44}. The Cauchy relations which give the result that $c_{12}=c_{44}$ so that we only have two such elastic constants.

The matrix of the coefficient has then the following form

$$\begin{bmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{bmatrix}.$$

[1.4.6]

We can split the matrix above into characteristic determinants into two products

$$\begin{vmatrix} c_{11} & c_{12} & c_{12} \\ c_{12} & c_{11} & c_{12} \\ c_{12} & c_{12} & c_{11} \end{vmatrix} \begin{vmatrix} c_{44} & 0 & 0 \\ 0 & c_{44} & 0 \\ 0 & 0 & c_{44} \end{vmatrix} =$$

$$= (c_{11} + 2c_{12})(c_{11} - c_{12})^2 c_{44}^3.$$

[1.4.7]

For these to be positive definite we must have that

$$c_{11} + 2c_{12} > 0 \qquad c_{11} - c_{12} > 0 \qquad c_{44} = c_{12} > 0$$

[1.4.8]

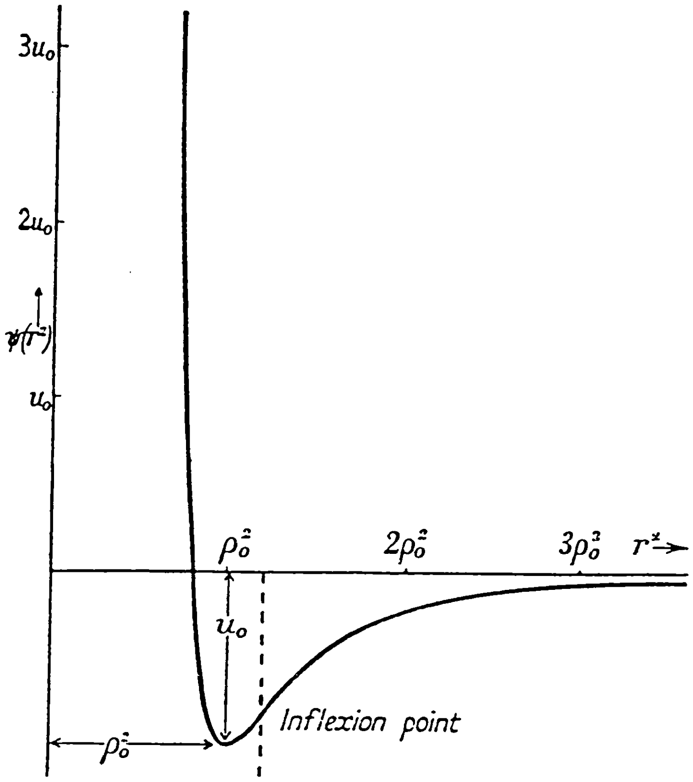


Fig. [1.4.1]

A typical curve for the potential function ψ is depicted above in fig. [1.4.1]. We suppose that the potential ψ is of the usual form assumed for explaining the binding energy of a diatomic molecule : it has a sharp minimum $-u_0$ at $r=\rho_0$, at which repulsive and attractive forces balance out and $\psi'=0$.

If we consider as Born does the grouping of lattice points according to their distances from the origin then different groups will lie on successive shells with an associated radii. The nearest neighbour distance which is equal to the innermost non-vanishing shell of a lattice is in general very close to ρ_0, since the particles interact predominantly with their nearest neighbours. If the shell next to the to the innermost one falls beyond the inflexion point where $\psi''(r^2)$ is negative then it will contribute a negative force constant value.

The size of the contribution of this next shell will then determine whether the elastic constants [1.4.8] obey the inequalities so that the matrix [1.4.6] is then positive definite and hence the crystal structure stable.

Since the gap between ρ_0^2 and the inflexion point is very narrow for central force potentials some lattice structures such as the simple cubic will always find themselves unstable since the second shell is always found to lie beyond the inflexion point and hence give a large negative contribution so that the inequalities are no longer valid. This is not found to be the case for the b.c.c. or f.c.c. where the contributions by the second shell of atoms although still negative are not large so that the inequalities are still obeyed.

1.5 ELASTIC CONSTANTS

When we are considering the problem of finding formal relations between elastic constants of a crystal and the interatomic forces through which the atoms are supposed to interact the question arises as to the choice of whether to use infinitesimal or Lagrangian strain. We can make a distinction between three different types of elastic constants (Martin 1975) depending on whether we use the infinitesimal or Lagrangian description of strain these are:

C_{IJ}	C'_{ijkl}	$\bar{C}_{ijkl}$
Brugger Elastic Constant	Linear Elastic Constant	Effective Elastic Constant

(i) The Brugger constants are coefficients in the expansion of the energy density in powers of the Lagrangian strain. Wallace (1972) in his definitions has these constants written down in his expansion as the $\tilde{C}_{ijkl}$ coefficients.

(ii) The linear elastic constants are the coefficients in the corresponding expansion in the infinitesimal strain. Wallace has these written down as the $\tilde{A}_{ijkl}$ coefficients.

(ii) The effective elastic constants are the coefficients determined from the velocity of sound waves whose theoretical values come from the method of long waves.

The thermodynamic definitions of the Brugger elastic constants are:

$$C_I = \rho_0 \frac{\partial F}{\partial \eta_I}, \qquad C_{IJ} = \rho_0 \frac{\partial^2 F}{\partial \eta_I \partial \eta_J}. \qquad [1.5.1]$$

The isothermal constants are found by taking F as the Helmholtz free energy and differentiating at constant temperature. The major advantage of using the Brugger constants over the linear constants is that they have the symmetry properties associated with rotational invariance.[1]

If we have a vector r^0 in the unstrained crystal then under a strain the vector r^0 goes to r and we can write down the change in the vector as

---

[1] In his discussion Stakgold (Stakgold 1950) never acknowledges the existence of strain tensors other than Lagrangian or Brugger elastic constants and consequently in discussing Born's work he interprets his results as approximate to that of the Brugger constants never as the exact results of the linear constants that they are.

$$r^2 - (r^0)^2 = 2 \sum_{ij} \eta_{ij} r_i^0 r_j^0 .$$

[1.5.2]

Where the derivatives of r^2 is (we also make a Voigt contraction ij=I)

$$\frac{\partial r^2}{\partial \eta_I} = 2 r_i^0 r_j^0 = 2X_I , \qquad \frac{\partial r^2}{\partial \eta_I \partial \eta_J} = 0.$$

[1.5.3]

We can see that the first derivatives are independent of the final state of strain while the second derivatives are zero. This is true for both final state of zero or finite strain. We can write down the derivatives of the many body potential Φ_M as

$$\frac{\partial \Phi_M}{\partial \eta_I} = \sum_{i=1}^{\frac{1}{2}M(M-1)} \frac{\partial \Phi_M}{\partial s_i} \frac{\partial s_i}{\partial \eta_I} = 2X_I \frac{\partial \Phi_M}{\partial s_i} .$$

[1.5.4]

The derivatives with respect to s_i are taken with other components of s fixed and the derivatives with respect to η_I with other components of η fixed. We simplify the notation slightly by defining the operator

$$D_I^M = 2X_I \frac{\partial}{\partial s_i} .$$

[1.5.5]

The expression for the elastic constants may be written as

$$C_I = \sum_{M=2}^{\infty} L_M D_I^M \Phi_M,$$

[1.5.6]

$$C_{IJ} = \sum_{M=2}^{\infty} L_M D_I^M D_J^M \Phi_M.$$

[1.5.7]

Where L_M is the inverse volume of the unit cell which is defined later on in [2.1.7]. The rotational invariance reduces the number of elastic constants from 81 to 21 and the crystal symmetry reduces the number further still. The second order elastic constants have the following symmetry properties

$$C_{ijkl} = C_{jikl}, \qquad [1.5.8a]$$

$$C_{ijkl} = C_{ijlk}, \qquad [1.5.8b]$$

$$C_{ijkl} = C_{klij}. \qquad [1.5.8c]$$

The first order elastic constants are also symmetric under interchange of indices

$$C_{ij} = C_{ji}.$$

[1.5.9]

This reduces the number of independent first order constants from nine to six. Examining the Brugger, linear and effective constants will show that the elastic constants do not always have the symmetry properties of [1.5.8] and [1.5.9] and certain specific conditions have to be met before any of the elastic constants can have such symmetry.

The Brugger elastic constants always have all the above symmetry properties, that is the use of the Lagrangian strains automatically ensures that the symmetry properties [1.5.8a] and [1.5.8b] hold. Also from the definition of the operator in [1.5.5] we see that the operators D^M_I and D^M_J commute so that $C_{IJ} = C_{JI}$ so that condition [1.5.8c] is also fulfilled.

The linear elastic constants are defined analogously to the Brugger constants [1.5.1]

$$C'_{ij} = \frac{\partial\Psi}{\partial u_{ij}}, \qquad\qquad C'_{ijkl} = \frac{\partial^2\Psi}{\partial u_{ij}\partial u_{kl}}.$$

[1.5.10]

Where the energy density Ψ is defined later on in [2.1.8]. We have the differential of the configuration vector s analogous to [1.5.4]

$$\frac{\partial s}{\partial u_{ij}} = 2(\delta_{ki} + u_{ki})\text{æ}^0_i\text{æ}^0_j.$$

[1.5.11]

Which is in agreement with the Lagrangian strain result at zero strain

$$\frac{\partial s}{\partial \eta_I} = \frac{\partial s}{\partial u_{ij}} = 2r^0_i r^0_j = 2X_{ij}.$$

[1.5.12]

Again we define an operator D^{M}_{ij} so that for the first order linear constants at zero strain order we have the analogous result of [1.5.6]

$$C'_{ij} = \sum_{M=2}^{\infty} L_{M} D^{M}_{ij} \Phi_{M}.$$

[1.5.13]

The operator D^{M}_{ij} is symmetric under interchange of indices i and j and hence at zero strain only

$$C'_{ij} = C'_{ij}.$$

[1.5.14]

Hence from [1.5.11] we can see that this symmetry is destroyed at finite strain except in the special case of a uniform dilation $u_{ij} = \lambda\delta_{ij}$ then the symmetry still holds

$$2(\delta_{ki}+u_{ki})\text{æ}^{0}_{k}\text{æ}^{0}_{j} = 2(\delta_{ki}+\lambda)\text{æ}^{0}_{k}\text{æ}^{0}_{j} = 2(1+\lambda)\text{æ}^{0}_{i}\text{æ}^{0}_{j}.$$

[1.5.15]

For the second order linear constants we require the evaluation of the equation

$$\frac{\partial^2\Phi_M}{\partial u_{ij}\partial u_{kl}} = \frac{\partial\Phi_M}{\partial s_i}.\frac{\partial^2 s_i}{\partial u_{ij}\partial u_{kl}} + \frac{\partial^2\Phi_M}{\partial s_i\partial s_j}.\frac{\partial s_i}{\partial u_{ij}}.\frac{\partial s_j}{\partial u_{kl}}.$$

[1.5.16]

The derivative with respect to the strain of the configuration vector is

$$\frac{\partial^2 s_i}{\partial u_{ij}\partial u_{kl}} = 2\delta_{ij}X_{kl}.$$

[1.5.17]

At zero strain only we can use [1.5.12] to obtain.

$$\frac{\partial^2\Phi_M}{\partial u_{ij}\partial u_{kl}} = (D^M_{ij}D^M_{kl} + \delta_{ik}D^M_{jl})\Phi_M.$$

[1.5.18]

Hence we have an expression for the second order linear elastic constants (at zero strain only)

$$C'_{ijkl} = \sum_{M=2}^{\infty} L_M(D^M_{ij}D^M_{kl}\Phi_M + \delta_{ik}D^M_{jl}\Phi_M).$$

[1.5.19]

The first term in [1.5.19], $D^M_{ij}D^M_{kl}\Phi_M$ corresponds at zero strain to the Lagrangian expression [1.5.7] and has therefore all the associated symmetry. The second term $\delta_{ik}D^{M}_{jl}\Phi_{M}$ has a more restricted symmetry which is the interchange of i and k and of j and l. For the full set of symmetry properties to apply the condition of zero strain is identified as the equilibrium state of the crystal as well as the state of zero stress. At zero stress the first order elastic constants C'_{ij} are zero (from the equilibrium condition) so that the term $\delta_{ik}D^{M}_{jl}\Phi_{M}$ in [1.5.19] also vanishes so that under this condition so that

$$C'_{ijkl} \equiv C_{IJ}. \qquad \text{(at zero strain, at zero stress)}$$

[1.5.20]

Hence under the condition of zero strain and zero stress all the symmetry properties of the linear elastic constants become equivalent to those of the Brugger elastic constants. The effective elastic constants are defined by (Hedin 1960)

$$\bar{C}_{ijkl} = C'_{ijkl} + C'_{il}\delta_{jk} - C'_{ij}\delta_{kl}.$$

[1.5.21]

At zero strain, $u = 0$, which need not correspond to the state of zero stress, we can use [1.5.19] to obtain

$$\bar{C}_{ijkl} = C^{B}_{ijkl} + (C^{B}_{il}\delta_{jk} + C^{B}_{jl}\delta_{ik} - C^{B}_{ij}\delta_{kl}).$$

[1.5.22]

Where the subscript B indicates a Brugger elastic constant. We can see that from [1.5.21] that the effective elastic constants posses only the symmetry property [1.5.8a]. In the state of zero stress or under uniform pressure the full set of symmetries [1.5.8a], [1.5.8b] and [1.5.8c] are recovered.

CHAPTER 2

THREE BODY POTENTIAL I

2.1 INTRODUCTION

The potential energy of an assembly of N identical atoms at positions $R_1,R_2 \cdots R_N$ can be written as a sum of contributions from different orders of many body interactions. Thus quite generally we can write

$$\Phi(R_1,R_2 \cdots R_N) = \Phi_0 + \sum_{i=1}^{N}\Phi_1(R_i) + \frac{1}{2!}\sum_{i=1}^{N}\sum_{j=1}^{N}\Phi_2(R_i,R_j) + \ldots$$

$$\ldots + \frac{1}{N!}\sum_{i=1}^{N}\sum_{j=1}^{N}\cdots\sum_{n=1}^{N}\Phi_N(R_i,R_j \cdots R_n), \qquad [2.1.1]$$

where the summations are restricted so that no two indices take the same value. Terms Φ_0 and Φ_1 are only included for generality, since Φ_0 can be set to zero by suitable choice of arbitrary origin of energy while Φ_1 accounts for the potential changes due to external fields. The terms Φ_2, Φ_3 etc are contributions to the energy from two atoms three atoms etc.

Each term in the expansion has a simple interpretation; Φ_2 is the interaction of two isolated atoms and Φ_3 is the excess energy of an isolated triplet of atoms, not accounted for by the pair term Φ_2. In general Φ_M is that part of the energy of an isolated cluster of M atoms not accounted for by lower order terms. This definition is an extension of the concept of a test particle to measure the field strength of a field corresponding to term Φ_1. Here we employ 2,3...N particles to measure the strengths of the many body interactions $\Phi_2,\Phi_3 \cdots \Phi_N$. There are other ways in which many-body interaction terms may be defined, examples are valence potentials and expansions of the lattice energy in terms of displacements.

The geometry of a cluster of M atoms is completely specified by M vectors $R_1, R_2 \ldots R_M$ that is by 3M real numbers. However, it is desirable to specify the cluster configuration in a way which is manifestly invariant under rotation and translations. In this work we are interested in the three body term and hence if we consider a triplet of atoms, where M=3

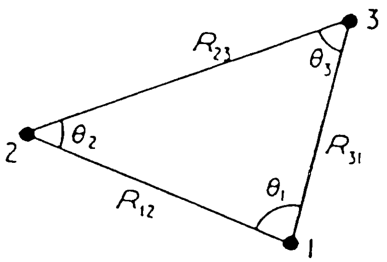


Fig. [2.1.1]

we can see that three numbers are needed to describe this triplet sufficiently to determine the energy and these numbers are clearly those required to specify the triangle formed by the three atoms. From the geometry of the triplet we have three possible sets to choose from:

i. the lengths of the three sides R_{12}, R_{23} and R_{31},
ii. the lengths of the two sides and included angle eg. R_{12} R_{13} and θ_1
iii. two angles and the length of one side, e.g. R_{12}, θ_1 and θ_2.

The first set (i) has coordinate system which treats the three atoms as equivalent and hence exhibits symmetry between the indices while set (ii) is preferable when valence potentials are used to describe the triplet of atoms.

If we use relative coordinates R_{12}, R_{23} and R_{31} of the atoms and take scalar products of these vectors we can see that the lengths R_{12}, R_{23}, R_{31} and angles θ_1, θ_2 and θ_3 are expressible in terms of scalar products of the three vectors. There are six such scalar products of which only three are independent, since any cross term can be written in terms of the square of the vectors.

For example

$$2R_{12}.R_{13} = R_{12}^2 + R_{31}^2 - R_{23}^2. \tag{2.1.2}$$

Thus the three body interaction term Φ_3 can be written as a function of R_{12}^2, R_{23}^2 and R_{13}^2 which in turn is describes a vector s in a configuration space

$$s = (s_1, s_2, s_3) = (R_{12}^2, R_{23}^2, R_{31}^2). \tag{2.1.3}$$

which is a point in a three-dimensional scalar product space. Each term in the cluster expansion [2.1.1] can be written as a function of a configuration vector s

$$\Phi = \frac{1}{2!}\sum_{i=1}^{N}\sum_{j=1}^{N}\Phi_2\Big[s(i,j)\Big] + \frac{1}{3!}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N}\Phi_3\Big[s(i,j,k)\Big] + \ldots$$

$$\ldots + \frac{1}{N!}\sum_{i=1}^{N}\sum_{j=1}^{N}\cdots\sum_{n=1}^{N}\Phi_N\Big[s(i,j\ldots n)\Big], \tag{2.1.4}$$

where s(i,j...) is the vector describing the configuration of the atoms i,j....

When we take the special case of the general assembly of N atoms, where the atoms occupy the lattice sites l of a space lattice then the cluster expansion becomes

$$\Phi = \frac{1}{2!}\sum_{l_1}\sum_{l_2}\Phi_2(s) + \frac{1}{3!}\sum_{l_1}\sum_{l_2}\sum_{l_3}\Phi_3(s) + \ldots$$

$$\ldots + \frac{1}{M!}\sum_{l_1}\ldots\sum_{l_M}\Phi_M(s) + \ldots. \qquad [2.1.5]$$

The number of terms is allowed to tend into infinity, and each term is summed over labels l_1, l_2 etc. which run over the entire lattice. In each summation the lattice site l_1 can be used as the origin of coordinates. We can thus rewrite Φ as a potential energy per atom:

$$\Phi/N = \frac{1}{2!}\sum_{l_2}\Phi_2(s) + \frac{1}{3!}\sum_{l_2}\sum_{l_3}\Phi_3(s) + \ldots$$

$$\ldots + \frac{1}{M!}\sum_{l_2}\ldots\sum_{l_M}\Phi_M(s) + \ldots. \qquad [2.1.6]$$

It is assumed that the interaction terms are such that [2.1.6] converges. We can make the notation simpler by denoting the operator L_M so that

$$L_M = \frac{1}{M!v_a} \sum_{l_2} \cdots \sum_{l_M} ,$$

[2.1.7]

where v_a is the volume of the unit cell. Then the energy density Ψ becomes

$$\Psi = L_2\Phi_2 + L_3\Phi_3 + L_4\Phi_4 + \ldots .$$

[2.1.8]

and this series can be extended to an infinite number of terms. This reduction in the number of summations is possible only in a perfect lattice, since in that case the sumands can be expressed in a form independent of l_1.

