SOME THEORETICAL CALCULATIONS
ON THE FREE ENERGY AND THE ELASTIC CONSTANTS
OF THE INERT GAS CRYSTALS

A thesis submitted to the University of Surrey
in partial fulfilment of the requirements
for the degree of Doctor of Philosophy

by

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ABSTRACT

The sphericalisation approximation in the cell model of a crystal is investigated for the three cubic lattices and various inverse power potential functions. It is shown that for most purposes the approximation is a good one.

The contributions to various properties of the inert gas solids Ne, A, kr and Xe of a long-range three-body force of the form given by Axilrod and Teller are calculated. It is shown that the three-body lattice energy is not negligible in these solids and that the three-body force contribution to the harmonic zero point vibrational energy is of the same order of magnitude as, but opposite in sign to, the two-body anharmonic energy. The elastic constants $C_{11}$, $C_{12}$ and $C_{44}$ and related elastic properties are calculated at the absolute zero assuming only two-body forces. A second calculation is then presented in which the three-body force is included. It is shown that the quantity $B = (C_{44} - C_{12})C_{12}^{-1}$ which is always positive when calculated with only two-body forces is reduced when the three-body interaction is included. In the cases of A, kr and Xe $B$ in fact becomes negative. It should be possible to test this experimentally and if $B$ were found negative this would provide strong evidence for the existence of three-body forces.

The zero point vibrational and free energy at finite temperatures are calculated using the Bethe approximation. The harmonic and quartic anharmonic energies are in good
agreement with the results of standard lattice dynamical methods. However the cubic and some of the non-leading anharmonic terms appear to be less accurately determined. The zero point energy results are applied to the inert gas solids to investigate various crystal models. The bulk moduli are also determined at 0°C.

All the investigations indicate that three-body forces play an important role in determining the theoretical properties of the inert gas solids, especially anisotropic properties.

The research on which this thesis is based was carried out at the University of Surrey between October 1965 and October 1968. Some portions of this work have already been discussed in the following publications:


Acknowledgements

The author wishes to sincerely thank his supervisor, Dr. I.J. Zucker, for suggesting the problems that have lead to the present work and also for his help and encouragement throughout its duration. Thanks are also due to Dr. M.C. Jones for many useful discussions, Mr. K. Knight for his advice on computing and Mr. M.O. Tucker for typing the thesis. The author also wishes to thank the Science Research Council for a maintenance grant for the period during which the work was done.
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1. Foreword

Any reasonable lattice dynamical theory, whether it be quantum or classical, should be capable of including in its formulation anharmonicity. This is especially true if the theory is to be applied calculating the properties of the inert gas solids. Anharmonic effects are present at all temperatures including absolute zero, the largest anharmonicity being exhibited by the lighter elements helium, neon and argon.

Anharmonicity is responsible for the linear dependence of the specific heat at high temperatures and thus the deviation from the Dulong-Petit Law. It also has pronounced effects on the equilibrium volume, bulk modulus and expansivity and becomes more important the higher the temperature.

Most theories are based on treating the anharmonicity as a perturbation on the harmonic energy. This must be done with caution as perturbation theory is only applicable in cases where one knows that it will work. Thus the theory outlined in the chapters below is applicable only to the inert gas solids neon, argon, krypton and xenon, helium being outside of its scope.

It was decided to apply the theory to calculating properties of the inert gas solids for several reasons.
(i) The availability at present of plenty of experimental solid state data with which to compare the results of the theory.  (ii) These solids are simple, for example there are none of the complications of electron interactions.  Further single phenomena of interest are more easily isolated and studied theoretically.  (iii) The electronic energy of these solids is in the ground state and therefore the Born-Oppenheimer (1927) or adiabatic approximation can be used.  (iv) They represent a reasonable testing ground for a theory of lattice dynamics ranging from the strongly anharmonic neon to the weakly anharmonic xenon.  (v) Before calculations can be made it is necessary to have representations of the interactions between atoms.  For the inert gas solids reasonable forms of interactions between pairs of atoms are available.  They appear to represent, at least qualitatively, the actual interactions although the choice of a given form may be purely for its convenience in calculations.  In the present work a Lennard-Jones \((m,6)\) representation of the pair potential will be used.  Although opposition has recently been expressed to this potential function it still appears to represent the pair interactions of inert gas atoms over considerable atomic separations and yet only two parameters are required to specify it.  We further have a fairly well established formula representing the long-range triple-dipole interaction between these atoms and hence the effect of these may also be studied.

The reasons for the development of the theories in the following chapters was threefold.  Firstly it was thought profitable to seek out a theory allowing the calculation of thermodynamic and thermoelastic properties in
a relatively simple manner. More complicated theories are already available based, for example, on the formal expressions derived by Ludwig (1958) for the free energy of a crystal. But these are only suitably adapted to ease of calculation at high and low temperature limits and no results at intermediate temperatures have yet been given. Even then approximations have to be made which to some extent limit the usefulness of the theories. It would therefore be very useful to have a theory based on the minimum of assumptions. Secondly many-body effects are now considered important in the inert gas solids (Coulson, 1965). A means of representing these forces, especially the three-body forces, was therefore sought and for various reasons given in the main text below a potential function first derived by Axilrod and Teller (1943) was chosen. Determining the effects of these forces and how they might be substantiated or otherwise has been another purpose of this investigation. Thirdly, a way of combining the theory and the techniques developed using the three-body forces was sought so that many-body forces could be incorporated into the lattice dynamics. It is thought that all three of these aims have been achieved and the means of achievement are contained in the following chapters.

Besides those references given in the main text the author has also found the following references useful for general background knowledge and information, Dobbs and Jones (1957), Pollack (1964), Boato (1964), Born and Huang (1954) and Hirschfelder et al. (1954).
2. Presentation of Thesis

In Chapter 2 we deviate slightly from the main theme of the thesis and discuss the sphericalisation approximation in the cell model of the crystal.

In Chapter 3 the three-body potential function of Axilrod and Teller (1943) is introduced and its contribution to the static and zero point vibrational energy of the inert gas solids is calculated. In Chapter 4 the calculations are extended to the elastic constants and related properties. Expressions are derived for the three-body contribution to the elastic constants using the method of small homogeneous deformations. The bulk modulus, Debye characteristic temperature at $T = 0^\circ K$ and the velocities of elastic waves are also determined.

In Chapter 5 we show how the Bethe approximation may be adapted so that the anharmonic zero point vibrational energy for the three cubic lattices may be calculated. The results are applied to investigate the errors involved in making the approximation that there are central, nearest neighbour interactions only between atoms in a crystal. It is shown how a non-central, three-body force can be included in the theory. Chapter 6 is a natural extension of the method used in Chapter 5 and expressions for the free energy at finite temperatures are derived. In Chapter 7 the results of Chapter 5 are applied in calculating the bulk moduli of the inert gas solids. The results obtained in the theories are summarised and possible extensions of the theory are suggested. Wherever possible the mathematics involved in derivations is placed at the end.
of each chapter. It is hoped this will provide for more fluent reading.
CHAPTER 2

THE SPHERICALISATION APPROXIMATION

1. Introduction

The cell model was first introduced by Lennard-Jones and Devonshire (1937) - abbreviated L.D.J. - and applied to the liquid state. Later L.D.J. recognised that the model was more applicable to the liquid state. Since then it has been used extensively in theories of the solid state, for example Henkel (1954), Levett and Hurst (1960), Guggenheim and McGlashan (1964), Zucker (1956, 1961) and Hillier and Walkley (1964). Barker (1963) has reviewed the model extensively and gives more references.

The fundamental assumptions of the cell model are:
(1) the available volume is divided into identical cells with one particle per cell, the centres of which are the classical lattices sites; (2) the particles move in their cells independently of one another and in the mean field produced by all the other particles at rest on the cell centres. The total energy of a crystal is thus just the sum of single particle energies and correlational effects are neglected. The cell model is thus entirely equivalent to an Einstein model of a crystal.