One such term is the $L_2\Phi_2$ which is

$$L_2\Phi_2 = \frac{1}{2v_a} \sum_{l_2} \Phi_2(s) = \frac{1}{2v_a} \sum_{l_2} \Phi_2(l_2^2) = \frac{1}{2v_a} \sum_{j} \Phi_2(r_j^2).$$

[2.1.9]

This gives the bond energy per unit volume of a crystal, assuming a pair potential $\Phi_2(r^2)$ interacting between atoms a distance r apart. The label j labels all the atoms of the crystal: r_j is the distance of the atom j from the origin, which is some lattice site.

2.2 DEFINITION OF ENERGY DENSITY

If an elastic body is considered as a continuum, the existence of a "strain energy density" can be ascertained.

From the atomic theory of elasticity, we can deduce the existence of an energy function of the internal forces between particles. This energy function can be expressed as a function of a defined strain. In the case of a monatomic crystalline body, this energy function corresponds to the strain energy density of a continuous body. We can write the energy density as

$$\Psi = \Psi(u_{\alpha\beta}). \qquad [2.2.1]$$

We assume the existence of a suitably convergent series expansion for $\Psi(u_{\alpha\beta})$,

$$\Psi = \Psi_0 + \Omega_{\alpha\beta}\, u_{\alpha\beta} + \Lambda_{\alpha\beta\gamma\lambda}\, u_{\alpha\beta} u_{\gamma\lambda} + \ldots. \qquad [2.2.2]$$

A feature of a two-body interaction is that special relationships apply. Examples are the Cauchy relations between the elastic constants (of which the coefficients $\Lambda_{\alpha\beta\gamma\lambda}$ of the quadratic term in our expansion are involved) which lead in an appropriate cubic crystal case to their being two independent elastic constants instead of three. These features are not expected to persist for three atom interactions and it is part of the objective of the present work to give a full account, parallel to that of Born and Huang (1954), for the three body case. Ostoskii and Efros (1961) write down general expressions for the energy density in a lattice with respect to such non central interactions.

Extending our previous notation to include different atoms in the unit cell the two body interactions lead to a potential energy function of the form

$$\Phi = \frac{1}{2}\sum_{l'k'}\sum_{lk} \Psi\begin{pmatrix} l' & l \\ k' & k \end{pmatrix}.$$

[2.2.3]

Here l denotes a unit cell and k labels the atom within the unit cell. Summing over all atoms in the crystal has the effect of counting all pairs of atoms twice. It simplifies the notation if the one atom term

$$\Psi\begin{pmatrix} l & l \\ k & k \end{pmatrix},$$

[2.2.4]

is left in the sum but is formally regarded as a null function. This limitation on the potential function is sufficient to enable an energy density function to be defined for homogeneous deformations. For an assembly of N atoms the energy function is given as

$$\Phi = \frac{N}{2}\sum_{l'k'}\sum_{k} \Psi\begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix},$$

[2.2.5]

so that the energy density can be written down as

$$\Psi = \Phi/Nv_a$$

[2.2.6]

where v_a is the volume of the unit cell. Combining [2.2.5] and [2.2.6] we have an analogous expression for [2.1.9] for more than one atom per unit cell

$$\Psi = \frac{1}{2v_a} \sum_{l'k'} \sum_{k} \Psi\begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix}.$$

[2.2.7]

The corresponding equations for three atoms interactions are readily written down

$$\Phi = \frac{N}{6} \sum_{l''k''} \sum_{l'k'} \sum_{k} \Psi\begin{pmatrix} l'' & l' & 0 \\ k'' & k' & k \end{pmatrix}.$$

[2.2.8]

The corresponding energy density expression is given by

$$\Psi = \frac{1}{6v_a} \sum_{l''k''} \sum_{l'k'} \sum_{k} \Psi\begin{pmatrix} l'' & l' & l \\ k'' & k' & k \end{pmatrix}.$$

[2.2.9]

The usual way of developing these functions involves a series expansion for the energy density in terms of the Cartesian displacement components of the individual particles. After such an expansion is obtained, the displacement is expressed in terms of the local strain and then substituted in the expansion.

2.3 FORCE CONSTANTS AND INTERNAL STRAIN

In this section we collect some of the expressions for the contribution of the three body interactions to the Taylor expansion of the potential energy function Φ. These would be necessary for calculations of lattice vibrations but they can also be related to the internal strain constants which are of interest here.

Assuming for simplicity that only three body interactions contribute, the potential energy may be written

$$\Phi = \frac{1}{6}\sum_{lk}\ \sum_{l'k'}\ \sum_{l''k''}\Psi\begin{pmatrix} l'' & l' & l \\ k'' & k' & k \end{pmatrix}.$$

[2.3.1]

A linear coefficient in the expansion is simply represented by

$$\Phi_{\alpha}\begin{pmatrix} l \\ k \end{pmatrix} = \frac{1}{2}\sum_{l'k'}\ \sum_{l''k''}\Psi\begin{pmatrix} l'' & l' & l \\ k'' & k' & k \end{pmatrix}_{\alpha}(lk).$$

[2.3.2]

Taking account of the fact that the triple potential depends only on the squares of the length s of the sides of the triangle

$$\Phi_{\alpha}\begin{pmatrix} l \\ k \end{pmatrix} = 2\sum_{l'k'}\ \sum_{l''k''}\Psi'_{(kk')}\begin{pmatrix} l'' & l' & l \\ k'' & k' & k \end{pmatrix}æ_{\alpha}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix},$$

[2.3.3]

in which

$$\Psi'_{(kk')}\begin{pmatrix} l'' & l' & l \\ k'' & k' & k \end{pmatrix} \equiv \left(\partial\Psi\begin{pmatrix} l'' & l' & l \\ k'' & k' & k \end{pmatrix} \Big/ \partial\left[r\begin{pmatrix} l & l' \\ k & k' \end{pmatrix}^2\right]\right)_0 .$$

[2.3.4]

For quadratic coefficients, only a term coupling two different atoms is written explicitly. In the notation of [2.3.2]

$$\Phi_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} = \sum_{l''k''} \Psi\begin{pmatrix} l'' & l' & l \\ k'' & k' & k \end{pmatrix}_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix},$$

[2.3.5]

and in the form corresponding to [2.3.3]

$$\begin{aligned} \Phi_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} = -4 \sum_{l''k''} \Bigg\{ & \Psi''_{(kk')(kk')}\begin{pmatrix} l'' & l' & l \\ k'' & k' & k \end{pmatrix} \text{æ}_{\alpha}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} \text{æ}_{\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} + \\ & + \Psi''_{(kk')(k'k'')}\begin{pmatrix} l'' & l' & l \\ k'' & k' & k \end{pmatrix} \text{æ}_{\alpha}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} \text{æ}_{\beta}\begin{pmatrix} l'' & l' \\ k'' & k' \end{pmatrix} + \\ & + \Psi''_{(kk'')(kk')}\begin{pmatrix} l'' & l' & l \\ k'' & k' & k \end{pmatrix} \text{æ}_{\alpha}\begin{pmatrix} l & l'' \\ k & k'' \end{pmatrix} \text{æ}_{\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} + \\ & + \Psi''_{(kk'')(k'k'')}\begin{pmatrix} l'' & l' & l \\ k'' & k' & k \end{pmatrix} \text{æ}_{\alpha}\begin{pmatrix} l & l'' \\ k & k'' \end{pmatrix} \text{æ}_{\beta}\begin{pmatrix} l'' & l' \\ k'' & k' \end{pmatrix} \Bigg\} - \\ & - 2\delta_{\alpha\beta} \sum_{l''k''} \Psi'_{(kk')}\begin{pmatrix} l'' & l' & l \\ k'' & k' & k \end{pmatrix} . \end{aligned}$$

[2.3.6]

Second derivative coefficients are indicated by an extension of the notation in [2.3.4].

$$\Psi''_{(kk')(kk'')}\begin{pmatrix} l'' & l' & l \\ k'' & k' & k \end{pmatrix} \equiv \left(\partial^2\Psi\begin{pmatrix} l'' & l' & l \\ k'' & k' & k \end{pmatrix} \Big/ \partial\left[r\begin{pmatrix} l & l' \\ k & k' \end{pmatrix}^2\right] \partial\left[r\begin{pmatrix} l & l'' \\ k & k'' \end{pmatrix}^2\right] \right)_0 .$$

[2.3.7]

The term in (l'k')≡(lk) may be deduced from the translation invariance condition [1.1.4]

$$\Phi_{\alpha\beta}\begin{pmatrix} l & l \\ k & k \end{pmatrix} = -\sum_{l'k'} \Phi_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} .$$

[2.3.8]

In which the sum excludes (lk) i.e. the sum is taken over all atoms in the lattice except (lk).

In the context of this thesis, attention is being focused on the elastic properties. In the general form of homogeneous deformation theory developed in section 1.2, the internal stain parameters are defined in terms of force constants in [1.2.15] which is repeated here.

$$\begin{Bmatrix} k & k' \\ \alpha & \beta \end{Bmatrix} = v_a^{-1} \sum_{l} \Phi_{\alpha\beta}\begin{pmatrix} l & 0 \\ k & k' \end{pmatrix}$$

[2.3.9]

in which it is recalled that v_a is the volume of the unit cell. When k≠k' the complete expression is obtained by substitution of [2.3.6] into [2.3.8]. When k=k', a few elementary manipulations lead to

$$\left\{ \begin{matrix} k & k' \\ \alpha & \beta \end{matrix} \right\} = - v_a^{-1} \sum_{l'} \sum_{k' \neq k} \Phi_{\alpha\beta} \left(\begin{matrix} l' & 0 \\ k' & k \end{matrix} \right) \quad . \qquad [2.3.10]$$

Examination of this expression shows that the sum is taken over atoms in all sublattices except that of the origin atom. Comparison of [2.3.8] and [2.3.9] shows that the lattice invariance relation for internal strain parameters is

$$\sum_{k'} \left\{ \begin{matrix} k & k' \\ \alpha & \beta \end{matrix} \right\} = 0 \qquad [2.3.11]$$

and this leads to a matrix of rank (3n-3) as expected.

2.4 HOMOGENEOUS DEFORMATION

The parametric theory of homogeneous deformation developed in section 1.2 is now given its specific form when three body interactions are assumed. The treatment will parallel that given in section 1.3 for the case of two body interactions.

The energy density is given by

$$\Psi = \frac{1}{6v_a} \sum_{lk} \sum_{l'k'} \sum_{l''k''} \Psi \left(\begin{matrix} l & l' & l'' \\ k & k' & k'' \end{matrix} \right) , \qquad [2.4.1]$$

and its change is determined for a homogeneous deformation in which each atom is displaced by an amount

$$u_{\alpha}\begin{pmatrix} l \\ k \end{pmatrix} = u_{\alpha}(k) + \sum_{\beta} u_{\alpha\beta} x_{\beta}\begin{pmatrix} l \\ k \end{pmatrix} .$$

[2.4.2]

As with the two body case, the expansion is expressed in terms of the derivatives of three body terms with respect to the square of a distance. For two bodies only one distance is concerned, but for three bodies there are three distances, the lengths of the sides of the triangle formed by the three atoms.

First, all terms derived from first derivatives are collected. These correspond to the first two lines of [1.3.7] in the two body case.

$$-2 \sum_{k\alpha}\left(u_{\alpha}(k) + \sum_{\beta} u_{\beta}(k) u_{\beta\alpha}\right)\left[\sum_{l''k''} \sum_{l'k'} \sum_{k} \Psi'_{(kk')}\begin{pmatrix} l'' & l' & 0 \\ k'' & k' & k \end{pmatrix} x_{\alpha}\begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix}\right] +$$

$$+ \sum_{\alpha\beta}\left(u_{\alpha\beta} + \frac{1}{2} \sum_{\gamma} u_{\gamma\alpha} u_{\gamma\beta}\right)\left[\sum_{l''k''} \sum_{l'k'} \sum_{k}\right.$$

$$\left. \Psi'_{(k'k)}\begin{pmatrix} l'' & l' & 0 \\ k'' & k' & k \end{pmatrix} x_{\alpha}\begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix} x_{\beta}\begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix}\right] .$$

[2.4.3]

Careful examination of this expression shows that it is exactly parallel to the two body case except that there is an additional lattice sum (over l''k''). It is also seen that the same coefficient (in the large square brackets) multiplies the linear deformation and some quadratic terms. The equilibrium conditions demand that the system is both stress free and force free and this in turn leads to the condition that the sums in square brackets vanish corresponding to the earlier [1.3.8].

Assuming the system is initially in equilibrium, expressions for the general elasticity parameters using the notation of [1.2.2] may be written.

$$\{\alpha\beta,\gamma\lambda\} = \frac{2}{v_a} \sum_{l''k''} \sum_{l'k'} \sum_{k}$$

$$\Bigg[\Psi''_{(k'k)(k'k)}\begin{pmatrix} l'' & l' & 0 \\ k'' & k' & k \end{pmatrix} \text{\ae}_{\alpha}\begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix} \text{\ae}_{\beta}\begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix} \text{\ae}_{\gamma}\begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix} \text{\ae}_{\lambda}\begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix}$$

$$+2\Psi''_{(k'k)(k''k)}\begin{pmatrix} l'' & l' & 0 \\ k'' & k' & k \end{pmatrix} \text{\ae}_{\alpha}\begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix} \text{\ae}_{\beta}\begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix} \text{\ae}_{\gamma}\begin{pmatrix} l'' & 0 \\ k'' & k \end{pmatrix} \text{\ae}_{\lambda}\begin{pmatrix} l'' & 0 \\ k'' & k \end{pmatrix}\Bigg]$$

[2.4.4]

and for the cross term between external and internal strain

$$\left\{ \begin{matrix} k \\ \alpha \end{matrix} \beta\gamma \right\} = - \frac{4}{V_a} \sum_{l''k'} \sum_{l'k'} \text{æ}_\alpha \begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix}$$

$$\Bigg[\Psi''_{(k'k)(k'k)} \begin{pmatrix} l'' & l' & 0 \\ k'' & k' & k \end{pmatrix} \text{æ}_\beta \begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix} \text{æ}_\gamma \begin{pmatrix} l' & 0 \\ k' & k \end{pmatrix}$$

$$+ \Psi''_{(k'k)(k''k)} \begin{pmatrix} l'' & l' & 0 \\ k'' & k' & k \end{pmatrix} \text{æ}_\beta \begin{pmatrix} l'' & 0 \\ k'' & k \end{pmatrix} \text{æ}_\gamma \begin{pmatrix} l'' & 0 \\ k'' & k \end{pmatrix}$$

$$+ \Psi''_{(k'k)(k''k')} \begin{pmatrix} l'' & l' & 0 \\ k'' & k' & k \end{pmatrix} \text{æ}_\beta \begin{pmatrix} l'' & l' \\ k'' & k' \end{pmatrix} \text{æ}_\gamma \begin{pmatrix} l'' & l' \\ k'' & k' \end{pmatrix} \Bigg] .$$

[2.4.5]

The final coefficient, coupling the internal strains, has been given explicitly in the last section equation [2.3.9] and preceding expressions.

It will be seen that the coefficients satisfy the symmetry relations [1.2.5] to [1.2.7]. These arise from rotational invariance. Closer examination shows that the first term in both [2.4.4] and [2.4.5] corresponds to a two body term and exhibits the characteristic additional symmetry in the Greek indices. In these terms the second derivatives is taken with respect to the same square distance twice and is multiplied by components of this distance with respect to coordinate axes. The three body interactions enters only through the numerical value assigned to the derivative and the effect is only to change the magnitude of the two body effect. On the other hand it is seen that the way in which three body effects are directly manifested is by the occurrence of products of Cartesian coordinates for different pairs.

As in general parametric theory, expressions for the elastic moduli can be worked out using [1.2.11]. The three body contributions to the various parameters having been given in this and the preceding section.

CHAPTER 3

THREE BODY POTENTIAL II

3.1 INTRODUCTION

For convenience we switch to a slightly different notation (Wallace 1972) than in previous chapters. We now label the atoms by the letters M,N..., the unit cell by the Greek letters μ,ν... and use the subscripts i,j... for the Cartesian indicies. The equilibrium position of the atoms are given by the vectors R(M) and the displacement are denoted by U(M). The potential energy of the crystal due to the interactions amongst the atoms in a given configuration is Φ; this is presumed to be an analytical function of the positions of the atoms and hence it may be expanded in the displacement from an arbitary initial configuration

$$\Phi = \Phi_0 + \sum_{M}\sum_{i} \Phi_i(M)U_i(U) + \frac{1}{2}\sum_{MN}\sum_{ij} \Phi_{ij}(MN)U_i(M)U_j(N) + \dots. \qquad [3.1.1]$$

Here Φ_0 is the potential of the interaction among the atoms where they are all located at their initial equilibrium position R(M). The coefficients $\Phi_i(M)$, $\Phi_{ij}(MN)$... are derivatives of the potential defined at the equilibrium configuration

$$\Phi_i(M) = \left(\frac{\partial\Phi}{\partial U_i(M)}\right)_0,$$

$$\Phi_{ij}(MN) = \left(\frac{\partial^2\Phi}{\partial U_i(M)\partial U_j(M)}\right)_0. \qquad [3.1.2]$$

We now extend the above expression so as to include a general three body potential expression for the energy density. Before this is possible we need to choose a set of coordinates so that we define the geometry of a triplet of atoms in our crystal stucture. There are various sets of coordinates for defining the geometry of the triplet and for example spectroscopists will generally favour valence coordinates that is a mixture of bond length and bond angles. Our triatomic system can have any of the three possible coordinate systems as shown below

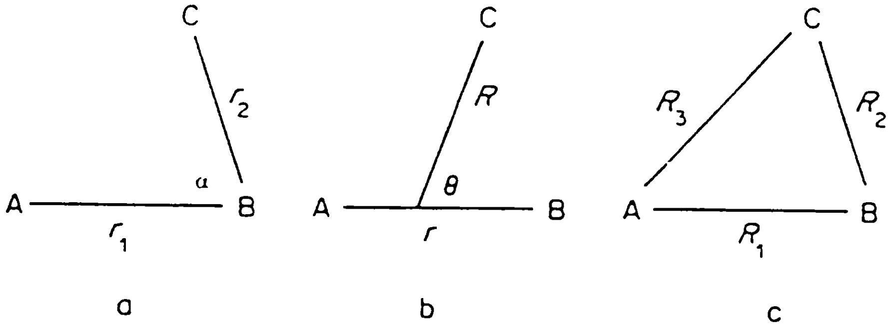


Fig. [3.1.1]

In (a) and (b) one of the atoms has been placed in different context than the other two and only in (c) do we have a coordinate system which treats the three atoms as equivalent.

Coordinates (a) are most favoured for analysing the vibrational states of ABC triatomic molecule because for small displacements from equilibrium the potential energy can, to a first approximation be written as sum of quadratic terms in the displacements

$$2V = k_1\Delta r_1^2 + k_2\Delta r_2^2 + k_\alpha\Delta\alpha^2.$$

[3.1.3]

The force constants are now derivatives of the potential with respect to changes in bond lengths Δr_1, Δr_2 and angle changes $\Delta\alpha$.

If the coordinates (c) are used then because of the symmetry the most general expression for the expansion of the potential energy of the system in powers of the displacements of the nuclei from their equlibrium separation position is

$$V = V_0 + \frac{1}{2} k_1\left[(\Delta r_1)^2 + (\Delta r_2)^2 + (\Delta r_3)^2\right] + $$

$$+ k_2\left[\Delta r_1\Delta r_2 + \Delta r_1\Delta r_3 + \Delta r_2\Delta r_3\right], \qquad [3.1.4]$$

where k_1 and k_2 are the force constants. In the central force approximation the cross terms vanish so that k_2 is taken to be zero.

We can define the force constants from [3.1.4] in terms of the Taylor coefficients [3.1.2] such that for a three body potential $\Phi(MNO)$ the coefficients can be written as

$$k_1 = \Phi_{ij}(MNO)(MN)(MN) = \frac{\partial^2\Phi(MNO)}{\partial U_i(MN)\partial U_j(MN)},$$

$$k_2 = \Phi_{ij}(MNO)(MN)(NO) = \frac{\partial^2\Phi(MNO)}{\partial U_i(MN)\partial U_j(NO)}. \qquad [3.1.5]$$

Where the force constants above correspond to k_1 and k_2 in [3.1.4] respectively.

3.2 DEFINITION OF ENERGY DENSITY

The elastic moduli are now developed by a different route. This follows the ideas of Wallace (1972) who deals with the problems arising from infinite lattice model differently from Born, although the results ultimately have the same algebraic form as the method of long waves.

Wallace (1972) considers a finite crystal which has perfect lattice periodicity in the bulk, with departures from the regular structure near to the surface. It is assumed that the detailed effect of the surface is negligible in the bulk and that its overall effect can be represented in terms of a stress field arising from the external forces acting on the crystal surface.

In this way a strain expansion of the potential energy is made with only the surface forces assumed to be present. These surface forces represent arbitrary mechanical stresses applied to the crystal.

From the initial equilibrium configuration we let the ions undergo a homogeneous deformation given by the displacements

$$U_i(M\mu) = S_i(\mu) + \sum_j u_{ij} R_j(M\mu) \qquad [3.2.1]$$

Here the u_{ij} are displacements gradients i.e. the strains and $S(\mu)$ are the sublattice displacements which occur during the homogeneous strain. Because of the lattice distortions near the crystal surface, the displacement gradients may not be constant in the surface region, but this effect will be neglected so that we may consider the u_{ij} displacement gradients as constants. The crystal potential Φ may be expanded as

$$\Phi = \Phi_0 + V \sum_{ij} \tilde{A}_{ij} u_{ij} + \frac{1}{2} V \sum_{ijkl} \tilde{A}_{ijkl} u_{ij} u_{kl} + \dots\dots \qquad [3.2.2]$$

This equation defines formally the $\tilde{A}$ coefficients in terms of the potential energy coefficients.

To simplify the treatment, which is given in detail in this chapter, attention is confined to the example of one atom per unit cell. The homogeneous deformation is then given by

$$U_i(M) = \sum_j u_{ij} R_j(M), \qquad [3.2.3]$$

and from the expansion of the potential we place [3.2.2] into [3.1.1] so that

$$\Phi = \Phi_0 + \sum_M \sum_{ij} \Phi_i(M) R_j(M) u_{ij} + \frac{1}{2} \sum_{MN} \sum_{ijkl} \Phi_{ij}(M,N) R_k(M) R_l(N) u_{ik} u_{jl} + \dots\dots \qquad [3.2.4]$$

Comparing the above expression [3.2.2] the $\tilde{A}$ coefficients are seen to be

$$\tilde{A}_{ij} = V^{-1} \sum_M \Phi_i(M) R_j(M),$$

$$\tilde{A}_{ijkl} = V^{-1} \sum_{MN} \Phi_{ik}(M,N) R_j(M) R_l(M) \qquad [3.2.5]$$

We can interchange the origin of the coordinates within the crystal without altering the potential energy (this comes about as a consequence of the translational invariance) so that if we add an arbitrary vector we have

$$\sum_{M} \Phi_i(M)R_j(M) = \sum_{M} \Phi_i(M)[R_j(M) - R_j],$$

[3.2.6]

where R_j are the components of the vector. Hence it follows that $\tilde{A}_{ijkl}$ is independent of the origin.

We now wish to eliminate surface effects. This can be done from $\tilde{A}_{ijkl}$ (Wallace 1972) by first calculating Φ per unit volume evaluated in the interior and then differentiating with respect to strain. Surface effects can be eliminated from $\tilde{A}_{ijkl}$ by taking the combination symmetric in j,l and evaluating in the interior. Defining this combination as $\hat{A}_{ijkl}$ we have

$$\hat{A}_{ikjl} = \frac{1}{2}(\tilde{A}_{ijkl} + \tilde{A}_{ilkj}),$$

[3.2.7]

so that from [3.2.5] we have

$$\begin{aligned}\hat{A}_{ikjl} &= \frac{1}{2} V^{-1} \sum_{MN} \Phi_{ik}(MN)\ [R_j(M)R_l(N) + R_l(M)R_j(N)] \\ &= -\frac{1}{2} V^{-1} \sum_{MN} \Phi_{ik}(MN)\ [R_j(N) - R_j(M)][R_l(N) - R_l(M)].\end{aligned}$$

[3.2.8]

The last expression follows from the translational invariance conditions. If the volume per unit cell is V_c then $V_c = V/N_0$ and the expression for $\hat{A}_{ijkl}$ can be written as

$$\hat{A}_{ikjl} = -\frac{1}{2} V_c^{-1} \sum_{N} \Phi_{ik}(N,O)R_j(N)R_l(N).$$

[3.2.9]

The above expression can be compared with Born's expression which is written for more than one atom per unit cell (substituting $C^{(2)}_{\alpha\beta,\gamma\lambda}$ from [1.3.13] into [1.3.17])

$$[\alpha\beta,\gamma\lambda] = -\frac{1}{2v_a} \sum_{lkk'} \Phi_{\alpha\beta}\begin{pmatrix} l & 0 \\ k & k' \end{pmatrix} \text{æ}_{\gamma}\begin{pmatrix} l & 0 \\ k & k' \end{pmatrix} \text{æ}_{\lambda}\begin{pmatrix} l & 0 \\ k & k' \end{pmatrix}.$$

[3.2.10]

We can express our original expansion [3.2.2] in terms of the symmetric (Lagrangian strains) finite strain parameters η_{ij} which are given by

$$\eta_{ij} = \frac{1}{2}\left(u_{ij} + u_{ji} + \sum_{k} u_{ki}u_{kj} \right).$$

[3.2.11]

We can see that the tensor η_{ij} is symmetric $\eta_{ij} = \eta_{ji}$. The crystal potential can be expanded in η_{ij}

$$\Phi = \Phi_0 + V \sum_{ij} \tilde{C}_{ij}\eta_{ij} + \frac{1}{2} V \sum_{ijkl} \tilde{C}_{ijkl}\eta_{ij}\eta_{kl} + \ldots.$$

[3.2.12]

The equation defines the $\tilde{C}$ coefficients and because of the symmetry of η_{ij} these coefficients must have complete Voigt symmetry

$$\tilde{C}_{ij} = \tilde{C}_{ji}, \qquad [3.2.13]$$

$$\tilde{C}_{ijkl} = \tilde{C}_{jikl} = \tilde{C}_{klij} = \ldots . \qquad [3.2.14]$$

By substituting [3.2.11] into [3.2.12] we write out the expansion and compare it to the expansion [3.2.2], then comparing coefficients

$$\tilde{A}_{ij} = \tilde{C}_{ij}, \qquad [3.2.15]$$

$$\tilde{A}_{ijkl} = \tilde{C}_{jl}\delta_{ik} + \tilde{C}_{ijkl}. \qquad [3.2.16]$$

The $\tilde{C}_{ij}$ and $\tilde{C}_{ijkl}$ are the mechanical analogs of the stress and second order elastic constants respectively.

Wallace (1972) describes three important symmetry properties of the $\hat{A}_{ijkl}$ coefficients (as defined in [3.2.7]). These properties are equivalent to the Voigt symmetry of the second order elastic constants

$$\hat{A}_{ijkl} = \hat{A}_{ijlk}, \qquad [3.2.17]$$

$$\hat{A}_{ijkl} = \hat{A}_{jikl}, \qquad [3.2.18]$$

$$\hat{A}_{ikjl} + \tilde{C}_{ik}\delta_{jl} = \hat{A}_{jlik} + \tilde{C}_{jl}\delta_{ik}. \qquad [3.2.19]$$

Also he defines the elastic constants $\tilde{C}_{ijkl}$ as a combination of force constants such that

$$\tilde{C}_{ijkl} = \tilde{A}_{ikjl} + \tilde{A}_{jkil} - \tilde{A}_{ijkl} - \tilde{C}_{jl}\delta_{ik} - \tilde{C}_{il}\delta_{jk} + \tilde{C}_{kl}\delta_{ij}. \tag{3.2.20}$$

Which is analogous to the result of Born and Huang (1954)

$$c_{\alpha\gamma,\beta\lambda} = [\alpha\beta,\gamma\lambda] + [\gamma\beta,\alpha\lambda] - [\alpha\gamma,\beta\lambda] + (\alpha\gamma,\beta\lambda).$$

Where the round bracket gives the contribution of the internal strains to the elastic contants which is zero for the one atom unit cell considered here.

3.3 CALCULATION OF $\hat{A}_{ijkl}$ FOR THREE BODY POTENTIAL

We now go on to calculate an expression for $\hat{A}_{ijkl}$ using a general three body potential which describes the interactions amongst three particles in an arbitrary triplet configuration.

Following the general expression given in [3.2.9] and assuming throughout our calculation that the crystal under consideration has one atom per unit cell we go on to write down the general expression in which we label the three atoms as P, N and O so that we have

$$\hat{A}_{ijkl} = -\frac{1}{2v_a}\sum_N \sum_P \Phi_{ij}(P,N,O)(N,O)\ R_k(N)R_l(N). \tag{3.3.1}$$

Where the general three body potential $\Phi(P,N,O)$ has its derivatives taken over one of the sides of the triangle only, which we have chosen arbitrarily as the side NO.

We now take as our origin the particle which we have labelled as O, so that all other triplet configurations will have two of their sides originating from the particle labeled O. Thus we can write [3.3.1] to include the side PO in our expression for $\hat{A}_{ijkl}$ (we multiply our expression by a factor of one half 1/2 so that we do not count both sides twice)

$$\hat{A}_{ijkl} = -\frac{1}{4V_a}\sum_N \sum_P \left\{ \Phi_{ij}(P,N,O)(N,O)\ R_k(N)R_l(N) \right.$$
$$\left. \Phi_{ij}(P,N,O)(P,O)\ R_k(P)R_l(P) \right\}. \qquad [3.3.2]$$

From fig. [3.3.1] we can see that there will be more than one such triplet with its apex at the origin.

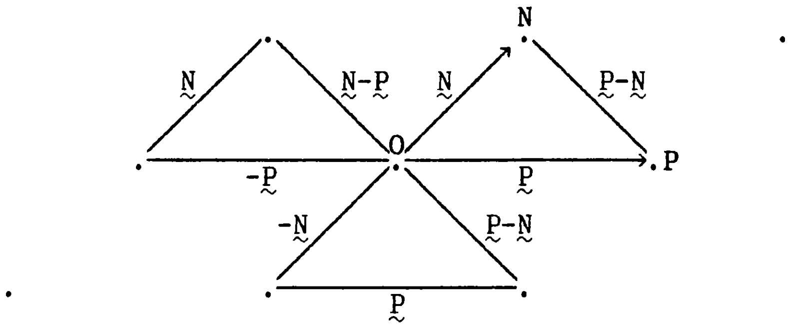


Fig. [3.3.1]

Hence it is possible to write down the third side of our triplet in terms of the two sides originating from O. We can also write down the potential energy function for all the triplets including the third side

$$\Phi(P,N,O) = \Phi(P-N,-N,O) = \Phi(N-P,-P,O). \qquad [3.3.3]$$

We now count over three triplets so that we now multiply our expression by a factor of a third so that our expression for $\hat{A}_{ijkl}$ written out in full is

$$\begin{aligned}\hat{A}_{ijkl} = -\frac{1}{12v_a} \sum_N \sum_P \Big\{ & \Phi_{ij}(P,N,O)(N,O)\; R_k(NO)R_l(NO) \\ & + \Phi_{ij}(P,N,O)(P,O)\; R_k(PO)R_l(PO) \\ & + \Phi_{ij}(P-N,-N,O)(P-N,O)\; R_k(PN)R_l(PN) \\ & + \Phi_{ij}(P-N,-N,O)(-N,O)\; R_k(ON)R_l(ON) \\ & + \Phi_{ij}(N-P,-P,O)(N-P,O)\; R_k(NP)R_l(NP) \\ & + \Phi_{ij}(N-P,-P,O)(-P,O)\; R_k(OP)R_l(OP) \Big\}. \end{aligned} \qquad [3.3.4]$$

We can use the translational symmetry of our crystal so that we can rewrite the expression [3.3.4] in terms of the same triplet. The translational symmetry allows us to rewrite the terms as

$$\begin{aligned} R_k(-P,O) &= -R_k(P) + R_k(O) & R_k(N-P,O) &= R_k(N-P) - R_k(O) \\ &= R_k(O) - R_k(P) & &= R_k(N) - R_k(P) - R_k(O) \\ &= R_k(OP), & &= R_k(NP), \end{aligned} \qquad [3.3.5]$$

so that if write $\hat{A}_{ijkl}$ explicitly we have

$$\begin{aligned}\hat{A}_{ijkl} = -\frac{1}{12v_a}\sum_N\sum_P \Big\{ & \Phi_{ij}(P,N,O)(N,O)\ R_k(NO)R_l(NO) \\ & + \Phi_{ij}(P,N,O)(P,O)\ R_k(PO)R_l(PO) \\ & + \Phi_{ij}(P,N,O)(P,N)\ R_k(PN)R_l(PN) \\ & + \Phi_{ij}(P,N,O)(O,N)\ R_k(ON)R_l(ON) \\ & + \Phi_{ij}(P,N,O)(N,P)\ R_k(NP)R_l(NP) \\ & + \Phi_{ij}(P,N,O)(O,P)\ R_k(OP)R_l(OP) \Big\}.\end{aligned}$$

[3.3.6]

We now write down explicitly the terms $\Phi_{ij}(PNO)(NO)$, $\Phi_{ij}(PNO)(PO)$, and $\Phi_{ij}(PNO)(PN)$. The term $\Phi_{ij}(PNO)(NO)$ is the second order differential of the general potential $\Phi(PNO)$ taken over the side NO. We calculate this term explicitly

$$\Phi_{ij}(PNO)(NO) = \frac{\partial^2\Phi(PNO)}{\partial u_i(N)\partial u_j(O)}.$$

[3.3.7]

Our potential function $\Phi(PNO)$ is written down as a function of the square of the distances making up the three sides of our triplet of particles

$$\Phi_{ij}(PNO) = \Psi\Big[s(NO),\ s(PO),\ s(PN)\Big],$$

[3.3.8]

$$s(NO) = \left[R_i(NO)\right]^2 = \left[R_i(N) - R_i(O)\right]^2. \qquad [3.3.9]$$

From the definitions of [3.3.8] and [3.3.9] we can calculate [3.3.7] explicitly

$$\Phi_{ij}(PNO)(NO) = \frac{\partial}{\partial u_i(N)} \left\{ \frac{\partial}{\partial u_j(O)} \Psi\left[s(NO),\ s(PO),\ s(PN)\right]\right\}, \qquad [3.3.10]$$

$$\Phi_{ij}(PNO)(NO) = \frac{\partial}{\partial u_i(N)} \left\{\frac{\partial \Psi}{\partial s(NO)} \frac{\partial s(NO)}{\partial u_j(O)} + \frac{\partial \Psi}{\partial s(PO)} \frac{\partial s(PO)}{\partial u_j(O)} + \frac{\partial \Psi}{\partial s(PN)} \frac{\partial s(PN)}{\partial u_j(O)}\right\}. \qquad [3.3.11]$$

In equation [3.3.11] all three sides of our triplet configuration are derivatives with respect to the side NO. Similarly we need to take the derivatives of $\Phi(PNO)$ for all three coefficients $\Phi_{ij}(PNO)(NO)$, $\Phi_{ij}(PNO)(PO)$ and $\Phi_{ij}(PNO)(PN)$.