The central problem in the cell model is to calculate the potential energy, $\Phi$, of a particle displaced a distance $\rho$ from its cell centre, due to its interactions via a pair potential $\phi(R)$ with all the other particles at rest on their lattice sites. $\Phi$ may be expanded in a power series
in \( \rho \), the coefficients of which depend on summations of various derivatives of \( \phi \) over all the lattice sites, \( s \), and the angles \( \psi_s \) between the displaced particle and the lattice sites. L.D.J. proposed the removal of this angular dependence to leave a spherically symmetric function depending only on \( \rho \). The removal of the angular dependence by averaging over a sphere was termed the "smearing" or "sphericalisation" approximation. This approximation has been examined by Buehler et al. (1951) for hard sphere molecules in a f.c.c. lattice and by Barker (1956) for particles interacting with a Lennard-Jones (12,6) potential also in a f.c.c. lattice. They showed that the smearing approximation was valid provided the particles were confined to regions in their cells where \( V/V_0 < 2 \), where \( V \) was the actual cell volume and \( V_0 \) the cell volume at closest possible packing. Here we investigate the sphericalisation approximation for the three cubic lattices and particles interacting with arbitrary pair potentials.

2. Theory

Let \( O \) be the cell centre (Figure 1) of some typical particle and let \( \rho \) be its displacement from equilibrium. Let \( R_s \) be the position vector of any lattice site with respect to \( O \). Then \( \mathcal{I} \) may be written

\[
\mathcal{I} = \sum_s \phi(|R_s - \rho|) \quad (2.1)
\]

where the sum is over all lattice sites.
sites. Expanding in a Taylor series we have

\[ \Phi = \sum_{s} \left\{ \phi - \rho \cos \psi \phi^{(1)} + \frac{\rho^2}{2} \left[ \frac{\phi^{(1)}}{R_s} + \cos^2 \psi \phi^{(2)} - \frac{\phi^{(1)}}{R_s} \right] \right. \\
- \frac{\rho^3}{6} \left[ 3 \cos \psi \left( \frac{\phi^{(2)}}{R_s} - \frac{\phi^{(1)}}{R_s^2} \right) + \cos^3 \psi \left( \frac{\phi^{(3)}}{R_s} - \frac{3\phi^{(2)}}{R_s^2} + \frac{3\phi^{(1)}}{R_s^3} \right) \right] \\
+ \frac{\rho^4}{24} \left[ 3 \cos \psi \left( \frac{\phi^{(2)}}{R_s^2} - \frac{\phi^{(1)}}{R_s^3} \right) + 6 \cos^2 \psi \left( \frac{\phi^{(3)}}{R_s} - \frac{2\phi^{(2)}}{R_s^2} + \frac{3\phi^{(1)}}{R_s^3} \right) \right] \\
+ \cos^4 \psi \left( \frac{\phi^{(4)}}{R_s} - \frac{5\phi^{(3)}}{R_s^2} + \frac{15\phi^{(2)}}{R_s^2} - \frac{15\phi^{(1)}}{R_s^3} \right) + \ldots \right\} \right\} (2.2) \]

Superscript \( n \) indicates the \( n \)th derivative.

Higher order terms are easily obtained. The summations over all lattice points thus involve terms such as \( \cos^m \psi f(R_s) \) where \( f(R_s) \) is some combination of derivatives of \( \phi \), and depends on \( R_s \) only. The smearing approximation removed the \( \cos^m \psi \) from the summation and replaced it by its average over a sphere, i.e.

\[ \sum_{s} \cos^m \psi f(R_s) = \cos^m \psi \sum_{s} f(R_s) \]

where \( \cos^m \psi = \frac{1}{4\pi} \int_{0}^{2\pi} \int_{0}^{\pi} \cos^m \psi \sin \psi \, d\psi \, d\chi \)

Hence \( \cos^m \psi \) was zero for odd \( m \) and equal to \( 1/(m+1) \) for even \( m \). All odd terms in (2.2) thus vanished and it can be shown that (2.2) becomes

\[ \Phi = \sum_{n=0}^{\infty} \rho^{2n} \phi_{2n} \]  

(2.3)

where

\[ \phi_{2n} = \frac{1}{(2n+1)!} \sum_{s} \left[ \phi^{(2n)} + 2n \phi^{(2n-1)} \right] \]
and this is the sphericalised potential energy. It is rare to consider terms of \( n > 2 \) in (2.3) since truncating the series at \( n = 1 \), i.e. at the \( \rho^2 \) term, is the normal harmonic approximation and usually only the first order anharmonic term is considered.

Now for the cubic lattices

\[
\mathbf{R}_s = (\ell_1 i + \ell_2 j + \ell_3 k) \frac{\mathbf{d}}{2}, \quad \mathbf{r} = xi + yj + zk
\]

where \( i, j \) and \( k \) are the cartesian unit vectors, \( d \) the nearest neighbour separation, \( \ell_1, \ell_2 \) and \( \ell_3 \) are integers and \( \ell \) a number characterising the given cubic lattice. For the s.c. lattice \( \ell = 1 \) and \( \ell_1, \ell_2, \ell_3 \) can take on any integer values. For the b.c.c. lattice \( \ell = \sqrt{3} \) and \( \ell_1, \ell_2, \ell_3 \) are either all odd or all even integers. For the f.c.c. lattice \( \ell = \sqrt{2} \) and \( (\ell_1 + \ell_2 + \ell_3) \) must be an even integer.

Cos \( \psi_s \) is then written as

\[
\cos \psi_s = \frac{\mathbf{r} \cdot \mathbf{R}_s}{\rho R_s} = \frac{1}{\rho} \frac{\ell_1 x + \ell_2 y + \ell_3 z}{(\ell_1^2 + \ell_2^2 + \ell_3^2)^{\frac{3}{2}}}
\]

The corrected expression for \( \cos^m \psi_s \) is then

\[
\cos^m \psi_s = \sum_s \cos^m \psi_s f(R_s)/\sum_s f(R_s)
\]

\[
= \frac{1}{\rho \sum_s (\ell_1^2 + \ell_2^2 + \ell_3^2)^{\frac{m}{2}}} \frac{f(\ell_1^2 + \ell_2^2 + \ell_3^2)}{\sum_s f(\ell_1^2 + \ell_2^2 + \ell_3^2)} (2.4)
\]

where \( \sum_s \) now implies summation over \( \ell_1, \ell_2, \ell_3 \) consistent with the particular cubic lattice considered.

It is evident that if \( m \) is odd that (2.4) will vanish since the summation operation performed on any terms con-
taining odd powers of \( \ell_1, \ell_2, \ell_3 \) will yield zero because of the symmetry of cubic lattices. Further as \( \ell_1, \ell_2, \ell_3 \) are completely interchangeable certain simplifications may be made. For example

\[
\sum_s (\ell_1^m x^m + \ell_2^m y^m + \ell_3^m z^m) = \frac{1}{3}(x^m+y^m+z^m) \sum_s (\ell_1^m+\ell_2^m+\ell_3^m).
\]

Thus for \( m=2 \)

\[
\cos^2 \psi_s = \frac{1}{\rho^2} \sum_s (\ell_1^2 x^2 + \ell_2^2 y^2 + \ell_3^2 z^2) \frac{f/\sum f}{(\ell_1^2+\ell_2^2+\ell_3^2)} = \frac{1}{3} \frac{(x^2+y^2+z^2)}{\rho^2} = \frac{1}{3}.
\]

Hence for all odd order terms and for \( \cos^2 \psi_s \) the sphericalisation approximation is exact. Now as the highest power of \( \cos \psi_s \) appearing in terms up to \( \rho^2 \) is \( \cos^2 \psi_s \) the sphericalised and exact cell model potential energy are identical for all potentials and all cubic lattices up to the harmonic approximation. This agrees with Barker's (1963) conclusion.

The quartic term in \( \rho \) contains an expression with \( \cos^4 \psi_s \), the sextic term \( \cos^6 \psi_s \) and so on. Higher order anharmonic terms will not be considered, for if they became of importance the cell model as such would hardly be applicable, so we now consider \( \cos^4 \psi_s \) and \( \cos^6 \psi_s \) only. If the following expressions are defined as

\[
S_{nqr}^{pq} = \sum_s \frac{\ell_1^p \ell_2^q \ell_3^r}{(\ell_1^2+\ell_2^2+\ell_3^2)^{n/2}} \cdot f(\ell_1^2+\ell_2^2+\ell_3^2)
\]

then the following relations hold for cubic lattices
After some manipulation it may be shown that

\[
\frac{\cos^4 \psi}{S_0} = \frac{S_0^4}{S_0} + (1 - \frac{5S_0^4}{S_0^4}) \frac{x^2y^2 + y^2z^2 + z^2x^2}{\rho^4}
\]

(2.5)

\[
\frac{\cos^6 \psi}{S_0} = \frac{S_0^6}{S_0} + \frac{(15S_0^{42} - 3S_0^6)}{S_0^6} \frac{x^2y^4 + y^2x^4 + x^2z^4 + z^2x^4 + y^2z^4 + z^2y^4}{\rho^6}
\]

+ \left(15 - \frac{51S_0^6}{S_0^6} - 270 \frac{S_0^{42}}{S_0^6}\right) \frac{x^2y^2z^2}{\rho^2}
\]

(2.6)

3. Discussion

The exact value of $\Phi$ depends explicitly on $x$, $y$ and $z$ separately as well as on $\rho$. But though this is true of $\Phi$ itself, many thermodynamic properties calculated from it depend on certain averages over $x, y, z$ and $\rho$. Two examples in particular are of interest. First consider the high temperature properties of the crystal. These will be determined from the partition function, which at high temperatures can be written as the phase integral

\[
Z = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \int e^{-\beta \Phi(\rho, x, y, z)} d\rho
\]

\[
= \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \int_0^{2\pi} \int_0^{\pi} \int_0^\infty e^{-\beta \Phi(\rho, \theta, \phi)} \rho^2 \sin \theta \, d\phi \, d\theta \, d\rho
\]

where $m$ is the atomic mass, $k$ Boltzmann's constant, $T$ temperature and $h$ Planck's constant. Now treating the anharmonic terms as perturbations, on expanding the expon-
ential and keeping only first order terms, the integrals over $\theta$ and $\phi$ can easily be carried out. The effect is to average the terms of (2.5) and (2.6) containing $x$, $y$ and $z$ over a sphere. If this is done then $\cos^4 \psi_s$ becomes equal to $1/5$ and $\cos^6 \psi_s = 1/7$ — in exact agreement with the smearing approximation.

At the other end of the temperature scale, the zero point energy can also be found with the anharmonic terms as perturbations. The anharmonic zero point energy is obtained by averaging the anharmonic terms over the square of the zeroth-order harmonic wavefunctions. But the latter is spherically symmetrical, hence again to first order we get the same result with the smearing approximation.

At both low and high temperatures with the anharmonic terms treated as perturbations, then to first order the sphericalisation approximation is exact. It thus seems highly plausible that at all temperatures, if the anharmonic terms are perturbations then the smearing approximation is good.

Further deductions may be made by considering the extreme values that $\cos^4 \psi_s$ and $\cos^6 \psi_s$ may have. For the expressions with $x$, $y$, $z$ and $\rho$ have extreme values when $x=y=z=0$ and when $x=y=z=\rho/\sqrt{3}$. Then

$$\frac{S_4^4}{S_0} \leq \cos^4 \psi_s \leq \frac{1}{3} - \frac{2}{3} \cdot \frac{S_4^4}{S_0}$$

$$\frac{S_6^6}{S_0} \leq \cos^6 \psi_s \leq \frac{5}{9} - \frac{14}{9} \cdot \frac{S_6^6}{S_0} - \frac{20}{3} \cdot \frac{S_4^2}{S_0}.$$
It may be argued that as in the cell model one particle is considered typical of all the others the most likely value of \(\cos^4\psi_s\) and \(\cos^6\psi_s\) lies between the extreme values. A reasonable assumption then is to take the mean of these two values, that is

\[
\cos^4\psi_s (m.v) = \frac{1}{6} (1 + \frac{S_4^4}{S_0})
\]

\[
\cos^6\psi_s (m.v) = \frac{5}{18} - \frac{5}{18} \frac{S_6^6}{S_0} - \frac{10}{3} \frac{S_6^4}{S_0}
\]

<table>
<thead>
<tr>
<th>Lattice</th>
<th>m=6</th>
<th>m=12</th>
<th>m=(\infty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.C.</td>
<td>0.2204</td>
<td>0.2220</td>
<td>2/9 = 0.2222</td>
</tr>
<tr>
<td>B.C.C.</td>
<td>0.1908</td>
<td>0.1878</td>
<td>5/27 = 0.1852</td>
</tr>
<tr>
<td>F.C.C.</td>
<td>0.1949</td>
<td>0.1945</td>
<td>7/36 = 0.1944</td>
</tr>
</tbody>
</table>

Sphericalised value = 1/5 = 0.2000

Table 1 \(\cos^4\psi_s (m.v)\)

<table>
<thead>
<tr>
<th>Lattice</th>
<th>m=6</th>
<th>m=12</th>
<th>m=(\infty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.C.</td>
<td>0.1830</td>
<td>0.1849</td>
<td>5/27 = 0.1852</td>
</tr>
<tr>
<td>B.C.C.</td>
<td>0.1488</td>
<td>0.1464</td>
<td>35/243 = 0.1440</td>
</tr>
<tr>
<td>F.C.C.</td>
<td>0.1164</td>
<td>0.1159</td>
<td>25/216 = 0.1152</td>
</tr>
</tbody>
</table>

Sphericalised value = 1/7 = 0.1428

Table 2 \(\cos^6\psi_s (m.v)\)

These can be evaluated once a given form of \(\phi(R)\) is chosen. We have considered \(\phi(R) = 1/R^m\) and have tabulated the mean values of \(\cos^4\psi_s\) and \(\cos^6\psi_s\) for the three cubic lattices and for different values of \(m\) (Tables 1 and 2).

For all three lattices \(\cos^4\psi_s (m.v)\) is near the sphericalised...
values but \( \cos^6 \psi_s \) is only so for the b.c.c. lattice. But as we have to go to the sixth order term in \( \rho \) before \( \cos^6 \psi_s \) appears it seems reasonable to conclude that the sphericalisation approximation is a very good one.

To summarise the conclusions: (1) the sphericalisation approximation is exact up to the harmonic term in the potential expansion; (2) if the anharmonic terms are treated as perturbations then to first order the sphericalisation approximation gives exact thermodynamic results in the low and high temperature limits; (3) if we take the mean of the extreme possible values of \( \cos^4 \psi_s \) and \( \cos^6 \psi_s \) as the most likely values in the potential energy then with potentials of the form of \( 1/R^m \) the sphericalisation approximation is good for the quartic term in \( \rho \), but not too good for the sextic term. Since the sextic term is a second order anharmonic term it may be said that for the cubic lattices the sphericalisation approximation is very good.
CHAPTER 3

THE EFFECT OF A LONG-RANGE, NON-CENTRAL THREE-BODY
POTENTIAL FUNCTION ON THE ZERO POINT ENERGY
OF CUBIC CRYSTALS

1. Introduction

For central two-body, pair-wise additive potential interactions between atoms theory predicts that for the inert gas solids the hexagonal close-packed (h.c.p.) structure is more stable than the face-centred cubic (f.c.c.) structure. As these solids condense into f.c.c. crystals there is an obvious discrepancy between theory and experiment. Because the difference in the static lattice energies of the two structures is very small many workers have considered other effects (such as vibrational energy) to try and theoretically stabilize the f.c.c. with respect to the h.c.p. lattice. A theoretical investigation by Baron and Domb (1955) into the inert gas solids for this specific purpose concluded that the only plausible theoretical explanation was that many-body forces must be present in these solids but they did not do any calculations on these forces. More recently it has been recognised (Coulson, 1965) that three-body forces are of considerable importance in the solid state of the inert gases.