Writing out $\Phi_{ij}(PNO)(NO)$ we have

$$\begin{aligned}\Phi_{ij}(PNO)(NO) = -\ 2\delta_{ij}\Psi(PNO)(NO) &+ 4\Psi(PNO)(PN)(NO)\ R_i(PN)\ R_j(NO) \\ &+ 4\Psi(PNO)(PN)(PO)\ R_i(PN)\ R_j(PO) \\ &+ 4\Psi(PNO)(NO)(NO)\ R_i(ON)\ R_j(ON) \\ &+ 4\Psi(PNO)(NO)(PO)\ R_i(ON)\ R_j(PO).\end{aligned} \qquad [3.3.12]$$

The remaining terms $\Phi_{ij}(PNO)(PO)$ and $\Phi_{ij}(PNO)(PN)$ are written similarly and the remaining terms from [3.3.6] are given by simply by interchanging i and j so that

$$\Phi_{ij}(PNO)(ON) = \Phi_{ji}(PNO)(NO).$$

[3.3.13]

We then collect all coefficients $\Psi(PNO)(PN)(NO)$, $\Psi(PNO)(PN)(PO)$, $\Psi(PNO)(NO)(NO)$ and $\Psi(PNO)(NO)(PO)$ in [3.3.12] and all the rest of the terms. If for example we take the coefficients of $\Psi(PNO)(PO)(NO)$ which are written out as

$$[R_i(PO)R_j(ON) + R_i(ON)R_j(PO)]\ R_k(NO)R_l(NO),$$
$$[R_i(NO)R_j(OP) + R_i(OP)R_j(NO)]\ R_k(PO)R_l(PO),$$
$$[R_i(ON)R_j(OP) + R_i(OP)R_j(ON)]\ R_k(PN)R_l(PN).$$

[3.3.14]

We have six such coefficients, one from each of the terms from equation [3.3.4]. We can rewrite the last of the terms in [3.3.14] which contains the third side not originating from the origin particle O. The side $R_k(PN)$ is given by

$$R_k(PN) = R_k(PO) - R_k(NO)$$

[3.3.15]

so that [3.3.14] can be written as

$$\begin{aligned}
&- [R_i(PO)R_j(NO) + R_i(NO)R_j(PO)]\ R_k(NO)R_l(NO)\\
&- [R_i(NO)R_j(PO) + R_i(PO)R_j(NO)]\ R_k(PO)R_l(PO)\\
&+ [R_i(NO)R_j(PO) + R_i(PO)R_j(NO)]\ R_k(PO)R_l(PO)\\
&+ [R_i(NO)R_j(PO) + R_i(PO)R_j(NO)]\ R_k(NO)R_l(NO)\\
&- [R_i(NO)R_j(PO) + R_i(PO)R_j(NO)]\ R_k(NO)R_l(PO)\\
&- [R_i(NO)R_j(PO) + R_i(PO)R_j(NO)]\ R_k(PO)R_l(NO).
\end{aligned}$$

[3.3.16]

The first four terms cancel. The last two that are left and may be written as

$$-[R_i(NO)R_j(PO) + R_i(PO)R_j(NO)][R_k(NO)R_l(PO) + R_k(PO)R_l(NO)].$$

[3.3.17]

An equivalent procedure will give the remaining coefficients for the terms coming from $\Psi(PNO)(PN)(NO)$ and $\Psi(PNO)(PN)(PO)$. We have the remaining terms $\Psi(PNO)(NO)(NO)$, $\Psi(PNO)(PO)(PO)$ and $\Psi(PNO)(PN)(PN)$ whose coefficients are given by the term

$$\begin{aligned}
\Psi(PNO)(NO)(NO) &= R_i(ON)R_j(NO)\ R_k(NO)R_l(NO) + R_i(NO)R_j(ON)\ R_k(NO)R_l(NO)\\
&= -2R_i(NO)R_j(NO)R_k(NO)R_l(NO).
\end{aligned}$$

[3.3.18]

Similarly we can write out the coefficients for $\Psi(PNO)(PO)(PO)$ and $\Psi(PNO)(PN)(PN)$. Finally we are left with the coefficients of $2\Psi(PNO)(NO)$ which are simply given by $-2\delta_{ij}$. Hence gathering all the terms together $\hat{A}_{ijkl}$ may be written as

$$\begin{aligned}\hat{A}_{ijkl} = \frac{1}{12v_a} \sum_N \sum_P \Big\{ & \\ & 4\delta_{ij}\Psi(PNO)(NO)\ R_k(NO)R_l(NO) \\ & + 4\delta_{ij}\Psi(PNO)(PO)\ R_k(PO)R_l(PO) \\ & + 4\delta_{ij}\Psi(PNO)(PN)\ R_k(PN)R_l(PN) \\ & + 8\Psi(PNO)(NO)(NO)\ R_i(NO)R_j(NO)R_k(NO)R_l(NO) \\ & + 8\Psi(PNO)(PO)(PO)\ R_i(PO)R_j(PO)R_k(PO)R_l(PO) \\ & + 8\Psi(PNO)(PN)(PN)\ R_i(PN)R_j(PN)R_k(PN)R_l(PN) \\ & + 4\Psi(PNO)(NO)(PO)\ [R_i(NO)R_j(PO) + R_i(PO)R_j(NO)] \\ & \qquad \times [R_k(NO)R_l(PO) + R_k(PO)R_l(NO)] \\ & + 4\Psi(PNO)(NO)(PN)\ [R_i(NO)R_j(PN) + R_i(PO)R_j(NO)] \\ & \qquad \times [R_k(NO)R_l(PN) + R_k(PN)R_l(NO)] \\ & + 4\Psi(PNO)(PO)(PN)\ [R_i(PO)R_j(PN) + R_i(PN)R_j(PO)] \\ & \qquad \times [R_k(PO)R_l(PN) + R_k(PN)R_l(PO)] \Big\}. \end{aligned}$$

[3.3.19]

The first three terms in [3.3.19] collectively make up the terms $\tilde{C}_{kl}\delta_{ij}$ where

$$\begin{aligned}\tilde{C}_{kl} = \frac{1}{12v_a} \sum_N \sum_P \Big\{ & 4\delta_{ij}\Psi(PNO)(NO)\ R_k(NO)R_l(NO) \\ & + 4\delta_{ij}\Psi(PNO)(PO)\ R_k(PO)R_l(PO) \\ & + 4\delta_{ij}\Psi(PNO)(PN)\ R_k(PN)R_l(PN) \Big\}. \end{aligned}$$

[3.3.20]

If we assume that all three sums are identical (that is all three sides of our triangle are identical) then

$$\tilde{C}_{kl} = \frac{1}{v_a} \sum_N \sum_P \Psi_{ij}(PNO)(NO)\ R_k(NO)R_l(NO) \qquad [3.3.21]$$

where we have counted over all triangles twice. We can now go on to simplify $\hat{A}_{ijkl}$ to the final expression

$$\begin{aligned}\hat{A}_{ijkl} = \frac{1}{v_c} \sum_N \sum_P \Big\{ & \Psi(PNO)(NO)\delta_{ij}\ R_k(NO)R_l(NO) \\ & + 2\ (PNO)(NO)(NO)\ R_i(NO)R_j(NO)R_k(NO)R_l(NO) \\ & + \Psi(PNO)(NO)(PO)\ [R_i(NO)R_j(PO) + R_i(PO)R_j(NO)] \\ & \times [R_k(NO)R_l(PO) + R_k(PO)R_l(NO)] \Big\}. \end{aligned} \qquad [3.3.22]$$

The first term in the sum is recognised as $\delta_{ij}\tilde{C}_{kl}$. The elastic moduli can now be determined using [3.2.20]. The terms like $\delta_{ij}\tilde{C}_{kl}$ cancel and the remainder simplifies to

$$\begin{aligned}\tilde{C}_{ijkl} = \frac{2}{v_a} \sum_{NP} \Big[& \Psi(PNO)(NO)(NO)\ R_i(NO)R_j(NO)R_k(NO)R_l(NO) \\ & + 2\Psi(PNO)(NO)(PO)\ R_i(NO)R_j(NO)R_k(PO)R_l(PO) \Big]. \end{aligned} \qquad [3.3.23]$$

This can now be connected with the previous treatments. A general expression for an elastic modulus in terms of energy density expansion parameters is given in [1.2.11]. In the case treated in this section, that of one atom per unit cell, there is no internal stress contribution and the equation reduces to

$$c_{\alpha\beta,\gamma\lambda} = \{\alpha\beta,\gamma\lambda\}.$$

[3.3.24]

This is given for the many atom per unit cell case [2.4.4], which on examination can be seen to be equivalent to [3.3.23].

3.4 TRANSLATIONAL INVARIANCE

For any given initial configuration of a crystal (or any particular configuration within the crystal structure such as a triplet of atoms) not necessarily coinciding with the equilibrium configuration, the i^{th} component of the total force acting on an atom must remain unchanged when the crystal undergoes a uniform translation. So that if we let our system undergo the translation ε, i.e.

$$U_i(M) = \varepsilon_i,$$

[3.4.1]

for all M the corresponding value of the derivative of the total potential $\partial\Phi/\partial U_i(M)$ in equation [3.1.1] is given by

$$\frac{\partial\Phi}{\partial U_i(M)} = \Phi_i(M) + \sum_N \sum_j \Phi_{ij}(M,N)\varepsilon_j + \ldots.$$

[3.4.2]

Since the ε_j is arbitrary, so the coefficients of each power of ε_j in [3.4.2] must vanish, leading to the translational invariance condition

$$\sum_{N} \Phi_{ij}(M,N) = 0.$$

[3.4.3]

Which may be rewritten as

$$\Phi_{ij}(M,M) = -\sum_{M\neq N} \Phi_{ij}(M,N).$$

[3.4.4]

So that the diagonal block force constant is expressed in terms of the off-diagonal block force constant. The term on the left hand side of equation [3.4.4] is sometimes called the "self force constant" which defines the force constant connecting two Cartesian displacements on the same atom. For our three body potential we have the expression for the potential energy

$$\Phi = \frac{1}{6}\sum_{M}\sum_{N\neq M}\sum_{P\neq M,N} \Phi(M,N,P).$$

[3.4.5]

We now write down an analogous expression as in [3.4.5] which includes our three body potential [3.4.6]. For M≠N, $\Phi_{ij}(M,N)$ can be written out as

$$\Phi_{ij}(M,N) = \sum_{P\neq M,N} \Phi_{ij}(M,N,P)(M,N).$$

[3.4.6]

Substituting [3.4.6] in the right hand side of the equation [3.4.4] we have

$$-\sum_{M\neq N}\Phi_{ij}(M,N) = -\sum_{M\neq N}\ \sum_{P\neq M,N}\Phi_{ij}(M,N,P)(M,N),$$

[3.4.7]

the left hand side of the equation can be written for M≠N as

$$\Phi_{ij}(M,M) = -\sum_{M\neq N}\ \sum_{P\neq M,N}\Phi_{ij}(M,N,P)(M,M).$$

[3.4.8]

From using equations [3.3.7] to [3.3.11] we can calculate the right hand side of equation [3.4.4]

$$\begin{aligned}-\sum_{M\neq N}\ \sum_{P\neq M,N}\Phi_{ij}(M,N,P)(M,N) = -\sum_{M\neq N}\ \sum_{P\neq M,N}\Big\{ & \\ & -2\delta_{ij}\ \Phi(MNP)(MN)\ + \\ & -4\Phi(MNP)(MN)(MN)\ R_i(MN)R_j(MN) \\ & +4\Phi(MNP)(MN)(NP)\ R_i(MN)R_j(NP) \\ & +4\Phi(MNP)(MP)(MN)\ R_i(MP)R_j(MN) \\ & +4\Phi(MNP)(MP)(NP)\ R_i(MP)R_j(NP)\Big\}.\end{aligned}$$

[3.4.9]

The left hand side of equation [3.4.4] is given by

$$\sum_{M\neq N}\sum_{P\neq M,N}\Phi_{ij}(M,N,P)(M,M) = \sum_{M\neq N}\sum_{P\neq M,N}\Bigg\{ \begin{aligned}[t] & 2\delta_{ij}\Phi(MNP)(MN) + 2\delta_{ij}\Phi(MNP)(MP) + \\ & + 4\Phi(MNP)(MN)(MN)\ R_i(MN)R_j(MN) \\ & + 4\Phi(MNP)(MN)(MP)\ R_i(MN)R_j(MP) \\ & + 4\Phi(MNP)(MP)(MN)\ R_i(MP)R_j(MN) \\ & + 4\Phi(MNP)(MP)(MP)\ R_i(MP)R_j(MP)\Bigg\}. \end{aligned} \qquad [3.4.10]$$

Working out the remaining term $\Phi(MNP)(MP)$ in a similar way to [3.4.9] we can write out the terms explicitly and then add them together so that we have

$$\begin{aligned} \Phi_{ij}(MNP)(MM) = {} & 2\delta_{ij}[\Phi(MN) + \Phi(MP)] \\ & + 4\Phi(MNP)(MN)(MN)\ R_i(MN)R_j(MN) \\ & + 4\Phi(MNP)(MN)(MP)\ R_i(MN)R_j(MP) \\ & + 4\Phi(MNP)(MP)(MN)\ R_i(MP)R_j(MN) \\ & + 4\Phi(MNP)(MP)(MP)\ R_i(MP)R_j(MP), \end{aligned} \qquad [3.4.11a]$$

$$\begin{aligned} \Phi_{ij}(MNP)(MN) = {} & -\ 2\delta_{ij}\Phi(MN) \\ & - 4\Phi(MNP)(MN)(MN)\ R_i(MN)R_j(MN) \\ & + 4\Phi(MNP)(MN)(NP)\ R_i(MN)R_j(NP) \\ & - 4\Phi(MNP)(MP)(MN)\ R_i(MP)R_j(MN) \\ & + 4\Phi(MNP)(MP)(NP)\ R_i(MP)R_j(NP), \end{aligned} \qquad [3.4.11b]$$

$$\begin{aligned}\Phi_{ij}(MNP)(MP) = &- 2\delta_{ij}\Phi(MP) \\ &- 4\Phi(MNP)(MP)(MP)\ R_i(MP)R_j(MP) \\ &- 4\Phi(MNP)(MP)(NP)\ R_i(MP)R_j(NP) \\ &- 4\Phi(MNP)(MN)(MP)\ R_i(MN)R_j(MP) \\ &- 4\Phi(MNP)(MN)(NP)\ R_i(MN)R_j(NP).\end{aligned}$$

[3.4.11c]

Adding terms together

$$\Phi_{ij}(MNP)(MM) + \Phi_{ij}(MNP)(MN) + \Phi_{ij}(MNP)(MP) = 0.$$

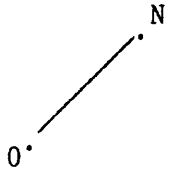
[3.4.12]

Which satisfies equation [3.4.3] and hence the translational invariance conditions.

3.5 DEFINITION OF THREE BODY PARAMETERS

We take a closer look at the definitions of the three body force constants with a view at arriving at a more physical interpretation of the force constants. One such interpretation (as mentioned in section 2.1) is to think of the sides of the triangle of particles as belonging to a three dimensional coordinate space. This way any derivatives of the potential energy are simply taken over the various coordinates of this configuration space.

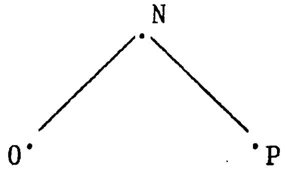
The expression given in [3.3.12] may be interpreted schematically by considering each of the terms on the right hand side of the equation. The first term $\Psi(PNO)(NO)$ is the first derivative of the general potential taken over the side NO of the triangle



$$\Psi(PNO)(NO) = \frac{\partial\Psi(PNO)}{\partial s(NO)}.$$

[3.5.1]

The second term Ψ(PNO)(PN)(NO) is the force constant (second derivative of the potential Ψ(PNO) which describes the interactions of two of the sides of our triangle in our triplet configuration)

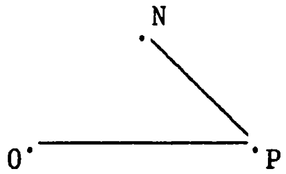


$\partial s(PN)\partial s(NO)$

$$\Psi(PNO)(PN)(NO) = \frac{\partial^2\Psi(PNO)}{\partial s(PN)\partial s(NO)}.$$

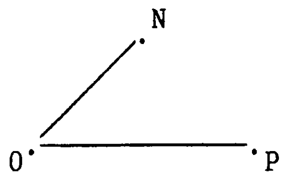
[3.5.2]

Similarly the third and fifth terms in [3.3.12] also describe similar force constants to the one described above and can also be interpreted schematically



$$\Psi(PNO)(PN)(PO) = \frac{\partial^2\Psi(PNO)}{\partial s(PN)\partial s(PO)},$$

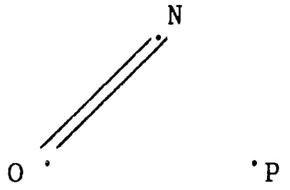
[3.5.3]



$$\Psi(PNO)(NO)(PO) = \frac{\partial^2\Psi(PNO)}{\partial s(NO)\partial s(PO)}.$$

[3.5.4]

The fourth term is a force constant which describes interactions between two atoms in our triplet configuration



$$\Psi(PNO)(NO)(NO) = \frac{\partial^2\Psi(PNO)}{\partial s(NO)\partial s(NO)}.$$

[3.5.5]

We can see that from [3.5.2], [3.5.3] and [3.5.4] that the force constants describe the interactions amongst all three atoms simultaneously while in [3.5.5] we have a pseudo two body interaction since there we are describing the interaction between two particles under a three body potential.

If we take a more specific configuration then such as an equilateral triangular configuration then all three force constants [3.5.2], [3.5.3] and [3.5.4] will be equivalent. We can use these definitions of force constants when we go on to calculate the elastic constants (linear combinations of force constants) of such systems as the cubic lattice and then go on to the diamond lattice where the resulting expressions for the force constants using valence potential are well described. This will allow comparison between the resulting expressions of the elastic force constants.

CHAPTER 4

SQUARE and CUBIC LATTICE

4.1 Introduction

4.2 Elastic Constants for Square and Cubic Lattices

4.3 Discussion

4.1 INTRODUCTION

The results from the previous chapter are now applied to two model systems: the square net and the simple cubic lattice. In fact, the two are closely related and the two dimensional system can be used as a stepping stone to the physically more realistic three dimensional crystal. At this stage, the constants arising from the three body interactions are parameters, the magnitudes of which are not readily estimated so that only general qualitative conclusions can be expected. As throughout this work, attention will be focused on elastic moduli and the corresponding stability conditions.

4.2 ELASTIC CONSTANTS FOR SQUARE and CUBIC LATTICES

Both the systems under consideration have only one atom per unit cell, so that for three body interactions the simplified formula [3.3.23] derived in the last chapter can be used as a starting point. According to this an elastic constant is represented by

$$c_{ijkl} = \frac{2}{v_a} \sum_{NP} \Big[\Psi(PNO)(NO)(NO)R_i(NO)R_j(NO)R_k(NO)R_l(NO) + 2\Psi(PNO)(NO)(PO)R_i(NO)R_j(NO)R_k(PO)R_l(PO) \Big]. \qquad [4.2.1]$$

Examination of this equation shows that each triangle containing the atom O is summed over twice. The equation can be symmetrised with respect to N and P and the summation adjusted so that each triangle is summed over once.

$$
\begin{aligned}
C_{ijkl} = \frac{2}{V_a} \sum_{N} \sum_{P>N} \Big[& \Psi(PNO)(NO)(NO)R_i(NO)R_j(NO)R_k(NO)R_l(NO) \\
& + \Psi(PNO)(PO)(PO)R_i(PO)R_j(PO)R_k(PO)R_l(PO) \\
& + 2\Psi(PNO)(NO)(PO)R_i(NO)R_j(NO)R_k(PO)R_l(PO) \\
& + 2\Psi(PNO)(PO)(NO)R_i(PO)R_j(PO)R_k(NO)R_l(NO) \Big] .
\end{aligned}
$$

[4.2.2]

In the case of the square net, two body interactions for first and second nearest neighbours will be included. In addition, three body terms arising from the smallest possible triangle will be taken into account.