As early as 1943 Axilrod and Teller gave the form of a triple-dipole interaction which they derived using third order perturbation theory (Axilrod, 1951a). Axilrod (1951b) applied this potential to determine the relative stability
of the close-packed structures for the inert gas solids and although he found that the three-body force favoured the f.c.c. lattice the difference in the two energies of the structures was too small to account for the actual structure. The potential derived by Axilrod was long-range.

The short-range, non-additive three-body interaction due to the electron exchange interactions of triplets of atoms was investigated by Jansen (1964). A calculation based on his results favoured the f.c.c. structure and appeared to remove the structural discrepancy. Earlier Jansen (1963) had calculated the three-body contribution to the free energy of vacancy formation in solid argon and Foreman (1963) had followed this work up by determining the volume of a vacancy including these effects.

Swenberg (1967) has cast doubts on the approximation used by Jansen. In other respects also Jansen's results have been questioned. Thus Graben et al. (1966) find that in their calculations of the third virial coefficient Jansen's choice of $\beta$, the width parameter in the Gaussian wave function for a given atom, is too large. A result supporting Swenberg's view. Using Axilrod's potential Graben et al. calculated the third virial coefficient in reduced form and showed that the discrepancy between theory and experiment could be removed. Bullough et al. (1966) performed calculations on the stacking fault energy of solid argon and found this to be $1/15^{th}$ of the value given by Jansen and Zimering (1963). Further calculations by Present (1967) seem to support the view that Jansen's results are too large. He determined the non-additive overlap
energy of interaction between three atoms using the Thomas-Fermi-Dirac approximation and found that for krypton, at a nuclear separation equal to the Van der Waals minimum, this was smaller even than the triple-dipole interaction of Axilrod. He concluded that the non-additive overlap interaction appeared too small to explain the structure of krypton and to produce any substantial correction to the third virial coefficient. Because of these factors of uncertainty in Jansen's approximations plus the fact that no analytical form is given for the short-range interaction we shall neglect this effect here.

Singh et al. (1967) tried to represent the short-range three-body non-additive interaction empirically by a function approximately representing the results obtained by Jansen. However, there seems no justification for the choice of their form of the non-central potential function except convenience. Higher order long-range triplet interactions such as the dipole-dipole-quadrupole interaction have been evaluated by Ayres and Tredgold (1956) but we shall also neglect these as being of a higher order. Lucas (1967) has derived a closed expression for the long-range many-body binding energy and in considering only two and three-body forces we have taken the first two terms in the perturbation expansion of this.

Therefore we consider only the long-range interaction potential of Axilrod and Teller (1943) given as

\[
\phi(3) = \frac{(3\cos \Theta_i \cos \Theta_j \cos \Theta_k + 1)}{R_{ij}^3 R_{jk}^3 R_{ki}^3} \quad (1.1)
\]
where $R_{ij}, R_{jk}$ and $R_{ki}$ are the sides of a triangle with atoms at its vertices and with interior angles $\Theta_i$, $\Theta_j$ and $\Theta_k$. Equation (1.1) can be rewritten as

$$
\phi(3) = \frac{v (3c_{ij}c_{jk}c_{ki} + 8R_{ij}R_{jk}R_{ki})}{8R_{ij}R_{jk}R_{ki}}
$$

where

$$
c_{ij} = R_{jk}^2 + R_{ki}^2 - R_{ij}^2.
$$

The constant $v$ was given by Axilrod (1949) as $\frac{9\alpha^3}{16}$ where $I$ is the ionisation potential and $\alpha$ the polarizability of the given atom.

The expression (1.1) has also been derived by Midzuno and Kihara (1956) using both perturbation and variational methods and more recently by Goetze and Schmidt (1966) using a more elegant technique, and by Graben (1968) using elementary electrostatics. The constant $v$ in (1.1) has been given by Kihara (1958) but in the calculations that follow we use the values given by Bell and Kingston (1966). Using Kihara's Rossi and Danon (1965) have calculated the three-body contribution to the cohesive energy of the inert gas solids. They find that this is between 20 and 30 per cent of the total cohesive energy which would appear to be too large. Bell and Kingston (1966) used recent data from spectroscopic, refractive index and Verdet constant measurements together with a simple method of evaluating oscillator strengths to calculate $v$ for the inert gas solids within an accuracy claimed to be 10% or less. Within this limit their values agree with those given by Axilrod (1951b).

In the present chapter we recalculate the contribution
of the three-body long-range potential to the static lattice energy using a new, more accurate value for the lattice sum. Later in this chapter it is then shown how the contribution of (1.1) to the zero point vibrational energy may be calculated in the Einstein approximation. The results of both these calculations will be used in a later chapter to investigate the effect of the non-central potential on the properties of the inert gas solids.

2. Static Lattice Energy

The three-body static lattice energy for a crystal of $N$ atoms is obtained by summing (1.1) over the whole lattice,

$$E(3L) = \frac{1}{6} \sum_{i \neq j \neq k} (3)(R_{ij}, R_{jk}, R_{ki})$$

$$= \frac{N}{6} \sum_{i \neq j} (3)$$

$$= \frac{NT}{3}$$

(2.1)

where we have taken the $k^{th}$ atom as origin. The factor $1/6^{th}$ appears because all triplets are counted 6 times in the sum over the whole lattice. Axilrod (1951b) has evaluated the lattice sum, $T_0$, occurring in (2.1) by direct summation of triplets out to about four nearest neighbour distances. His result for the static lattice energy of a f.c.c. lattice was

$$E(3L) = \frac{N}{3} \sqrt[6]{56.7} \frac{R_0}{R}$$

(2.2)
where \( R_0 \) was the nearest neighbour distance. We have re-calculated this and find that the result given by Axilrod for the sum over nearest neighbour triplets as 14.7113 is wrong and should be 35.1653. We have further extended the summation over all triplets out to about ten nearest neighbour distances and obtained the result 57.41. From a plot of the partial sums against the reciprocal of the nearest neighbour distance the sum to infinity was estimated to be 57.60 ± 0.05. It is therefore clear that the triplet interaction is long-range, the interaction due to nearest neighbours providing only 60% of the total lattice interaction energy. Therefore the non-nearest neighbours are just as important and must be included in any calculation.

The contribution to the lattice energy at \( T=0^\circ\text{K} \) due to triplet interactions is easily evaluated from equation (2.2) using the values for \( v \) given by Bell and Kingston (1966). These are given in Table 1 together with the experimental heat of sublimation.

<table>
<thead>
<tr>
<th>Gas</th>
<th>( H_0 ) cals/gm.mole</th>
<th>( R_0 ) angstroms</th>
<th>( v )</th>
<th>( \bar{f}(\mathbf{3L}) ) cals/gm.mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neon</td>
<td>448</td>
<td>3.1563</td>
<td>1.677</td>
<td>14.91</td>
</tr>
<tr>
<td>Argon</td>
<td>1846</td>
<td>3.7549</td>
<td>74.48</td>
<td>138.8</td>
</tr>
<tr>
<td>Krypton</td>
<td>2666</td>
<td>3.9910</td>
<td>223.7</td>
<td>239.4</td>
</tr>
<tr>
<td>Xenon</td>
<td>3828</td>
<td>4.3356</td>
<td>749.0</td>
<td>382.6</td>
</tr>
</tbody>
</table>

\( v \) is given in erg. (angstroms)\(^9\)x10\(^{12}\) and derived from values given by Bell and Kingston (1966). Experimental values for \( H_0 \) and \( R_0 \) obtained from Pollack (1964).

Table 1
It is apparent from these values that even the long-range triplet interactions are of considerable importance. It is very difficult to measure $E(3L)$ experimentally because of the difficulty in isolating the two-body lattice energy $E(2L)$. Only one experimental result obtained by Lasee and Simmons (1967) for krypton by measurements of vacancy concentration is as yet known. The difficulties of the experiment are illustrated by the result given for the many-body interaction of krypton as $650 \pm 300 \text{ cals/gm.mole}$. Further the experiment cannot distinguish between the various possibilities of the origin of the three-body and higher order forces or give their relative importance. However, it clearly gives evidence of the importance of many-body interactions and it is reasonable to assume that triplet interactions are the most important of these.

3. Zero Point Vibrational Energy

Goetze and Schmidt (1966) first made a calculation on the effect of triplet interactions on the zero point energy and other properties of argon. In this section we give explicit formulae for the zero point energy and extend the work to include results for the other inert gas solids. Following Goetze and Schmidt we employ an Einstein model of a crystal to evaluate the harmonic contribution to the zero point energy. This model is used for the following reasons. Although exact expressions have been given for the harmonic zero point energy of a f.c.c. lattice by Domb and Salter (1952) and Isenberg (1963) only nearest neighbour interactions were considered. This is a reasonable approximation for two-body forces but as already demon-
stromed in the static lattice energy calculations it is a very bad approximation for triplet interactions. With the Einstein model the calculations may be done including all neighbour interactions and even for two-body forces the error in ignoring non-nearest neighbour interactions is at least as great as that of the Einstein approximation for the nearest neighbour interactions.

As mentioned in the previous chapter, the Einstein model considers the vibration of one atom of the crystal moving in a potential produced by all the others at rest on their equilibrium sites. In the appendix we calculate the potential energy of a typical atom due to its displacement \( \rho \) from its lattice position; up to the quadratic term in \( \rho \) this is

\[
K = \frac{1}{6}(P_2 + 2T_2)\rho^2 \tag{3.1}
\]

where

\[
P_2 = \sum_{\text{pairs}} (\phi''(2) + \frac{2}{R_{ij}} \phi'(2))
\]

\[
T_2 = \sum_{\text{triplets}} (\phi''(3) + \frac{2}{R_{ij}} \phi'(3)).
\]

\( \phi(2) \) is the pair potential function and superscripts indicate differentiation with respect to \( R_{ij} \). Putting the potential energy \( K \) in the Schrodinger equation for a typical atom the harmonic zero point energy may be written down immediately

\[
\phi^H(2Z + 3Z) = \frac{3}{2}\hbar \left( \frac{P_2 + 2T_2}{3m} \right)^{\frac{1}{2}}. \tag{3.2}
\]

With no three-body force \( T_2 \) is zero and
For the f.c.c. lattice with only nearest neighbour interactions and neglecting \( \phi(2)'/R \) compared with \( \phi(2)'' \), \( P_2 = 12\phi(2)'' \) and \( \phi^H(2Z) = 1.061\phi(2)''/m \). The exact result in these circumstances is 1.022\( \phi(2)''/m \), so that the Einstein result is only \( 3\% \) different. However, we shall not neglect \( \phi(2)'/R \) and include all neighbour interactions in our calculations.

For the two-body potential \( \phi^{(2)} \) we shall assume a Lennard-Jones (12,6) potential as typical. This may be written

\[
\phi^{(2)}(r) = 4\xi\left\{(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6\right\}
\]

(3.4)

The parameter \( \xi \) is the depth of the potential at the minimum and \( \sigma \) the distance at which \( \phi^{(2)} = 0 \). These parameters have been calculated elsewhere (Zucker, 1968) using the experimental heat of sublimation \( H_0 \) and the nearest neighbour distance, both at \( T = 0^\circ K \). Two sets of parameters were calculated for each element; in the first case only two-body interactions are considered and then the free energy at \( T = 0^\circ K \), \( F_0 \), is given by

\[
F_0 = -H_0 = \Phi(2L) + \Phi(2Z)
\]

where \( \Phi(2Z) \) is the total zero point energy, including both harmonic and anharmonic terms; in the second case the static triplet lattice energy is included, that is it is assumed that

\[
F_0 = \Phi(2L) + \Phi(2Z) + \Phi(3L).
\]
It should be noted that $\mathcal{I}(3Z)$ has not been included as it has a negligible effect on the pair potential parameters. The effect of $\mathcal{I}(3L)$ is, however, considerable and both sets of parameters for each element have been given in Table 2.

<table>
<thead>
<tr>
<th></th>
<th>$\epsilon/k$</th>
<th>$\sigma$</th>
<th>$\chi^*$</th>
<th>$N\epsilon$</th>
<th>$\nu^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Angstroms</td>
<td></td>
<td></td>
<td>cals/gm.mole</td>
<td></td>
</tr>
<tr>
<td>Neon (a)</td>
<td>36.46</td>
<td>2.776</td>
<td>.5809</td>
<td>72.48</td>
<td>.03401</td>
</tr>
<tr>
<td>(b)</td>
<td>37.54</td>
<td>2.765</td>
<td>.5749</td>
<td>74.63</td>
<td>.03429</td>
</tr>
<tr>
<td>Argon (a)</td>
<td>119.4</td>
<td>3.400</td>
<td>.1864</td>
<td>237.4</td>
<td>.07438</td>
</tr>
<tr>
<td>(b)</td>
<td>128.3</td>
<td>3.368</td>
<td>.1815</td>
<td>255.1</td>
<td>.07535</td>
</tr>
<tr>
<td>Krypton (a)</td>
<td>164.7</td>
<td>3.635</td>
<td>.1025</td>
<td>327.4</td>
<td>.08872</td>
</tr>
<tr>
<td>(b)</td>
<td>179.8</td>
<td>3.595</td>
<td>.0992</td>
<td>357.4</td>
<td>.08997</td>
</tr>
<tr>
<td>Xenon (a)</td>
<td>231.5</td>
<td>3.960</td>
<td>.06340</td>
<td>460.1</td>
<td>.09791</td>
</tr>
<tr>
<td>(b)</td>
<td>255.3</td>
<td>3.911</td>
<td>.06113</td>
<td>507.4</td>
<td>.09934</td>
</tr>
</tbody>
</table>

(a) $\mathcal{I}(3L)$ not included, (b) $\mathcal{I}(3L)$ included.

Table 2. Parameters of $4\epsilon[(\frac{\sigma}{R})^{12} - (\frac{\sigma}{R})^{6}]$

For the 12-6 potential and a f.c.c. lattice

$$P_2 = 4\epsilon \sum_{i \neq j} \left( 132 \frac{\sigma^{12}_{14}}{R_{ij}} - 30 \frac{\sigma^{6}_{8}}{R_{ij}} \right)$$

$$= 4\epsilon \left( 1591.9 \frac{\sigma^{12}_{14}}{R_0} - 384 \frac{\sigma^{6}_{8}}{R_0} \right)$$

(3.5)

The triplet term $T_2$ may also be found explicitly from
The importance of non-nearest neighbours in the sum over triplets for \( T_2 \) is made very clear when it is noted that the nearest neighbour contribution to the lattice sum of -567 is only -92.5. Even at five nearest neighbour distances the triplet sum is only -538.4, and at ten nearest neighbour distances -561.9. Extrapolation as before suggested the sum to infinity to be -567 \( \pm 1 \).