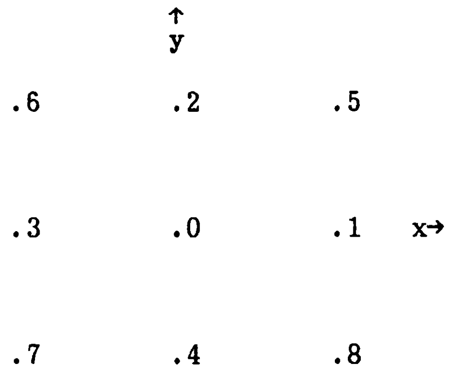


Fig. [4.2.1]

In terms of the diagram shown, there are four triangles such as (012) with the origin and two nearest neighbours and eight triangles such as (015) with the origin, one nearest and one second nearest neighbour. This illustrates the complication associated with three body interactions: the twelve triangles have the same shape and size and are therefore of potentially equal importance but there are two different arrangements when classified with respect to nearest neighbour interactions.

With respect to the simple cubic lattice, it is seen that the figure is a section of this lattice. Moreover, to a first approximation, only those interactions included in the square net will be taken into account for the simple cubic case. In this way, the three dimensional crystal is built up by a sum of contributions from the xy, xz and yz planes.

Strictly, the expression written in [4.2.2] for the elastic modulus contains the three atom contributions only. The corresponding two atom contribution was discussed in section 1.3 and may be written in a form corresponding to the notation in this chapter.

$$c_{ijkl} = \frac{2}{V_a} \sum_{N} \Psi''(NO)\ R_i(NO) R_j(NO) R_k(NO)_l R(NO), \qquad [4.2.3]$$

in which $\Psi''(NO)$ represents the value of the second derivative of the pair potential with respect to the square of the interparticle distance. The total elastic modulus is the sum of [4.2.2] and [4.2.3].

The results can be expressed in terms of a relatively small number of parameters which are defined as follows for two body terms.

$$k_F \equiv \Psi''(10), \qquad k_S \equiv \Psi''(50). \qquad [4.2.4]$$

Here k_F is the force constant for a first neighbour pair such as (10) and k_S for a second neighbour pair such as (50).

In a similar way for three body terms

$$k_{FF} \equiv \Psi''(012)(01)(01) \equiv \Psi''(015)(01)(01)$$

$$k_{SS} \equiv \Psi''(015)(05)(05)$$

$$k_{FG} \equiv \Psi''(012)(01)(02)$$

$$k_{FS} \equiv \Psi''(015)(01)(05)$$

[4.2.5]

Here k_{FF} is the force constant for a first neighbour pair from the triplet named. Note that the value is the same for triangles (012) and (015) because they have the same shape. In a similar way, k_{SS} refers to second nearest neighbours. k_{FG} is the cross term between two nearest neighbour pairs and k_{FS} for a first and second nearest pair. These cross terms do not arise for the two body interaction since this depends on only one distance.

The details of the derivation are given in an appendix at the end but the final results for the elastic moduli of the simple cubic atomic lattice are summarised below

$$c_{11} = 8a(k_F + 2k_S + 4k_{FF} + 4k_{SS} + 8k_{FS})$$

[4.2.6]

$$c_{12} = 8a(k_S + 2k_{SS} + 2k_{FG} + 4k_{FS})$$

[4.2.7]

$$c_{44} = 8a(k_S + 2k_{SS})$$

[4.2.8]

If a is the lattice constant, all force constant terms contain a factor a^4 which partially cancels with the unit cell volume v_a which is a^3.

4.3 DISCUSSION

The elastic moduli for an atomic simple cubic lattice have been determined for two and three body interactions restricted to near neighbours. The precise expressions are summarised in [4.2.4] to [4.2.6].

The three atom terms may be subdivided into two types. The constant k_{FF}, for example, is the value of a second differential made with respect to the same distance squared twice. It is multiplied by relative cartesian coordinates of this same distance. In this way it refers to only one pair of atoms explicitly and hence is effectively only a two body contribution to the elastic modulus. The constant k_{FS}, for example, on the other hand is the value of a second differential with respect to two different distances and is multiplied by cartesian coordinates referring to all three atoms. Constants of this type represent genuine three body contributions to the properties under consideration.

For elastic stability, following [1.4.8], three conditions are necessary for a cubic structure.

$$c_{11}+2c_{12}>0 \qquad c_{11}-c_{12}>0 \qquad c_{44}>0 \tag{4.3.1}$$

The simplest of these is the last: $c_{44}>0$. Neglecting three body potentials, this takes the value $8ak_S$. A typical form for the two body potential is illustrated in fig [1.4.1]. The nearest neighbour distance is likely to be in the region of the minimum where the value of the second derivative (and hence k_F) is positive. The second nearest neighbour distance is root two times the nearest neighbour distance. For the sort of potential functions used, the second derivative (and hence k_S) is now negative. In this way, c_{44} is negative in the two body model and the lattice is unstable. This constant represents a shear deformation. It is noted that addition of more distant two atom terms does not confer stability as the second derivative of the potential remains negative for large values of the distance.

When the three body potential is taken into account, a term $16ak_{SS}$ is added to c_{44}. It is then essential for stability that k_{SS} is positive and that

$$|k_{SS}| > \frac{1}{2}|k_S|. \qquad [4.3.2]$$

It is noted that, to this level of approximation, the three body contribution consists of effective two body terms only.

For the second stability condition

$$c_{11}-c_{12}= 8a(k_F+k_S+4k_{FF}+2k_{SS}-2k_{FG}+4k_{FS}), \qquad [4.3.3]$$

must be positive. For the two atom potential model, only k_F and k_S survive. It has already been stated that the first of these constants is likely to be positive and the second negative. The same potentials on which these arguments are based give values of k_F which are much greater in magnitude than k_S. Hence this second stability condition is expected to hold for the central interaction model.

The third stability condition is that

$$c_{11}+2c_{12}= 8a(k_F+4k_S+4k_{FF}+8k_{SS}+4k_{FG}+16k_{FS}),$$

[4.3.4]

is positive. By a similar argument, this stability condition is expected to hold for the two atom interaction model.

It can be seen that the role of the three atom interactions in both these last two conditions is complicated, there being four constants. It is required to estimate signs and magnitudes of the various terms. Since all four are derived from a single function, it may be possible to achieve this. A preliminary investigation is presented in chapter 6.

The most stringent requirement is that the three body interaction should lead to a positive value of c_{44} and it has been seen that a single parameter k_{SS} is the critical factor.

On the experimental side, it is noted that there is only one simple cubic atomic lattice known, that of α-polonium (J. Donohue 1974). An experimental consequence of the central model which is often quoted is that the Cauchy conditions hold i.e.

$$c_{12}= c_{44}$$

[4.3.5]

From the results given here

$$c_{12}-c_{44}= 16a(k_{FG}+2k_{FS})$$

[4.3.6]

Two comments may be made. The first is that the departure from the Cauchy result is due to genuine three body effects i.e. from force constants depending on two inter atomic distances and hence three atomic positions. The second is that the difference is due wholly to c_{12}.

CHAPTER 5

LATTICE DYNAMICS OF DIAMOND

5.1 INTRODUCTION

The lattice dynamics of diamond and diamond like structures has been discussed in the literature by Born (1914), his collaborator Smith (1948) and Warren *et al* (1957). Musgrave and Pople (1962) use spectroscopic data of molecules to calculate the force constants obtained by Born and Smith. More recently Cowley (1982) has proposed several models for the interatomic potential of silicon and uses them to generate the interatomic force constants.

The forces determining the structure of diamond arise from covalent bonding between carbon atoms. In molecules exhibiting such bonding a potential energy expression in terms of changes in bond distances, interbond angles, dihedral angles and similar internal coordinates (often called valence coordinates) frequently give close agreement between observed and calculated frequencies with relatively few force constants. One advantage of using valence coordinates is that the structures in the crystal closely resemble those in a molecule whose vibrations have been interpreted in terms of valence force functions.

Musgrave and Pople use the results of Smith in order to write down the elastic constants of diamond by the use of spectroscopic data obtained from the neopentane $C(CH_3)_4$ molecule. The values of force constants calculated from the data are then used to calculate theoretical values for the Raman frequency and values for elastic constants.

Born and Smith using a general potential function have obtained a set of coefficients from the potential energy expansion which were then used to calculate the force constants of diamond for first and second nearest neighbour interactions. These coefficients (parameters in the theory) were expressed by calculating the dymamical matrix whose elements they are. Similar calculations were also carried out by Ramathan (1947) and St James (1958). By using the symmetry operations belonging to the diamond structure and looking at solutions of the equation of motion at the long wavelength limit $q \rightarrow 0$ it is possible to express the values of the Raman frequency and elastic constants in terms of the parameters. Also expressions for the dispersion relations between the frequency and the wave vector are obtained in terms of the parameters so that a calculation of these relations is possible along certain directions of high symmetry along the Brillouin zone (Brillouin 1946).

The parameters obtained by Smith are the most general ones which occur in this type of analysis. Also the use of a general potential function gives the least number of parameters to which experimental data may be fitted. The number of parameters will of course increase sharply as we include more and more distant neighbour interactions. In case of diamond (Born 1946) it was thought that by simply extending the previous analysis to include second neighbour interactions that the calculated theoretical values of the elastic constants and Raman frequency would be brought to closer agreement with the experimental values. This was not found to be the case (Smith 1948). In fact it is necessary to go out to fifth nearest neighbours (Herman 1956) before such agreement is possible. Cousins (1982) gives a useful survey of various theoretical approaches in which the internal strain paramaters are extracted from various models of elasticity and lattice dynamics of diamond and diamond like structures.

The advantages of using valence coordinates over the more general parameters is that they give themselves more readily to physical interpretation that is the force constants can be attributed to bond and angle changes within the structure. The disadvantages of using valence coordinates become apparent when the need for mathematical manipulation becomes necessary and difficulties arise from the non orthogonal character of such coordinates.

It is suggested that perhaps the use of a coordinates system where the atoms are all treated equivalently might be more useful in terms of manipulation and flexibility when we include many body interactions in the analysis.

5.2 GENERAL THEORY

The expression for the potential energy of the crystal when the atoms are given small displacement is written down as

$$\Phi = \frac{1}{2}\sum_{lk}\sum_{l'k'}\sum_{\alpha\beta}\Phi_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix}u_{\alpha}\begin{pmatrix} l \\ k \end{pmatrix}u_{\beta}\begin{pmatrix} l' \\ k' \end{pmatrix}.$$

[5.2.1]

where l identifies a unit cell, k a particular atom in the unit cell. The equilibrium positions are given by

$$r\begin{pmatrix} l \\ k \end{pmatrix} = r^{l} + r_{k},$$

[5.2.2]

and rectangular components of $r\begin{pmatrix} l \\ k \end{pmatrix}$ are $æ_{\alpha}\begin{pmatrix} l \\ k \end{pmatrix}$ (α = 1,2,3). The index k runs from 1 to n, (n is the number of atoms in the unit cell) so the number of independent coordinates is 3nN. The equation of motion of a particle of type k and mass m_k is then

$$m_k \ddot{u}_\alpha\begin{pmatrix} l \\ k \end{pmatrix} = -\sum_{l'k'}\sum_{\beta} \Phi_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} u_\beta\begin{pmatrix} l' \\ k' \end{pmatrix},$$

[5.2.3]

which is formally solved by introducing the plane wave (Born and Begbie 1946)

$$v\begin{pmatrix} l \\ k \end{pmatrix} = V(k) \exp i(q.r^l - \omega t),$$

[5.2.4]

where $v\begin{pmatrix} l \\ k \end{pmatrix}$ is a reduced displacement vector $\sqrt{m_k}\, u\begin{pmatrix} l \\ k \end{pmatrix}$ and the coefficient $\Phi_{\alpha\beta}(ll':kk')$ is rewritten as

$$D_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} = \frac{1}{(m_k m_{k'})^{1/2}} \Phi_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix}.$$

[5.2.5]

So that the equation of motion becomes

$$\omega^2 V_\alpha(k) = \sum_{k'\beta} D_{\alpha\beta}\begin{pmatrix} & q & \\ k & & k' \end{pmatrix} V_\beta(k'),$$

[5.2.6]

where

$$D_{\alpha\beta}\begin{pmatrix} & q & \\ k & & k' \end{pmatrix} = \sum_{l'}\sum_{\beta} D_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} \exp -i(q.r^{l}),$$

[5.2.7]

where D(q) is the representation of the dynamical matrix in reciprocal space. In order to calculate the force constants we can use the symmetry of the crystal. If S represents the operation of a centre of symmetry (without translation) about $r\begin{pmatrix} l \\ k \end{pmatrix}$ which brings $r\begin{pmatrix} l' \\ k' \end{pmatrix}$ into coincidence with $r\begin{pmatrix} l'' \\ k' \end{pmatrix}$ and leaves $r\begin{pmatrix} l \\ k \end{pmatrix}$ unaffected then if

$$S = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix},$$

[5.2.8]

it follows then that the matrix $D_{\alpha\beta}(ll':kk')$ transforms as (Cochran 1966)

$$D_{\alpha\beta}\begin{pmatrix} l & l'' \\ k & k' \end{pmatrix} = SD_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix}\tilde{S},$$

[5.2.9]

where $\tilde{S}$ is the transpose of S. Certain symmetry operations will bring the atom (l'k') into self coincidence as well as the one at (lk). For these symmetry operations

$$D_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} = S_{o}D_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix}\tilde{S}_{o}.$$

[5.2.10]

This relation limits the number of independent force constants. The solution of the equation of motion [5.2.6] for long wavelength limit is used to find the elastic constants.

There is a different route which does not exploit the symmetry of the lattice directly but is more convenient when considering many body interactions. It is possible to write out an explicit expression for the elements (force constants) in the dynamical matrix and then go on to calculate the force constants for any pair, triplet or any other multibody interaction. The second derivatives of the potential energy can be written down for the simple case of one atom per unit cell and central interactions

$$\Phi_{\alpha\beta}(11') = \frac{\partial^2\Phi}{\partial u_\alpha(1)\partial u_\beta(1')},$$

$$\frac{\partial^2\Phi}{\partial u_\alpha(1)\partial u_\beta(1')} = \frac{\partial^2 s}{\partial u_\alpha(1)\partial u_\beta(1')} \cdot \frac{\partial\Phi}{\partial s} + \frac{\partial s}{\partial u_\alpha(1)} \cdot \frac{\partial s}{\partial u_\beta(1')} \cdot \frac{\partial^2\Phi}{\partial s^2},$$

[5.2.11]

where the configuration vector s is defined as

$$s = R^2_{11'} = \sum_\alpha \left[u_\alpha(1) - u_\alpha(1')\right]^2.$$

[5.2.12]

Hence the force constant is given by the expression

$$\Phi_{\alpha\beta}(11') = -2\delta_{\alpha\beta}\Psi' - 4\text{æ}_\alpha\text{æ}_\beta\Psi''.$$

[5.2.13]

where the terms $\varkappa_\alpha$ and $\varkappa_\beta$ are the Cartesian components of the distance between the atoms in the crystal usually taken from some reference atom point. The differential Ψ' and Ψ'' are the first and second order differential respectively of the potential over the configuration vector s.

5.3 CORRECTION TO THEORY

Before proceeding further, it should be pointed out that there is an error in Smith's treatment of the next nearest neighbour dynamical matrices. The general forces between nearest neighbours are described by the parameters α and β and in Smith's notation it is suggested that there are only three independent dynamical matrix elements μ,ν and λ. There is in fact a fourth which we shall call σ, which Smith has incorrectly set equal to zero. Thus the correct form of the matrix Smith calls D^9 is

$$-\frac{1}{m}\begin{vmatrix} \mu & \nu & \sigma \\ \nu & \mu & \sigma \\ -\sigma & -\sigma & \lambda \end{vmatrix},$$

rather than [5.3.1]

$$-\frac{1}{m}\begin{vmatrix} \mu & \nu & 0 \\ \nu & \mu & 0 \\ 0 & 0 & \lambda \end{vmatrix}.$$

[5.3.2]

We can see from the diagram below that

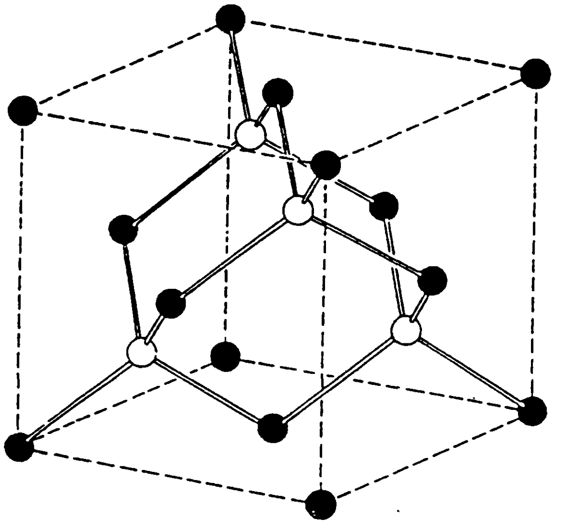


Fig. [5.3.1]

the atoms lying on the face centered cubic sites lie at a centre of octahedral symmetry while the remaining four atoms lie at a centre of tetrahedral symmetry.

When deriving the dynamical matrices of the face centred cubic lattice the reflexion planes $æ_\alpha = \pm æ_\beta$ and $æ_\alpha = 0$ are valid and so from the symmetry elements describing these planes the matrix [5.3.2] is obtained. Smith uses the same symmetry elements to derive her matrix elements for second nearest neighbours in the diamond structure, but because only half the tetrahedral holes are filled then the symmetry element $æ_\alpha = 0$ no longer exists and only the reflexion planes $æ_\alpha = \pm æ_\beta$ still hold. Consequently the extra element σ appears in the matrix as in [5.3.1].