For the purposes of calculation it was convenient to introduce the reduced notation:

\[
R^* = \frac{R}{\sigma}, \quad \Lambda^* = \frac{\hbar}{\sigma(\overline{m}\varepsilon)^{\frac{3}{2}}}, \quad F^* = \frac{F}{\overline{m}\varepsilon}, \quad v^* = \frac{v}{\sigma^3\varepsilon}.
\]

In this notation the zero point energy of a crystal of \( N \) atoms becomes

\[
E^H(2Z+3Z) = 3N(4\pi R_0^7)^{-1}(2122.56 - 512.08R_0^6 - 378v^*R_0^3)^{\frac{3}{2}}
\]

(3.7)

The zero point energy at \( T=0 \) was then calculated both with and without the triplet contribution and for both sets of potential parameters for each gas. The results have been given in Table 3 together with the contribution to the zero point energy due to anharmonicity calculated using only the pair potential with an Einstein model. The latter is
|                | $\Psi^H(2Z)$ | $\Psi^H(2^5+3Z)$ | $|\Psi^H(3Z)|$ | $\Psi^{Anh}(2Z)$ |
|----------------|--------------|------------------|----------------|-----------------|
| Neon (a)       | 130.6        | 129.3            | 1.3            | 14.4            |
| (b)            | 127.4        | 126.2            | 1.2            | 14.7            |
| Argon (a)      | 182.3        | 179.4            | 2.9            | 4.5             |
| (b)            | 174.4        | 171.4            | 3.0            | 4.7             |
| (c)            | 176.4        | 173.4            | 3.0            | -               |
| Krypton (a)    | 145.9        | 143.3            | 2.6            | 1.9             |
| (b)            | 138.7        | 136.0            | 2.7            | 1.9             |
| (c)            | 140.5        | 137.7            | 2.8            | -               |
| Xenon (a)      | 130.0        | 127.5            | 2.5            | 1.0             |
| (b)            | 123.1        | 120.4            | 2.7            | 1.0             |

(a) Calculated from parameters (a) Table 2,
(b) Calculated from parameters (b) Table 2,
(c) Calculated for the potential of Guggenheim and McGlashan (1960).

(All values are in cals/gm.mole)

Table 3

incorrect for calculating the anharmonic contribution but for consistency we calculate it this way and the order of magnitude is correct.

4. Discussion

It is evident that the inclusion of triplet interactions reduces the zero point energy. This was also found by Goetze and Schmidt (1966) who find that the Einstein frequency is lowered by three-body forces. In the case of neon the change is small and negligible compared with the anharmonic term. This is because the triplet
interaction coefficient for neon is relatively smaller than for the other elements, and the anharmonicity of neon is relatively larger. But for argon, krypton and xenon the effect of the triplet interaction is at least of the same order as the anharmonic term.

The choice of a given pair potential although affecting the absolute value of the total harmonic zero point energy has very little effect on \( |\frac{\theta H}{\theta} (32) | \). This is illustrated by using the pair potential suggested by Guggenheim and McGlashan (1960a,b) for inert gases. These authors are opposed to the Lennard-Jones (12,6) potential and give one entirely different. It is not possible to calculate \( P_2 \) completely for their potential since the part involving non-nearest neighbours is drawn in by hand. However, we have computed the zero point energy at \( T = 0^\circ \text{K} \) for argon and krypton from the formula given for the Einstein frequency obtained from the analytic portion of their potential. This is

\[
\nu_E^2 = 6(\pi^2 m_{\text{min}} R_{\text{min}}^2)^{-1} \frac{1}{2} K (1+\Delta)^{-1} (1+3) - \alpha \Delta (1+\Delta)^{-1} (1+2\Delta) \\
+ 2 \beta^2 (1+\Delta)^{-1} (1+2\Delta)^{-1} - \frac{5}{12} 0.802 \lambda (1+\Delta)^{-8}
\]

(4.1)

where

\[
\Delta = \frac{R_0 - R_{\text{min}}}{R_{\text{min}}}
\]

\( R_{\text{min}} \), \( K \), \( \alpha \), \( \beta \) and \( \lambda \) are given parameters and we have used the latest values of McGlashan (1965) for argon. The triplet interaction modifies \( \nu_E \) to a new frequency \( \nu_E' \) given by

\[
(\nu_E')^2 = \nu_E^2 + 2T_2 (12\pi^2 m)^{-1}
\]

(4.2)
The zero point energy is then given by $3N\hbar \nu_g/2$ and the values calculated from (4.2) both with and without the triplet contribution are also given in Table 3. As may be seen $|\mathbb{H}(3\zeta)|$ is virtually unchanged.

In conclusion it appears that the effect of triplet interactions on the zero point vibrational energy is independent of the pair potential. The size of the effect in neon is small but in argon, krypton and xenon it is of the same order as the anharmonic pair potential term but of opposite sign. If other three-body terms of importance - Jansen (1964) believes the short-range terms to be similar to the Axilrod and Teller formula - then not only must the triplet lattice energy be included in any solid state calculation, but also the triplet zero point contributions as well.

**APPENDIX**  The Potential Energy of a Particle Displaced from its Lattice Site

**Pair Interactions**

Let us consider a typical lattice point as the origin of a coordinate system (Figure 1). Let $\rho$ be the displacement of an atom from this point. The potential energy of the displaced atom with all the other atoms at rest on their lattice points due to pair-wise interactions is
Expanding as a Taylor series up to $\rho^2$ we have

$$K(\text{two-body}) = \sum_{i \neq j} \phi^{(2)}(\rho_{ij} - \rho) - \rho \cdot R_{ij} \frac{\phi^{(2)}}{R_{ij}}$$

$$+ \frac{1}{2} \left[ \rho \cdot R_{ij} \frac{\phi^{(2)}}{R_{ij}} + \left( \rho \cdot R_{ij} \right)^2 \left( \frac{\phi^{(2)''}}{R_{ij}^2} - \frac{\phi^{(2)'} \phi^{(2)}}{R_{ij}^3} \right) \right] + \ldots \right \} \text{(A.1)}$$

The first term is simply the lattice energy, $\rho \cdot R_{ij} = \rho R_{ij} \cos \Theta$ where $\Theta$ is the angle between $\rho$ and $R_{ij}$. Because of symmetry the sum over all lattice points of this term vanishes. Similarly $(\rho \cdot R_{ij})^2 = \rho^2 R_{ij}^2 \cos^2 \Theta$ and it has been shown in the previous chapter that $\cos^2 \Theta$ in the sum over all lattice points can be replaced by $1/3$ outside the sum. Hence

$$K(\text{two-body}) = \rho^2 \sum_{i \neq j} \left( \phi^{(2)''} + 2 \frac{\phi^{(2)'} \phi^{(2)}}{R_{ij}} \right) = \frac{\rho^2 P_2}{\Theta} \text{. (A.2)}$$

**Triplet Interactions**

![Figure 2](image-url)
Let us consider the triplet interaction of the displaced atom with all the others at rest on their lattice sites (Figure 2). This is

\[
\frac{1}{2} \sum_{i \neq j \neq k} \phi^{(3)}(|R_{ij}|, |R_{ik}|, |R_{jk}|)
\]

and again expanding in a Taylor series we have

\[
K(\text{three-body}) = \frac{1}{2} \sum_{i \neq j \neq k} \phi^{(3)}(|R_{ij}|, |R_{ik}|, |R_{jk}|)
\]

\[
- \frac{1}{3} \frac{\partial \phi^{(3)}}{\partial R_{ij}} \frac{\partial \phi^{(3)}}{\partial R_{ik}} + \frac{1}{3} \frac{\partial \phi^{(3)}}{\partial R_{ij}} \frac{\partial \phi^{(3)}}{\partial R_{ik}}
\]

\[
+ \frac{1}{3} \frac{\partial \phi^{(3)}}{\partial R_{ij}} + \frac{1}{3} \frac{\partial \phi^{(3)}}{\partial R_{ik}}
\]

\[
+ \frac{1}{6} \left( \frac{\partial \phi^{(3)}}{\partial R_{ij}} + \frac{\partial \phi^{(3)}}{\partial R_{ik}} \right)^2
\]

\[
+ \frac{1}{6} \left( \frac{\partial \phi^{(3)}}{\partial R_{ij}} + \frac{\partial \phi^{(3)}}{\partial R_{ik}} \right)^2
\]

\[
+ 2 \frac{\partial \phi^{(3)}}{\partial R_{ij}} \frac{\partial \phi^{(3)}}{\partial R_{ik}} \frac{\partial \phi^{(3)}}{\partial R_{ij}} \frac{\partial \phi^{(3)}}{\partial R_{ik}}
\]

The first term is again simply the lattice energy.