The additional matrix element must be taken into account in any of the expressions used to calculate the frequency spectrum and subsequent dispersion relations. The antisymmetric off diagonal elements of the dynamical matrix D(q) are given as

$$D_{12}\begin{pmatrix} q \\ 1\ \ 1 \end{pmatrix} = \frac{4\nu}{m} \sin \pi q_x \sin \pi q_y,$$

$$D_{13}\begin{pmatrix} q \\ 1\ \ 1 \end{pmatrix} = \frac{4\nu}{m} \sin \pi q_z \sin \pi q_x,$$

$$D_{23}\begin{pmatrix} q \\ 1\ \ 1 \end{pmatrix} = \frac{4\nu}{m} \sin \pi q_y \sin \pi q_z,$$

[5.3.3]

where these elements are taken over the q_x, q_y, q_z space. With the additional parameter σ we have the expressions

$$D_{12}\begin{pmatrix} q \\ 1\ \ 1 \end{pmatrix} = \frac{4\nu}{m} \sin \pi q_x \sin \pi q_y - i4\sigma \sin \pi q_z(\cos \pi q_x - \cos \pi q_y),$$

$$D_{13}\begin{pmatrix} q \\ 1\ \ 1 \end{pmatrix} = \frac{4\nu}{m} \sin \pi q_z \sin \pi q_x - i4\sigma \sin \pi q_y(\cos \pi q_z - \cos \pi q_x),$$

$$D_{23}\begin{pmatrix} q \\ 1\ \ 1 \end{pmatrix} = \frac{4\nu}{m} \sin \pi q_y \sin \pi q_z - i4\sigma \sin \pi q_x(\cos \pi q_y - \cos \pi q_z).$$

[5.3.4]

When the dispersion relations are calculated along symmetry directions of the Brillouin Zone it is found that the only direction where the the parameter σ appears is in the $[\frac{1}{2}\ \frac{1}{2}\ 0]$ direction, otherwise all other dispersion relations remain unaffected.

The relations between the macroscopic elastic constants and the atomic force are given by Smith (1948) as

$$2ac_{11} = (\alpha + 8\mu),$$

$$2ac_{12} = (\alpha - \frac{\beta^2}{2} + 4\lambda + 4\mu),$$

$$2ac_{44} = (2\beta - \alpha - 4\lambda - 4\mu + 8\nu).$$

[5.3.5]

The force constant σ appears in the secular equation but not in the long wavelength approximation from which the above relations are obtained.

5.4 THREE BODY POTENTIAL EXPRESSION

The diamond lattice can be thought of as two equivalent interpenetrating face centered cubic lattices, relatively displaced one quarter of the way along the cube diagonal. Diamond has the translational symmetry of face centered cubic lattice and at each point of the face centred cubic Bravais (space) lattice it has a basis consisting of two atoms at a distance of $\frac{\sqrt{3}}{2}a$, where 2a is the lattice constant.

If we go to a Cartesian coordinate system with the origin at a lattice point and axes parallel to the cube edges, the primitive (cell vectors) vectors of the the lattice are given by

$$a_1 = a(0,1,1), \quad a_2 = a(1,0,1), \quad a_3 = a(1,1,0). \qquad [5.4.1]$$

The coordinates of the two atoms in the unit cell are (0,0,0) and $(\frac{1}{2}a,\frac{1}{2}a,\frac{1}{2}a)$ which are labelled as 0 and 0′ respectively. The atoms lying on the same cubic lattice as 0 are labelled k=1, and those lying on the same lattice as 0′ are labelled k=2. Each of the atoms in the basis has four nearest neighbours arranged tetrahedral at a distance $\frac{\sqrt{3}}{2}a$ which sit on the other f.c.c lattice such that any interactions between these neighbours always involve relative sublattice displacements. When we go on to second nearest neighbours then the same atoms in the basis have twelve second nearest neighbours at a distance $\sqrt{2}a$ which lie on the same f.c.c. lattice.

In order to include a three body interaction in our diamond lattice we must first expand on the expression used by Smith for the force constant. We use an analogous expression to [5.2.11] for the Taylor coefficient as

$$\frac{\partial^2\Phi(abc)}{\partial u_\alpha(a)\partial u_\beta(b)}, \tag{5.4.2}$$

where

$$\Phi(abc) = \Phi[s(ab),s(bc),s(ca)]. \tag{5.4.3}$$

and

$$s(ab) = r^2(ab) = [r_x(ab)]^2 + [r_y(ab)]^2 + [r_z(ab)]^2, \tag{5.4.4}$$

where the atomic distances s(ab),s(bc),s(ca) are the nearest neighbour distances which together make up the sides of the triplet.

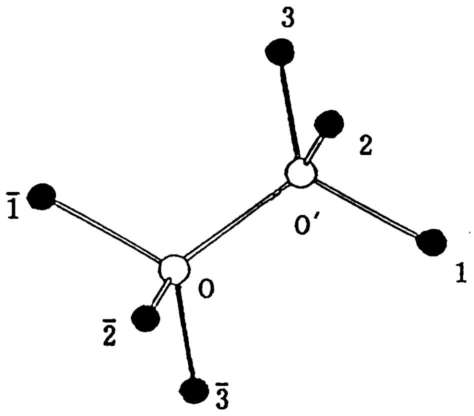


Fig. [5.4.1]

When we consider nearest neighbour interactions then the origin of our triangle is taken as the distance between the atoms at (0,0,0) and $(\frac{1}{2}a,\frac{1}{2}a,\frac{1}{2}a)$ so that all nearest neighbour triplet interactions have that side common to them. There are in common a total of six nearest neighbour triplet of atoms making up all nearest neighbour interactions. If we expand [5.4.2] then we have

$$\begin{aligned}\Phi = -\Psi'_{ab}2\delta_{\alpha\beta} &+ 4\ \text{æ}_{\alpha}(ab)\text{æ}_{\beta}(ba)\ \Psi''_{(ab)(ba)}\\ &+ 4\ \text{æ}_{\alpha}(ab)\text{æ}_{\beta}(bc)\ \Psi''_{(ab)(bc)}\\ &+ 4\ \text{æ}_{\alpha}(ac)\text{æ}_{\beta}(ba)\ \Psi''_{(ac)(ba)}\\ &+ 4\ \text{æ}_{\alpha}(ac)\text{æ}_{\beta}(bc)\ \Psi''_{(ab)(bc)}.\end{aligned} \tag{5.4.5}$$

We can rewrite the above expression so that the derivatives are taken over the triplet sides can be distinguished by whether they lie along a carbon, carbon bond or not. We rewrite [5.4.5] as

$$\begin{aligned}\Phi = -\Psi'_{N}\ 2\delta_{\alpha\beta} &+ 4\ \Psi_{NN}\text{æ}_{\alpha}(ab)\text{æ}_{\beta}(ba)\\ &+ 4\ \Psi_{NB}[\text{æ}_{\alpha}(ab)\text{æ}_{\beta}(bc) + \text{æ}_{\alpha}(ac)\text{æ}_{\beta}(ba)]\\ &+ 4\ \Psi_{BB'}\text{æ}_{\alpha}(ac)\text{æ}_{\beta}(bc)\end{aligned} \tag{5.4.6}$$

If we calculate the contribution of the triplet $D(O,O',1)$ (see fig. [5.4.1]) for nearest neighbour force constant then from equation [5.4.6] our triplets will correspond to D(abc) where all contributions from $D(O,O',1)$, $D(O,O',2)$ and $D(O,O',3)$ will have the side s(ac) as the non bonded side and s(ab) and s(bc) as the two bonded sides.

Contributions from the triplets D(O,O',$\bar{1}$), D(O,O',$\bar{2}$) and D(O,O',$\bar{3}$) will still have the side s(ab) as the bonded side but now the other bonded side is s(ac) and non bonded side is now s(bc). The second nearest neighbour interactions are considered in a similar way except that the common side to all triplets (there is in fact only one such configuration) is the non bonded side 01 (from fig. [5.4.1]).

k	l	$\varkappa_1$	$\varkappa_2$	$\varkappa_3$
k=1	O'	$\frac{1}{2}a$	$\frac{1}{2}a$	$\frac{1}{2}a$
	$\bar{1}$	$-\frac{1}{2}a$	$-\frac{1}{2}a$	$\frac{1}{2}a$
	$\bar{2}$	$-\frac{1}{2}a$	$\frac{1}{2}a$	$-\frac{1}{2}a$
	$\bar{3}$	$\frac{1}{2}a$	$-\frac{1}{2}a$	$-\frac{1}{2}a$

Table [5.4.1]

k	l	$\varkappa_1$	$\varkappa_2$	$\varkappa_3$
k=2	O	0	0	0
	1	a	a	0
	2	a	0	a
	3	0	a	a

Table [5.4.2]

Table [5.4.1] gives the coordinates of the first neighbours of 0 and table [5.4.2] gives the coordinates of first neighbours of 0′. Table [5.4.3] gives the various interatomic distances needed to calculate the triplet contributions given by $D(O,O',1)$, $D(O,O',2)$ and $D(O,O',3)$ using [5.4.6].

	æ_1	æ_2	æ_3
$\text{æ}_\alpha(ab)$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
$\text{æ}_\beta(ba)$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
$\text{æ}_\alpha(ac)$	-1	-1	0
$\text{æ}_\beta(ca)$	1	1	0
$\text{æ}_\beta(bc)$	$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$
$\text{æ}_\alpha(cb)$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$

Table [5.4.3]

Where the lattice constant factor, a is taken out for simplicity. From [4.5.6] we have

$$D(a,b,c) = D(O,O',1) = \begin{bmatrix} C_1 & C_3 & C_4 \\ C_3 & C_1 & C_4 \\ C_3 & C_3 & C_2 \end{bmatrix} . \qquad [5.4.7]$$

Where:

$C_1 = D_{xx}(O,O',1) = D_{yy}(O,O',1) = -2\Psi_B - \Psi_{BB} + \Psi_{BB'},$

$C_2 = D_{zz}(O,O',1) = -2\Psi_B - \Psi_{BB} - \Psi_{BB'},$

$C_3 = D_{xy}(O,O',1) = D_{yx}(O,O',1) = D_{zx}(O,O',1) = D_{zy}(O,O',1) = -\Psi_{BB} + \Psi_{BB'},$

$C_4 = D_{xz}(O,O',1) = D_{yz}(O,O',1) = -\Psi_{BB} - \Psi_{BB'}.$

Similar contributions are calculated for the remaining set of triplets $D(O,O',2)$, $D(O,O',3)$, $D(O,O',\bar{1})$, $D(O,O',\bar{2})$, and $D(O,O',\bar{3})$.

Thus for nearest neighbour triplets we have the force constant matrix

$$-2\begin{vmatrix} 6\Psi_B + 3\Psi_{BB} - \Psi_{BB'} & 3\Psi_{BB} + 4\Psi_{NB} - \Psi_{BB'} & 3\Psi_{BB} + 4\Psi_{NB} - \Psi_{BB'} \\ 3\Psi_{BB} + 4\Psi_{NB} - \Psi_{BB'} & 6\Psi_B + 3\Psi_{BB} - \Psi_{BB'} & 3\Psi_{BB} + 4\Psi_{NB} - \Psi_{BB'} \\ 3\Psi_{BB} + 4\Psi_{NB} - \Psi_{BB'} & 3\Psi_{BB} + 4\Psi_{NB} - \Psi_{BB'} & 6\Psi_B + 3\Psi_{BB} - \Psi_{BB'} \end{vmatrix}. \qquad [5.4.8]$$

For the second nearest neighbours the force constant matrix is

$$-\begin{vmatrix} 2\Psi_N + 4\Psi_{NN} + 4\Psi_{NB} + \Psi_{BB'} & 4\Psi_{NN} + 4\Psi_{NB} + \Psi_{BB'} & -2\Psi_{NB} - \Psi_{BB'} \\ 4\Psi_{NN} + 4\Psi_{NB} + \Psi_{BB'} & 2\Psi_N + 4\Psi_{NN} + 4\Psi_{NB} + \Psi_{BB'} & -2\Psi_{NB} - \Psi_{BB'} \\ 2\Psi_{NB} + \Psi_{BB'} & 2\Psi_{NB} + \Psi_{BB'} & 2\Psi_N - \Psi_{BB'} \end{vmatrix}. \qquad [5.4.9]$$

The force constants Ψ_{BB} and Ψ_{NN} are in fact pseudo-two body and describe interactions between pairs of atoms under a three body potential. We now write down the force constants resulting from two body interactions for nearest and next nearest neighbours in terms of our bonded and non bonded atoms in the triplet. These force constants are given in a more general form by Smith (1948). By using the expression [5.2.13] we can work out analogous force constant matrices in terms of our parameters.

Nearest neighbour interactions give the force matrix

$$-\frac{1}{m}\begin{vmatrix} 2\Phi_B + \Phi_{BB} & \Phi_{BB} & \Phi_{BB} \\ \Phi_{BB} & 2\Phi_B + \Phi_{BB} & \Phi_{BB} \\ \Phi_{BB} & \Phi_{BB} & 2\Phi_B + \Phi_{BB} \end{vmatrix}.$$

[5.4.10]

Which is analogous to the matrix given by Smith (1948)

$$-\frac{1}{m}\begin{vmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{vmatrix}.$$

[5.4.11]

The elastic constants are given by the expression (Smith 1948)

$$2ac_{11} = \alpha, \qquad 2ac_{12} = 2\beta - \alpha, \qquad 2ac_{44} = \alpha - \frac{\beta^2}{\alpha}.$$

[5.4.12]

In terms of our parameters the elastic constants may be rewritten (using the above result of Smith) as

$$2ac_{11} = 2\Phi_B + \Phi_{BB}, \qquad 2ac_{12} = \Phi_{BB} - 2\Phi_B, \qquad 2ac_{44} = \Phi_{BB} + 2\Phi_B - \frac{\Phi_{BB}^2}{\Phi_{BB} + 2\Phi_B}.$$

[5.4.13]

When we go on to consider second nearest neighbour interactions we have the matrix

$$-\frac{1}{m}\begin{vmatrix} 2\Phi_N + 4\Phi_{NN} & 4\Phi_{NN} & 0 \\ 4\Phi_{NN} & 2\Phi_N + \Phi_{NN} & 0 \\ 0 & 0 & 2\Phi_N \end{vmatrix}.$$

[5.4.14]

Which is analogous to the second nearest neighbour matrix

$$-\frac{1}{m}\begin{vmatrix} \mu & \nu & 0 \\ \nu & \mu & 0 \\ 0 & 0 & \lambda \end{vmatrix}.$$

[5.4.15]

The expression for the elastic constants for second nearest neighbour interactions are given again by Smith (1948):

$$2ac_{11} = \alpha + 8\mu$$
$$2ac_{12} = 2\beta - \alpha - 4\mu - 4\lambda + 8\nu$$
$$2ac_{44} = \alpha + 4\lambda + 4\mu - \frac{\beta^2}{\alpha}$$

[5.4.16]

Hence we can also write down the expressions for the elastic constants for second nearest neighbours:

$$2ac_{11} = \Phi_{BB} + 2\Phi_{B} + 16\Phi_{N} + 32\Phi_{NN},$$
$$2ac_{12} = \Phi_{BB} - 2\Phi_{B} - 16\Phi_{N} + 16\Phi_{NN},$$
$$2ac_{44} = \Phi_{BB} + 2\Phi_{B} + 16\Phi_{N} + 16\Phi_{NN} - \frac{\Phi_{BB}^2}{\Phi_{BB} + 2\Phi_{B}}.$$

[5.4.17]

From the condition of zero pressure as given by Born and Huang (1954) below:

$$\sum_{lkk'} \text{æ}_{\alpha}\begin{pmatrix} l \\ k\ \ k' \end{pmatrix} \text{æ}_{\beta}\begin{pmatrix} l \\ k\ \ k' \end{pmatrix} \Psi'\left(x\left|\begin{matrix} l \\ k\ \ k' \end{matrix}\right|^2\right) = 0.$$

[5.4.18]

We now have a relation between the forces (first derivatives of the potential) Φ_B and Φ_N such that

$$\Phi_N = -\frac{1}{8}\Phi_B.$$

[5.4.19]

Hence the expressions [5.4.17] can be simplified to

$$2ac_{11} = \Phi_{BB} + 32\Phi_{NN},$$

$$2ac_{12} = \Phi_{BB} + 16\Phi_{NN},$$

$$2ac_{44} = \Phi_{BB} + 16\Phi_{NN} - \frac{\Phi_{BB}^2}{\Phi_{BB} + 2\Phi_B}.$$

[5.4.20]

We can also write down linear combinations of elastic constants. One such combination is related to the compressibility of the crystal and is given in terms of the elastic constants c_{11} and c_{12}:

$$2a(c_{11} + 2c_{12}) = 3\Phi_{BB} + 64\Phi_{NN}.$$

[5.4.21]

Another such combination is related to the shearing deformations of the crystal and again is given in terms of the elastic constants c_{11} and c_{12}:

$$2a(c_{11} - c_{12}) = 16\Phi_{NN}.$$

[5.4.22]

We can now combine our results for two body force constants and three body force constants for nearest neighbours [5.4.10] and [5.4.8] so that the force constants α and β are given by:

$$\alpha = \Phi_{BB} + 2\Phi_{B} + 6\Psi_{BB} + 12\Psi_{B} - 2\Psi_{BB'},$$
$$\beta = \Phi_{BB} + 6\Psi_{BB} + 8\Psi_{NB} - 2\Psi_{BB'}.$$

[5.4.23]

The elastic constants can be written down from [5.4.12]

$$2ac_{11} = \Phi_{BB} + 2\Phi_{B} + 12\Psi_{B} - 2\Psi_{BB'},$$
$$2ac_{12} = \Phi_{BB} - 2\Phi_{B} - 12\Psi_{B} + 16\Psi_{NB} - 2\Psi_{BB'},$$
$$2ac_{44} = \Phi_{BB} - 2\Phi_{B} - 12\Psi_{B} - 2\Psi_{BB'} - \frac{\left[\Phi_{BB} + 8\Psi_{NB} - 2\Psi_{BB'}\right]^2}{\Phi_{BB} - 2\Phi_{B} - 12\Psi_{B} - 2\Psi_{BB'}}.$$

[5.4.24]

We can write down the force constants for the two body forces plus three body forces for second nearest neighbours as:

$$\alpha = \Phi_{BB} + 2\Phi_{B} + 6\Psi_{BB} + 12\Psi_{B} - 2\Psi_{BB'}$$
$$\beta = \Phi_{BB} + 6\Psi_{BB} + 8\Psi_{NB} - 2\Psi_{BB'}$$
$$\lambda = 2\Phi_{B} + 2\Psi_{N} - \Psi_{BB'}$$
$$\mu = 2\Phi_{B} + 2\Psi_{N} + 4\Phi_{NN} + 4\Psi_{NN} + 4\Psi_{NB} + \Psi_{BB'}$$
$$\nu = 4\Phi_{NN} + 4\Psi_{NN} + 4\Psi_{NB} + \Psi_{BB'}$$
$$\sigma = -\,2\Psi_{NB} - \Psi_{BB'}$$

[5.4.25]

The elastic constants can be rewritten for second nearest neighbour interactions

$$2ac_{11} = \Gamma_{BB} + 32\Gamma_{NN} + 32\Psi_{NB} + 6\Psi_{BB'},$$

$$2ac_{12} = \Gamma_{BB} + 16\Gamma_{NN} + 32\Psi_{NB} + 6\Psi_{BB'},$$

$$2ac_{44} = \Gamma_{BB} + 16\Gamma_{NN} - 16\Psi_{NB} - \frac{\left[\Gamma_{BB} + 8\Psi_{NB} - 2\Psi_{BB'}\right]^2}{\Gamma_{BB} - 2\Phi_{B} + 12\Phi_{B} - 2\Psi_{BB'}}.$$

[5.4.26]

Here for simplicity of notation the effective two body parameters are combined:

$$\Gamma_{BB} = \Phi_{BB} + 6\Psi_{BB'}$$

[5.4.27]

$$\Gamma_{NN} = \Phi_{NN} + \Phi_{NN}$$

[5.4.28]

In addition, the zero pressure condition [5.4.18] when applied to two and three body interactions is

$$2\Phi_{B} + 16\Phi_{N} + 12\Psi_{B} + 16\Psi_{N} = 0$$

[5.4.29]

This has been taken into account in expressions of elastic moduli [5.4.26].

5.5 ELASTIC CONSTANTS

We compare our results to those of Musgrave and Pople (1962). They have set up a general valence force field for diamond. The energy is expanded in terms of the bond length r_{ij} and bond angles θ_{ijk}.

They arrive at a total of seven interaction constants listed as:

(i) k_r, a point to point bond stretching constants for nearest neighbours i and j,

(ii) k_{rr}, an interaction constant for the bond pairs such that i and k are nearest neighbours of j,

(iii) k_θ, an angular rigidity for the angle θ_{ijk},

(iv) $k'_{r\theta}$, an interaction constant for the bond ij which forms an arm of the angle θ_{ijk},

(v) $k''_{r\theta}$, an interaction constant for the bond ij which does not form an arm of the angle θ_{kjl},

(vi) $k'_{\theta\theta}$, interaction constant between angles θ_{ijk} and θ_{ijl} which share a bond,

(vii) $k''_{\theta\theta}$, an interaction constant between angles θ_{ijk} and θ_{ljm} which do not share a bond.

The atom labelled j is the atom at the origin and i,j,l and m are nearest neighbour atoms. From the above definitions the interaction constants can be grouped into various many body interactions: k_r is a parameter of a two body potential, k_{rr}, k_θ, $k'_{r\theta}$, of a three body potential, $k''_{r\theta}$, $k'_{\theta\theta}$, of a four body potential and $k''_{\theta\theta}$ a parameter of a five body potential.

These seven interaction constants can be reduced to five, by making use of a single geometrical relation which holds amongst the bond angles

$$\sum_{ik} \delta\theta_{ijk} = 0, \qquad [5.5.1]$$

so that the interaction constants $k'_{r\theta}$, $k''_{r\theta}$, $k'_{\theta\theta}$ and $k''_{\theta\theta}$ can be written as the following combinations

$$k_{r\theta} = 2^{1/2}(k'_{r\theta} - k''_{r\theta}), \qquad k'_{\theta} = k_{\theta} - k'_{\theta\theta}, \qquad k''_{\theta} = k_{\theta} - k''_{\theta\theta}. \tag{5.5.2}$$

Musgrave and Pople derive expressions for the elastic constants in terms of their five interaction constants. They use the Born constants as Smith (1948) derives them, in order to write down equivalent expressions for the force constants using a combination of the valence force constants so that

$$\begin{aligned}
\alpha &= \tfrac{1}{3}\left[k_r - 2k_{rr} - 8k_{r\theta} + 8k''_{\theta} \right],\\
\beta &= \tfrac{1}{3}\left[k_r - 2k_{rr} - 2k_{r\theta} - 4k''_{\theta} \right],\\
\lambda &= \tfrac{1}{3}\left[- k_{rr} + 2k_{r\theta} - 3k'_{\theta} + k''_{\theta} \right],\\
\mu &= \tfrac{1}{6}\left[2k_{rr} + 2k_{r\theta} + 6k'_{\theta} - 5k''_{\theta} \right],\\
\nu &= \tfrac{1}{6}\left[2k_{rr} + 2k_{r\theta} - 3k'_{\theta} + 4k''_{\theta} \right],\\
\sigma &= \tfrac{1}{6}\left[- 2k_{rr} + k_{r\theta} + 3k'_{\theta} - k''_{\theta} \right].
\end{aligned} \tag{5.5.3}$$

This may be compared to the expression [5.4.25] for the parameters α through to σ in terms of two and three body constants.

We note that in the force constants of Musgrave and Pople the two body contribution to the overall force constant appears in α and β only. This contribution k_r (bond stretching constant) does not appear in the constants λ, ν, μ and σ since these constants take into account more distant neighbours where higher multibody interactions are present. This is also found to be the case for the force constants listed in [5.4.10] where the two body interaction constant Φ_{BB} only appears in α and β[1]. Herman (1958) in his discussion of the lattice vibrational spectrum of silicon, writes down the atomic force constant matrices for general, central, angular and torsional forces for up to the fifth nearest neighbour.

Assuming zero stress we can summarise the results as follows:

Herman (1958)

Nearest neighbour	General forces	Two body forces	Three body forces
1°	$\begin{vmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{vmatrix}$	$\begin{vmatrix} P_1 & P_1 & P_1 \\ P_1 & P_1 & P_1 \\ P_1 & P_1 & P_1 \end{vmatrix}$	$\begin{vmatrix} 16Q & -8Q & -8Q \\ -8Q & 16Q & -8Q \\ -8Q & -8Q & 16Q \end{vmatrix}$
2°	$\begin{vmatrix} \mu & \nu & \sigma \\ \nu & \mu & \sigma \\ -\sigma & -\sigma & \lambda \end{vmatrix}$	$\begin{vmatrix} P_2 & P_2 & 0 \\ P_2 & P_2 & 0 \\ 0 & 0 & 0 \end{vmatrix}$	$\begin{vmatrix} Q & Q & 2Q \\ Q & Q & 2Q \\ -2Q & -2Q & -4Q \end{vmatrix}$

[5.5.4]

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[1] The earliest model of the lattice dynamics of diamond was put forward in 1914 by Born (Born 1914). It is a force constant model, with all except the first nearest neighbour force constants set to zero. By making such an assumption we find that the expressions for the elastic constants are

$$c_{11} = c_{12} = \alpha/a, \qquad c_{44} = 0.$$

Which correspond to [5.5.4], [5.5.5] and [5.5.6] with only the two body term as a non zero term. These elastic constants as might be expected do not agree with the experimental values.

Musgrave and Pople (1962)

Nearest neighbour	General forces	Two body forces	Three body forces
1°	$\begin{vmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{vmatrix}$	$\begin{vmatrix} k_r & k_r & k_r \\ k_r & k_r & k_r \\ k_r & k_r & k_r \end{vmatrix}$	$\begin{vmatrix} 16k_\theta & -8k_\theta & -8k_\theta \\ -8k_\theta & 16k_\theta & -8k_\theta \\ -8k_\theta & -8k_\theta & 16k_\theta \end{vmatrix}$
2°	$\begin{vmatrix} \mu & \nu & \sigma \\ \nu & \mu & \sigma \\ -\sigma & -\sigma & \lambda \end{vmatrix}$	$\begin{vmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix}$	$\begin{vmatrix} k_\theta & k_\theta & 2k_\theta \\ k_\theta & k_\theta & 2k_\theta \\ -2k_\theta & -2k_\theta & -4k_\theta \end{vmatrix}$

[5.5.5]

The equivalent results of this work are:

Nearest neighbour	General forces	Two body forces	Three body forces
1°	$\begin{vmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{vmatrix}$	$\begin{vmatrix} \Phi_{BB} & \Phi_{BB} & \Phi_{BB} \\ \Phi_{BB} & \Phi_{BB} & \Phi_{BB} \\ \Phi_{BB} & \Phi_{BB} & \Phi_{BB} \end{vmatrix}$	$\begin{vmatrix} C_1 & C_2 & C_2 \\ C_2 & C_1 & C_2 \\ C_2 & C_2 & C_1 \end{vmatrix}$
2°	$\begin{vmatrix} \mu & \nu & \sigma \\ \nu & \mu & \sigma \\ -\sigma & -\sigma & \lambda \end{vmatrix}$	$\begin{vmatrix} \Phi_{NN} & \Phi_{NN} & 0 \\ \Phi_{NN} & \Phi_{NN} & 0 \\ 0 & 0 & 0 \end{vmatrix}$	$\begin{vmatrix} C_3 & C_3 & C_4 \\ C_3 & C_3 & C_4 \\ -C_4 & -C_4 & C_5 \end{vmatrix}$

[5.5.6]

Where (assuming zero stress):

$$C_1 = 6\Psi_{BB} - 2\Psi_{BB'}$$
$$C_2 = 6\Psi_{BB} + 8\Psi_{NB} - 2\Psi_{BB'}$$
$$C_3 = 4\Psi_{NN} + 4\Psi_{NB} + \Psi_{BB'}$$
$$C_4 = -\ 2\Psi_{NB} - \Psi_{BB'}$$
$$C_5 = -\ \Psi_{BB'}$$

[5.5.7]

If we focus attention on the nearest neighbour force constant matrices (two body forces only) we see that in all three works the results are equivalent, but when we come to consider second nearest neighbour force constants we find that Musgrave and Pople do not arrive at a force constants which is equivalent to P_2 in Herman's work or Φ_{NN} in this work. Both of these force constants describe the interaction of atoms through non bonded distances in the lattice and since Musgrave and Pople only consider a valence potential which is given in terms of two of the nearest neighbour bonded sides and the angle between them it is then not surprising that this form of interaction between second nearest neighbours is not described by the use of such a potential. Moving onto three body forces we can see that in Herman's work the first and second nearest neighbour interactions are described by only one parameter Q. This parameter describes pure angular forces which by definition tend to resist deformations of the angle formed by each pair of concurrent bonds. Musgrave and Pople give three parameters which they say describe three body interactions. Of these three only k_θ can be taken as equivalent to Herman's parameter Q (once equations [5.5.2] are substituted into [5.5.3] it is then a relatively trivial task to pick out the relevant force constants). When we come to consider the force constants listed in [5.5.7] we find that a straightforward comparison with either Herman's or Musgrave and Pople's force constants is no longer possible. One of the reasons for this is that the three body force constants in [5.5.7] are neither as general as the Born parameters (Smith 1948) and neither are they as specific[2] as the force constants that Musgrave and Pople use. We can see from [5.5.6] that the three body first and second nearest neighbour matrices are analogous to the general force constants [5.5.4] and also from [5.5.5] we can see that they are also analogous to the Musgrave constants.

From [5.5.6] and [5.5.7] we see that there are five force constants: Φ_{BB} Φ_{NN} Ψ_{NN} Ψ_{NB} and Ψ_{BB}, and six Born constants. The linear relation that exist between these two sets of force constants in given by Musgrave and Pople as

$$\sigma = \frac{1}{4}(\alpha - \beta) + \lambda + \mu - \nu. \tag{5.5.8}$$

When the two and three body force constants in [5.5.6] are placed into equation [5.5.8] the relation still holds.

5.6 CRYSTAL STABILITY

One of the problems in solid state theory is the explanation of the absolute stability of a given substance or the interpretation of

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[2] By specific we mean that the parameters that Musgrave and Pople have written down come from considering a valence potential. The results from such a potential should obey all of the translational and rotational conditions satisfied by the more general potential such as the one used by Born.

polymorphic transitions between different crystal structures exhibited by one and the same chemical compound. From the pioneering work of Born (1940) it is possible to show that for the simplest classes of solids such as those of the rare gas atoms that a two body pair potential leads to the result that all rare gas species should crystallise in the hexagonal close packed structure. Experimentally this configuration is found only with solid helium. In fact it is the f.c.c. lattice which is favoured and can be explained by taking into account many body interactions amongst the atoms.

Such a pair potential cannot stabilize the diamond structure. If we take a typical pair potential such as the Lennard-Jones (6,12) potential:

$$E(R) = 4\varepsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6} \right].$$

[5.6.1]

where $E(\sigma)=0$; $E_{min}=-\varepsilon$; for $R=R_0=2^{1/6}\sigma$. We can use the potential to calculate the elastic constants of diamond and then use the various inequalities which make the elastic constant matrix positive definite to test for stability.

From Born and Huang (1954) the expression for the elastic constants is derived from the method of long waves and is given by the expression

$$c_{\alpha\gamma,\beta\lambda} = [\alpha\beta,\gamma\lambda] + [\beta\gamma,\alpha\lambda] - [\beta\lambda,\alpha\gamma] + (\alpha\gamma,\beta\lambda).$$

[5.6.2]

The term $(\alpha\gamma,\beta\lambda)$ describes the internal strains within the crystal. This term is still present when we assume a pair potential interaction for our diamond crystal and hence must be taken into account when calculating the elastic constants. The terms in the square and round brackets are defined by

$$[\alpha\beta,\gamma\lambda] = \frac{1}{8\pi^2 v_a} \sum_{kk'} (m_k m_{k'})^{1/2} C^{(2)}_{\alpha\beta,\gamma\lambda}(kk'),$$

[5.6.3]

$$(\alpha\gamma,\beta\lambda) = -\frac{1}{4\pi^2 v_a} \sum_{kk'} \sum_{\mu\nu} \Gamma_{\nu\mu}(kk') \left[\sum_{k''} C^{(1)}_{\mu\nu}(kk'')m_{k''}\right] \left[\sum_{k'''} C^{(1)}_{\mu\nu}(kk''')m_{k'''}\right]$$

[5.6.4]

Where $C^{(2)}_{\alpha\beta,\gamma\lambda}(kk')$ and $C^{(1)}_{\mu\nu}(kk'')$ are defined in [1.3.13]. The matrix $\Gamma_{\nu\mu}(kk')$ is defined as the inverse of the matrix $C^{(0)}_{\alpha\beta}(kk')$ which satisfies by definition the relation

$$\sum_{\beta k'} \Gamma_{\alpha\beta}(kk')\ C^{(0)}_{\beta\lambda}(k'k'') = \sum_{\beta k'} C^{(0)}_{\alpha\beta}(kk')\ \Gamma_{\beta\lambda}(k'k'')$$

$$= \delta_{\alpha\beta}\delta_{kk'}.$$

[5.6.5]

If we assume a pair potential then the definitions of $C^{(0)}_{\alpha\beta}(kk')$, $C^{(1)}_{\alpha\beta,\gamma}(kk')$ and $C^{(2)}_{\alpha\beta,\gamma\lambda}(kk')$ can be written as (Born and Huang 1954)

$$C^{(0)}_{\alpha\beta}(kk) = \frac{1}{m_k}\left\{ 2\delta_{\alpha\beta} \sum_{k'(\neq k)} \sum_{l} [\Psi']_x + 4 \sum_{k'(\neq k)} \sum_{l} [\text{æ}_\alpha \text{æ}_\beta \Psi'']_x \right\},$$

[5.6.6]

$$C^{(1)}_{\alpha\beta,\gamma}(kk') = \frac{4\pi}{(m_k m_{k'})^{1/2}} \left\{ \delta_{\alpha\beta} \sum_{l} [\text{æ}_\gamma \Psi']_x + 2 \sum_{l} [\text{æ}_\alpha \text{æ}_\beta \text{æ}_\gamma \Psi'']_x \right\},$$

[5.6.7]

$$C^{(2)}_{\alpha\beta,\gamma\lambda}(kk') = \frac{8\pi^2}{(m_k m_{k'})^{1/2}} \left\{ \delta_{\alpha\beta} \sum_{l} [\text{æ}_\gamma \text{æ}_\lambda \Psi']_x + 2 \sum_{l} [\text{æ}_\alpha \text{æ}_\beta \text{æ}_\gamma \text{æ}_\lambda \Psi'']_x \right\}.$$

[5.6.8]

Assuming that the crystal is initially free of stress we can write $C^{(2)}_{\alpha\beta,\gamma\lambda}(kk')$ in [5.6.3] so that the square brackets reduce to

$$[\alpha\beta,\gamma\lambda] = \frac{2}{v_a} \sum_{lkk'} \left[\text{æ}_\alpha \text{æ}_\beta \text{æ}_\gamma \text{æ}_\lambda \Psi'' \right]_x$$

[5.6.9]

From [5.6.2] the elastic constants are given by

$$c_{11} = c_{xxxx} = [xx,xx],$$

$$c_{12} = c_{xxyy} = [xy,xy] + [xy,xy] - [xx,yy],$$

$$c_{44} = c_{xyxy} = [xx,yy] + [xy,xy] - [xy,xy] - (xy,xy).$$

[5.6.10]

The force constants given by the round brackets $(\alpha\gamma,\beta\lambda)$ are zero for the elastic constants c_{11} and c_{12} and hence do not contribute. From

[5.6.6], [5.6.7], [5.6.9] and [5.6.2] (assuming m=1 the unit mass of a carbon atom) we calculate the elastic constants for nearest and next nearest neighbours

$$\frac{2v_a}{a^4} c_{11} = \Psi''(r_1) + 32\Psi''(r_2),$$

$$\frac{2v_a}{a^4} c_{12} = \Psi''(r_1) + 16\Psi''(r_2),$$

$$\frac{2v_a}{a^4} c_{44} = \Psi''(r_1) + 16\Psi''(r_2) - \frac{\left(\Psi''(r_2) \right)^2}{2\Psi'(r_1) + \Psi''(r_2)}.$$

[5.6.11]

Hence the linear combinations of the elastic constants are given by

$$\frac{2v_a}{a^4} (c_{11} - c_{12}) = 16\Psi''(r_2)$$

$$\frac{2v_a}{a^4} (c_{11} + 2c_{12}) = 3\Psi''(r_1) + 64\Psi''(r_2)$$

[5.6.12]

Where Ψ'' is the second derivative of the Lennard-Jones potential taken with respect to the nearest neighbour distance r_1 and second nearest neighbour distance r_2.

One of the characteristics of such a potential function (see fig. 1.4.1) is the very narrow distance between the minimum and the point of inflexion. In this small gap the second derivative Ψ'' changes from a positive to a negative value. Hence derivatives with respect to second nearest neighbour distance will be negative if they lie outside the inflexion point. The nearest neighbours distance is close to the equilibrium distance since the atoms interact predominantly with nearest neighbours.