The first order term again vanishes in the summation because of symmetry. Similarly the mixed second order term reduces to

\[
K(\text{three-body}) = \frac{1}{2} \sum_{i \neq j \neq k} \frac{\partial^2 \phi^{(3)}}{\partial R_{ij}^2} + \frac{\partial^2 \phi^{(3)}}{\partial R_{ik}^2} + \frac{\partial^2 \phi^{(3)}}{\partial R_{jk}^2} + \frac{\partial^2 \phi^{(3)}}{\partial R_{ij} \partial R_{ik}}
\]

Again because of symmetry the terms with \( R_{ij} \) as variable in the summation are equivalent to those with \( R_{ik} \) as variable; hence
\[ K(\text{three-body}) = \frac{\rho^2}{12} \sum_{i \neq j \neq k} 2(\phi^{(2)})_{ij} + \frac{2}{R_{ij}} \phi^{(2)} \]  \hspace{1cm} (A.5)

\[ = 2T^2 \rho^2, \]

and also \[ K = K(\text{two-body}) + K(\text{three-body}) \]

\[ = \frac{\rho^2}{6} (p_2 + 2T^2). \]  \hspace{1cm} (A.6)

Besides evaluating \( T_0 \) and \( T_2 \) for the f.c.c. lattice we have also evaluated them for the b.c.c. and s.c. lattices. The results are 44.33 \( \pm \) 0.02, -420.3 \( \pm \) 0.5, 19.85 \( \pm \) 0.01 and -222.3 \( \pm \) 0.5 respectively, where we have extrapolated to obtain the sum to infinity.
CHAPTER 4

THE EFFECT OF A LONG-RANGE THREE-BODY FORCE ON
THE ELASTIC CONSTANTS OF THE INERT GAS SOLIDS
AT THE ABSOLUTE ZERO

1. Introduction

The long-range triple-dipole interaction potential function derived by Axilrod and Teller (1943) has already been described in the previous chapter. Although the potential appears from the application of third order perturbation theory to the pair-wise interaction of three dipoles only, it seems to be a genuine three-body interaction as it depends on all three mutual interatomic distances. The short-range interactions of triplets of atoms due to overlap exchange affects investigated by Jansen (1964) and co-workers will, for the reasons stated in the previous chapter, not be used here.

Rossi and Danon (1965), Goetze and Schmidt (1966) and Chell and Zucker (1968) have calculated the contribution from the triple-dipole interaction to the static lattice and zero point energies of the inert gas solids. Zucker (1968) investigated the effect of the long-range three-body force on the determination of the pair potential functions of the heavier inert gases from solid state data. He found that the inclusion of three-body forces affected the potential parameters of a given potential function considerably but did not appear to affect the theoretical isotherms obtained from them. However, all these calcu-
lations merely exhibited how certain isotropic thermodynamical properties of the rare gas crystals normally evaluated assuming only two-body interactions would be altered by the inclusion of the triple-dipole interaction. No genuine three-body effect which could be determined experimentally was considered apart from a reported calculation made by Goetze and Schmidt (1966) on the elastic constants of argon. Attempts to obtain information about three-body interactions from vacancy measurements have also led to conflicting reports. Thus Smith and Chapman (1967) state that the vacancy concentration of argon at the triple point was consistent with a simple two-body force calculation made by Glyde (1966). On the other hand Losee and Simmons (1967) interpreted their measurements on the energy of vacancy formation in krypton as showing a many-body contribution to the lattice energy of krypton estimated as 650±300 cal mole⁻¹.

It is the purpose of this chapter to present a theoretical calculation of the elastic constants and related thermoelastic properties of the inert gas solids. It will be shown how by including the triple-dipole interaction that the theory predicts a result depending unequivocally on this interaction and which should be capable of experimental proof or disproof. Expressions are derived for the triple-dipole contribution to the elastic constants which are defined from the expression for the free energy in terms of Lagrangian finite strain coordinates.

2. Theory

The heaviest inert gases Ne, A, kr and Xe condense into f.c.c. crystals. Because of their high symmetry
cubic crystals have only three independent non-zero elastic constants $C_{11}$, $C_{12}$ and $C_{44}$. It is well known that if only central pair-wise interactions are present between the particles making up the crystal and the latter is treated classically, that is zero point vibrations at $T = 0^\circ K$ are neglected, then the Cauchy relation $C_{12} = C_{44}$ holds for cubic structures. Expressions for the elastic constants in terms of a pair potential function $\phi^{(2)}(r)$ have been derived by Born (1940) using the method of homogeneous deformations. The pair potential that will be used will be the Lennard-Jones (12,6) function, given by equation (3.4) in Chapter 3. With this potential the following formulae for various thermoelastic expressions in the classical limit at $T = 0^\circ K$ may be derived in reduced notation. They are

\[
\Gamma^*(2L) = \frac{6.066}{V^*} - \frac{14.454}{V^*^2}
\]

\[
P^*(2L) = - \frac{3\Gamma^*}{V^*} = \frac{24.264}{V^*^3} - \frac{28.908}{V^*^2}
\]

\[
K^*(2L) = - V^* \frac{\partial P^*}{\partial V^*} = \frac{121.32}{V^*^2} - \frac{86.724}{V^*^3}
\]

\[
C_{11}^*(2L) = \frac{171.2}{V^*^3} - \frac{123.0}{V^*^2}
\]

\[
C_{12}^*(2L) = C_{44}^*(2L) = \frac{84.25}{V^*^5} - \frac{54.11}{V^*^3}
\]

where

\[
\Gamma^* = \frac{E}{NV}, \quad V^* = \frac{V}{N\sigma^3}
\]

\[
P^* = \frac{\sigma^3 P}{\varepsilon}, \quad C_{ij}^* = \frac{\sigma^3 C_{ij}}{\varepsilon}
\]

$E$ is the static lattice energy of a crystal of $N$ atoms, $V$ the volume, $P$ the pressure and $K$ the bulk modulus. $\varepsilon$ and $\sigma$ are the parameters occurring in the (12,6) potential func-
tion. There is a general relation which holds amongst the elastic constants of cubic crystals namely

\[ K = \frac{1}{3} (C_{11} + 2C_{12} + P). \]  

(Salter (1954) improved on the static lattice approximation. He considered zero point effects in the harmonic approximation and showed that the Cauchy relation was no longer valid. Although Baron and Klein (1965a) showed Salter's method was not correct for the elastic constants, their own more rigorous investigation confirmed Salter's conclusions. These were that if there are only pair interactions the effects of zero point vibrations was to make \( C_{44} > C_{12} \) at \( T = 0^\circ K \). The expressions derived by Barron and Klein for the contributions due to zero point effects were

\[ P^*(2Z) = \frac{f^*(2Z)}{V^*} \gamma(1) \]

\[ C_{11}^*(2Z) = \frac{f^*(2Z)}{V^*} \beta_{11}(1) + P^*(2Z) \]

\[ C_{12}^*(2Z) = \frac{f^*(2Z)}{V^*} \beta_{12}(1) \]

\[ C_{44}^*(2Z) = \frac{f^*(2Z)}{V^*} \beta_{44}(1) + \frac{P^*(2Z)}{2} \]  

(2.4,a-d)

\( f^*(2Z) \) was the reduced two-body zero point energy, and the \( \beta_{ij}(1) \) and \( \gamma(1) \) were volume dependent constants for a given \( \Phi(2)(r) \). The latter were obtained from the work of Barron and Klein (1965a) but \( f^*(2Z) \) was calculated on an all neighbour model by a method based on the Bethe approximation and developed by Chell (1967,1968b).