We can make a qualitative assessment of the stability of diamond. If we take the equilibrium distance of diamond as $R_0= 2^{1/6}\sigma$ (the distance of the nearest neighbour bonded atoms) which is also the nearest neighbour distance then the second nearest neighbour distance is given by $R_2=(8/3)^{1/2}R_0$. The distance of the inflexion point is given as $R_i=(13/7)^{1/6}R_0$ so that we can see that for diamond the second nearest neighbours lie outside the inflexion point since $R_2>R_i$. Hence we can see from [5.6.12] that $c_{11}- c_{12}$ is negative since this elastic constant is given by the second derivative of second nearest neighbour atoms only. It follows that the elastic constant c_{12} and $c_{11}+ 2c_{12}$ are also negative due to the larger contribution by the second nearest neighbour force constant $\Psi''(r_2)$. Thus from the conditions set out by Born for crystal stability we find that a pair potential such as a Lennard-Jones (6,12) potential cannot give stability to the diamond lattice and therefore it is necessary to look for higher orders of interactions such as three body interactions and see whether stability can be obtained.

Such a qualitative analysis is not possible when considering a multibody potential such as the three body potential considered here. One of the reasons for this is that no analogous potential exists, such as the Lennard-Jones pair potential, so that the same kind of analysis (which considers the sign of the force constant as we pass through the various neighbour distances) is not possible. We consider this problem in the next chapter.

CHAPTER 6

MURRELL AND MILLS POTENTIAL

6.1 Introduction

6.2 Expression for Three Body Potential

6.3 Application of Three Body Potential to Crystal Problem

6.4 Prospects for Further Work on Diamond

6.1 INTRODUCTION

In the course of the thesis so far, the lattice dynamics has been discussed either in the context of the potential expansion coefficients as parameters or in terms of a potential energy function with specified general properties. In the traditional work of Born and later workers, the potential function type considered has almost always been the two body or central interaction. Here the possibility of a many body classification has been explored and attention focused on the three body potential and its application to elastic properties.

It is clear that in any detailed application of the theory, a particular functional form must be assumed for the potential. In this chapter, such a function is described, the form chosen having hitherto been used only in the context of isolated molecules. The necessary expressions for the use of this potential in a crystal context are developed and its application to diamond considered. Further use of this type of potential will require extended numerical calculations, including optimisation of potential parameters as well as determination of the crystal properties of interest, and it is anticipated that this might form the basis of a future investigation.

6.2 EXPRESSION FOR THREE BODY POTENTIAL

One of the most popular potentials for a stable diatomic molecule in current use is that of Morse (1929) which is a three parameter potential, the parameters usually being fitted to the equilibrium bond length, the electronic dissociation energy (D_e) and the harmonic force constant (k).

$$V_M = D_e[\exp(2\alpha\rho) - 2\exp(-\alpha\rho)]$$

[6.2.1]

where

$$\alpha = \left(\frac{k}{2D_e}\right)$$

[6.2.2]

and ρ is the displacement of the internuclear distance from its equilibrium value.

It is generally found that the cubic force constant $k^{(3)}$ agrees closely with that deduced by spectroscopic analysis, but agreement with the quartic is poor. By introducing more parameters into a Morse type function it is possible to obtain agreement with D_e and with the higher force constant. The Morse function was extended in this way by Hulbert and Hirschfelder (Hulbert and Hirschfelder 1941). They proposed an analytical function in which the repulsive branch of the potential is multiplied by a polynomial in ρ as follows:

$$V_{HH} = D_e\left\{[1 + g\rho^3 + h\rho^4]\exp(-2\alpha\rho) - 2\exp(-\alpha\rho)\right\}$$

[6.2.3]

They were able, by suitable choice of g and h, to fit the cubic and quartic derivatives of the potential. However, as the attractive branch of the Morse potential is not modified by this procedure and the Hulbert and Hirschfelder was not found to be a great improvement over the simple Morse function.

A more satisfactory function which can be extended to fit higher derivatives of the potential was first suggested by Rydberg

$$V_R = -D_e[1 + a\rho] \exp [-a\rho] \qquad [6.2.4]$$

Like the Morse function it employs the same experimental data to determine the parameters but whereas the former involves two exponential constants, α and 2α, the Rydberg function uses, in effect, the geometric mean of these namely $2^{1/2}\alpha$. This function has a minimum of depth D_e at $\rho=0$ and the second derivative of the potential is given by

$$f_2 = a^2 D_e \qquad [6.2.5]$$

In the range of ρ generally covered by spectroscopic investigations there is in general little difference between V_M and V_R. The advantage of V_R is that it is easily extended to fit higher derivatives of the potential by simply increasing the order of the polynomial in equation [6.2.4]. The extended Rydberg function is defined as

$$V_{ER} = -D_e[1 + \sum_k a_k\rho^k] \exp [-\gamma\rho] \qquad [6.2.6]$$

which has a minimum at $\rho=0$ if $\gamma=a_1$. To fit f_2, f_3 and f_4 one requires terms in the polynomial to k=3. Expanding [6.2.6] up to k=3

$$V_{ER} = -D_e[1 + a_1\rho^1 + a_2\rho^2 + a_3\rho^3] \exp (-a_1\rho) \qquad [6.2.7]$$

The analytical potential used to describe our triatomic system is an extension of this type of function. In the triatomic case we have many more parameters in this functional form of the potential but also have more spectroscopic constants from which to determine them.

The variables for the potential of the ABC system are the three internuclear distances $R_1(R_{AB})$, $R_2(R_{BC})$ and $R_3(R_{AC})$. This is preferable to other independent sets (Fig. 3.1.1), such as the two distances and included angle, as the aim is to produce a potential which is appropriate for all shapes of the ABC triangle and all atom-atom dissociation limits. The three bond lengths are independent coordinates and must satisfy the triangular restriction $R_i \leq R_j + R_k$.

Following Murrell *et al* (1984) we can write the total potential as a sum of one, two and three body terms as

$$V_{ABC}(R_1,R_2,R_3) = V_A^{(1)} + V_B^{(1)} + V_C^{(1)} + R_{AB}^{(2)}(R_1) + R_{BC}^{(2)}(R_2) + R_{AC}^{(2)}(R_3) + V_I^{(3)}(R_1,R_2,R_3).$$

[6.2.8]

Atomic energies $V_A^{(1)}$ represent atomic excitation energies of the dissociated atoms. The two atom potentials $R_{AB}^{(2)}(R_1)$ etc., represent the potential curves of the corresponding diatomics which are modelled on the extended Rydberg function adjusted to fit the dissociation energy, bond length and quartic force constants if known.

The three body interaction term is taken in the form

$$V_I^{(3)}(R_1,R_2,R_3) = T(R_1,R_2,R_3).P(R_1,R_2,R_3)$$

[6.2.9]

where T is a range function that tends to zero as R_i becomes large. P is a polynomial in the displacement coordinates $\rho_i = \rho_i - \rho_i^0$, chosen from a reference configuration (R_1^0, R_2^0, R_3^0). The function T is written in the form

$$T = \prod_{i=1}^{3} \left[1 - \tanh\left(\frac{\gamma_i \rho_i}{2} \right) \right]. \qquad [6.2.10]$$

Where ρ_i is a parameter. The form which the P function takes is:

$$P = V_I^0 \left[1 + \sum_i c_i \rho_i + \sum_{i \le j} c_{ij} \rho_i \rho_j + \sum_{i \le j \le k} c_{ijk} \rho_i \rho_j \rho_k \right]. \qquad [6.2.11]$$

Where again c_i, c_{ij} and c_{ijk} are all parameters which are varied to give the best value for the surface potential calculated by Murrell and Mills.

6.3 APPLICATION OF THREE BODY POTENTIAL TO CRYSTAL PROBLEM

The potential to be developed is associated with the names of Murrell, Mills and Carter (1980) and has the advantage that it allows the possibility of any many body term in addition to the three atom interactions on which attention is focused here.

In the context of diatomic molecules, many approximate functional forms have been suggested for the two body potential. Murrell's approach is to choose one of these, which is found to be readily adapted in form to higher body interactions. The idea has been applied successively to two, three and four atom molecules so that in practice the potential has only been taken to a four body term.

In this chapter, it is the diamond problem which is taken as illustration. At the molecular level C_2 and C_3 have been considered, so that a molecular potential for three carbon atoms has already been found.

In order to use the Murrell potential in the context of crystals, a number of formulae must be developed. The potential is written in terms of radial displacement coordinates

$$\rho = r - r_o, \qquad [6.3.1]$$

in which r is the distance between the two atoms and r_o a reference value. In the crystal theories developed earlier in the thesis, the formulae are expressed in terms of s, the square of the distance between the two atoms. The form of the Murrell potential is sufficiently complicated that it is most natural to express its variations directly in terms of the radial displacement coordinates ρ and to use bridging formulae to get to the s coordinates used in the general theory. Elementary analysis leads to the formulae

$$\frac{\partial V}{\partial s} = \frac{1}{2r^2}\,\frac{\partial V}{\partial \rho}, \qquad [6.3.2]$$

$$\frac{\partial^2 V}{\partial s^2} = \frac{1}{4r^2}\left\{ \frac{\partial^2 V}{\partial \rho^2} - \frac{1}{r}\,\frac{\partial V}{\partial \rho} \right\}. \qquad [6.3.3]$$

The three body potential function is itself expressed in [6.2.9] as the product of a polynomial P and a "range" function T. The two body term [6.2.6] may also be expressed in this form by identifying the range function T as exp($-\gamma\rho$). The effect of this is to split the differentiation into two parts which can be determined separately and then combined. Again using elementary analysis

$$V=PT, \tag{6.3.4}$$

$$\frac{\partial V}{\partial s_i} = P\frac{\partial T}{\partial s_i} + \frac{\partial P}{\partial s_i}T, \tag{6.3.5}$$

$$\frac{\partial^2 V}{\partial s_i \partial s_j} = P\frac{\partial^2 T}{\partial s_i \partial s_j} + \frac{\partial P}{\partial s_i}\frac{\partial T}{\partial s_j} + \frac{\partial P}{\partial s_j}\frac{\partial T}{\partial s_i} + \frac{\partial^2 P}{\partial s_i \partial s_j}T. \tag{6.3.6}$$

Expressions for the derivatives are readily written down and are given in the following equations.

$$\begin{aligned}\frac{\partial P}{\partial \rho_1} = {} & c_1 + 2c_{11}\rho_1 + c_{12}\rho_2 + c_{13}\rho_3 + 3c_{111}\rho_1^2 + 2c_{113}\rho_1\rho_3 + 2c_{112}\rho_1\rho_2 \\ & + c_{123}\rho_2\rho_3 + 4c_{1111}\rho_1^3 + 3c_{1112}\rho_1^2\rho_2 + 3c_{1113}\rho_1^2\rho_3 + 2c_{1122}\rho_1\rho_2^2 \\ & + 2c_{1133}\rho_1\rho_3^2 + 2c_{1123}\rho_1\rho_2\rho_3.\end{aligned} \tag{6.3.7}$$

$$\begin{aligned}\frac{\partial P}{\partial \rho_2} = {} & c_2 + 2c_{22}\rho_2 + c_{12}\rho_1 + c_{23}\rho_3 + 3c_{222}\rho_2^2 + c_{112}\rho_1^2 + 2c_{223}\rho_2\rho_3 \\ & + c_{123}\rho_1\rho_3 + 4c_{2222}\rho_2^3 + c_{1112}\rho_1^3 + 3c_{2223}\rho_2^2\rho_3 \\ & + 2c_{1122}\rho_1^2\rho_2 + 2c_{2233}\rho_2\rho_3^2 + c_{1123}\rho_1^2\rho_3 .\end{aligned}$$

[6.3.8]

$$\begin{aligned}\frac{\partial P}{\partial \rho_3} = {} & c_3 + 2c_{33}\rho_3 + c_{13}\rho_1 + c_{23}\rho_2 + 3c_{333}\rho_3^2 + c_{113}\rho_1^2 + 2c_{223}\rho_2^2 \\ & + c_{123}\rho_1\rho_2 + 4c_{3333}\rho_3^3 + c_{1113}\rho_1^3 + c_{2223}\rho_2^3 \\ & + 2c_{1133}\rho_1^2\rho_3 + 2c_{2233}\rho_2^2\rho_3 + c_{1123}\rho_1^2\rho_2 .\end{aligned}$$

[6.3.9]

$$\begin{aligned}\frac{\partial^2 P}{\partial \rho_1^2} = {} & 2c_{11} + 6c_{111}\rho_1 + 2c_{113}\rho_3 + 2c_{112}\rho_2 + + 12c_{1111}\rho_1^2 + 6c_{1112}\rho_1\rho_2 \\ & + 6c_{1113}\rho_1\rho_3 + 2c_{1122}\rho_2^2 + 2c_{1133}\rho_3^2 + 2c_{1123}\rho_2\rho_3 .\end{aligned}$$

[6.3.10]

$$\begin{aligned}\frac{\partial^2 P}{\partial \rho_2^2} = {} & 2c_{22} + 6c_{222}\rho_2 + 2c_{223}\rho_3 + 12c_{2222}\rho_2^2 + 6c_{2223}\rho_2\rho_3 \\ & + 2c_{1122}\rho_1^2 + 2c_{2233}\rho_3^2 .\end{aligned}$$

[6.3.11]

$$\frac{\partial^2 P}{\partial \rho_3^2} = 2c_{33} + 6c_{333}\rho_3 + 12c_{3333}\rho_3^2 + 2c_{1133}\rho_1^2 + 2c_{2233}\rho_2^2 .$$

[6.3.12]

$$\frac{\partial^2 P}{\partial \rho_1 \partial \rho_2} = c_{12} + 2c_{112}\rho_1 + c_{123}\rho_3 + 3c_{1112}\rho_1^2 + 4c_{1122}\rho_1\rho_2 + 2c_{1123}\rho_1\rho_3 .$$

[6.3.13]

$$\frac{\partial^2 P}{\partial \rho_1 \partial \rho_3} = c_{13} + 2c_{113}\rho_1 + c_{123}\rho_2 + 3c_{1113}\rho_1^2 + 4c_{1133}\rho_1\rho_3 + 2c_{1123}\rho_1\rho_2 .$$

[6.3.14]

$$\frac{\partial^2 p}{\partial\rho_2\partial\rho_3} = c_{23} + 2c_{223}\rho_2 + c_{123}\rho_1 + 3c_{2223}\rho_2^2 + 4c_{2233}\rho_2\rho_3 + c_{1123}\rho_1^2. \qquad [6.3.15]$$

The first and second derivatives of T are given by

$$\frac{\partial T}{\partial\rho_i} = -\frac{\gamma_i}{2}\,\mathrm{sech}^2\left(\frac{\gamma_i\rho_i}{2}\right)\left[1 - \tanh\left(\frac{\gamma_j\rho_j}{2}\right)\right]\left[1 - \tanh\left(\frac{\gamma_k\rho_k}{2}\right)\right] \qquad [6.3.16]$$

$$\frac{\partial^2 T}{\partial\rho_i^2} = 2\,\mathrm{sech}\left(\frac{\gamma_i\rho_i}{2}\right)\tanh\left(\frac{\gamma_i\rho_i}{2}\right)\left(\frac{\gamma_i}{2}\right)^2 \times\left[1 - \tanh\left(\frac{\gamma_j\rho_j}{2}\right)\right]\left[1 - \tanh\left(\frac{\gamma_k\rho_k}{2}\right)\right] \qquad [6.3.17]$$

$$\frac{\partial^2 T}{\partial\rho_i\partial\rho_j} = \mathrm{sech}^2\left(\frac{\gamma_j\rho_j}{2}\right)\mathrm{sech}^2\left(\frac{\gamma_i\rho_i}{2}\right)\left(\frac{\gamma_j\gamma_i}{4}\right)\left[1 - \tanh\left(\frac{\gamma_k\rho_k}{2}\right)\right] \qquad [6.3.18]$$

When applied to systems such as diamond, these equations are considerably simplified because the c coefficients depend only on atom type. In this way, for example, $c_1=c_2=c_3$ with similar relationships for higher terms.

6.4 PROSPECT FOR FURTHER WORK ON DIAMOND

The potential functions and parameter values for C_2 and C_3 given by Murrell lead to totally unrealistic values of the elastic moduli of diamond. An improved model might be found by altering the parameter values and by extending the potential to include higher many body terms. Profitable continuation of the work in this thesis can be expected by developing this programme in the future.

The failure of the molecular parameters of C_2 and C_3 to give an adequate description of diamond is not surprising. In particular, C_3 is formally a linear molecule but has a very low bending force constant, whereas a C_3 fragment in diamond has a relatively high resistance to bending.

Herman (1959), using the Born von Karman theory of lattice dynamics, showed that the experimental elastic constants cannot be fitted to force constant models based only on first and second nearest neighbour interactions. Indeed, fifth neighbour interactions are required to reproduce the experimental pattern. This would suggest not only that the range of interactions must be extended, but it almost certainly means that four and perhaps five body forces must be considered.

APPENDIX

The three body parts of the elastic constants given in this chapter may be derived from two specimen triangles.

Triangle 1

$O \equiv (000)$ $N \equiv (100)$ $P \equiv (010)$

$R_x(NO) = 1$ $R_y(NO) = 0$ $R_z(NO) = 0$

$R_x(PO) = 0$ $R_y(PO) = 1$ $R_z(PO) = 0$

Contribution to c_{ijkl}

ijkl	k
xxxx	$2ak_{FF}$
yyyy	$2ak_{FF}$
xxyy	$4ak_{FG}$
xyxy	0

Table [A.1]

All other contributions zero.

Triangle 2

$O \equiv (000)$ $N \equiv (100)$ $P \equiv (110)$

$R_x(NO) = 1$ $R_y(NO) = 0$ $R_z(NO) = 0$

$R_x(PO) = 1$ $R_y(PO) = 1$ $R_z(PO) = 0$

Contribution to c_{ijkl}

ijkl	k
xxxx	$2a(k_{FF} + k_{SS} + 4k_{FS})$
yyyy	$2ak_{SS}$
xxyy	$2a(k_{SS} + 2k_{FS})$
xyxy	$2ak_{SS}$

Table [A.2]

All other contributions zero.

To get total contributions to square net in xy plane, sum over 4 triangles of type 1 (symmetric with respect to x and y) 4 of type 2 identical to above entry and 4 of type 2 with x and y entries interchanged. This leads to

$$c_{xxxx}=16a(k_{FF}+k_{SS}+2k_{FS}) \quad [A.1]$$

$$c_{yyyy}=c_{xxxx} \quad [A.2]$$

$$c_{xxyy}=16a(k_{SS}+k_{FG}+2k_{FS}) \quad [A.3]$$

$$c_{xyxy}=16ak_{SS} \quad [A.4]$$

To get the corresponding expressions for the simple cubic structure, add contributions like the above for the xy xz and yz planes.

$$c_{11} = 2c_{xxxx} \qquad c_{12} = c_{xxyy} \qquad c_{44} = c_{xyxy} \qquad [A.5]$$

A similar analysis for the two body terms leads to

$$c_{11} = 8a(k_F+k_S) \qquad c_{12} = 8ak_S \qquad c_{44} = 8ak_S \qquad [A.6]$$

Equations [4.2.6] to [4.2.8] are obtained by adding the two and three body contributions.

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