It is convenient here to introduce the dimensionless quantity, \( B \), defined by
B equals zero if the Cauchy relation holds and its value is a measure of the deviation of this relation. It was found by both Salter (1954) and Barron and Klein (1965a) that with only two-body forces the effect of zero-point energy was to make B a positive quantity at $T = 0^\circ K$.

Using the method of homogeneous deformations we have investigated the contribution to the elastic constants due to the triple-dipole interaction (given by equation (1.1) in Chapter 3) in the static lattice approximation. The elastic constants were then obtained from the expansion for the strained energy in powers of the Lagrangian strain coordinates. The relationships between the elastic constants defined in this way and those defined by other means has been discussed by Barron and Klein (1965b). The details of the calculation have been given in the appendix. The results obtained for a f.c.c. lattice in reduced notation were

$$\Phi^*(3L) = 6.776 \frac{v^*}{V^*}, \quad P^*(3L) = 20.32 \frac{v^*}{V^*}$$

$$K^*(3L) = 81.28 \frac{v^*}{V^*}, \quad C_{11}^*(3L) = 100.4 \frac{v^*}{V^*}$$

$$C_{12}^*(3L) = 61.56 \frac{v^*}{V^*}, \quad C_{44}^*(3L) = -20.52 \frac{v^*}{V^*} (2.6, a-g)$$

where $v^* = v/\sigma^O$ and $v$ is the constant appearing in the expression for the triple-dipole interaction.

The lattice sums evaluated to obtain the above formulae were all computed independently of one another. The triplet...
summations were very slow to converge and the results given are extrapolated values, the estimated errors being given in the appendix. It was thus most gratifying to find that the relation (2.3) was satisfied and hence corroborated the results of individual lattice sums.

It may be seen immediately that once again the Cauchy relation is not valid. But in this case

\[ C_{44}(3L) - C_{12}(3L) = -82.08 \frac{v^*}{v^*4} \]  

(2.7)

and as \( v^* \) and \( C_{12}(3L) \) are positive, \( B \) is negative. \( B \) at the absolute zero will thus depend on the relative sizes of the effects of the zero point vibrations calculated from two-body interactions and the static lattice contribution of the triple-dipole interaction. There is also a contribution from the triple-dipole interaction to the zero point vibrational effects but this is of a higher order and was thus neglected.

The absolute values of the elastic constants \( C_{11}, C_{12} \) and \( C_{44} \) and the dimensionless parameter \( B \) were thus evaluated using equations (2.2), (2.4) and (2.6). In addition \( \Theta^0 \) the limiting value of the Debye temperature as \( T \to 0 \) was calculated from the formula

\[ \Theta^0^3 = 9\pi\hbar(4\pi\nu k)^{-3/2} \frac{2}{18+7/3} f(s,t) \]  

(2.8)

where \[ s = \frac{c_{11} - c_{44}}{c_{12} + c_{44}}, \quad t = \frac{c_{12} - c_{44}}{c_{44}} \]

and \( c_{11} = C_{11} - P, c_{12} = C_{12} + P, c_{44} = C_{44} - P, \)
where $c_{ij}$ are the elastic constants derived from the stress-strain relations, and $f(s,t)$ is a function tabulated by de Launay (1954, 1956). The transverse and longitudinal velocities $v_t$ and $v_\ell$ of elastic waves in a polycrystalline specimen were also evaluated using the arithmetic mean, $G$ (Hill, 1952) of the shear moduli $G_V$ and $G_R$ defined by Voigt (1928) and Reuss (1929) respectively. These were

\[
G_V = \frac{1}{3}(c_{11} - c_{12} + 3c_{44})
\]

\[
G_V - G_R = \frac{3}{5}\left[\frac{2c_{44}}{4c_{44} + 3(c_{11} - c_{12})}\right]^2
\]

whence

\[
v_\ell^* = (\frac{1}{3}G^*)^2
\]

\[
v_t^* = G^*v^*\quad\text{and}\quad v^* = v\left(\frac{m}{\rho}\right)^{\frac{1}{2}}
\]

The results of these calculations at $P = 0$ and $T = 0$ have been exhibited in Table 1. Some calculations have been made for $B$ at $T = 0$ and elevated pressures and these results have been shown in Figure 1.

3. Discussion of Results

To make numerical calculations it was necessary to select a given pair potential. As previously indicated the chosen form was the Lennard-Jones (12,6) potential function. The main reason for this choice was that this is the only pair potential for which Barron and Klein have given $\beta_{ij}(1)$ and $\gamma(1)$ for all neighbour interactions. Two sets of the parameters $\sigma$ and $\epsilon$ were used for each element and these are given in Table 2 in Chapter 3. The first set labelled (a) were derived assuming only two-body inter-
<table>
<thead>
<tr>
<th>Element</th>
<th>C_{11}</th>
<th>C_{12}</th>
<th>C_{44}</th>
<th>Bx1000 K = \frac{1}{3}(C_{11} + 2C_{12} + P)</th>
<th>V_e'</th>
<th>V_t'</th>
<th>\theta^0(0^\circ K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neon</td>
<td>(a) 1.37</td>
<td>0.668</td>
<td>0.848</td>
<td>26.9</td>
<td>0.90</td>
<td>10.67</td>
<td>6.33</td>
</tr>
<tr>
<td></td>
<td>(b) 1.36</td>
<td>0.668</td>
<td>0.794</td>
<td>18.9</td>
<td>0.90</td>
<td>10.54</td>
<td>6.17</td>
</tr>
<tr>
<td>Argon</td>
<td>(a) 3.70</td>
<td>2.03</td>
<td>2.16</td>
<td>6.4</td>
<td>2.59</td>
<td>16.07</td>
<td>9.14</td>
</tr>
<tr>
<td></td>
<td>(b) 3.59</td>
<td>2.02</td>
<td>1.85</td>
<td>-8.4</td>
<td>2.54</td>
<td>15.60</td>
<td>8.62</td>
</tr>
<tr>
<td>Krypton</td>
<td>(a) 4.52</td>
<td>2.53</td>
<td>2.61</td>
<td>3.2</td>
<td>3.19</td>
<td>13.42</td>
<td>7.59</td>
</tr>
<tr>
<td></td>
<td>(b) 4.38</td>
<td>2.53</td>
<td>2.17</td>
<td>-14.2</td>
<td>3.15</td>
<td>12.99</td>
<td>7.07</td>
</tr>
<tr>
<td>Xenon</td>
<td>(a) 5.11</td>
<td>2.88</td>
<td>2.94</td>
<td>2.1</td>
<td>3.62</td>
<td>12.90</td>
<td>7.26</td>
</tr>
<tr>
<td></td>
<td>(b) 4.93</td>
<td>2.88</td>
<td>2.39</td>
<td>-17.0</td>
<td>3.56</td>
<td>12.43</td>
<td>6.71</td>
</tr>
</tbody>
</table>

(a) Calculated neglecting the three-body interaction.
(b) Calculated with the three-body interaction included.

The C_{ij} and K are given in units of 10^{10} \text{dyn/cm}^2.

Experimental values for \theta^0 obtained from Barron and Klein (1965).

TABLE 1. Elastic constants and related quantities at T = 0^\circ K and zero pressure.
Curves 1-4 were calculated without the three-body interaction term for neon, argon, krypton and xenon respectively. Curves 5-8 were calculated with the three-body interaction term included for neon, argon, krypton and xenon.
actions, and the values obtained are in excellent agreement with the results of Barron and Klein (1965a). The second set labelled (b) are the theoretical values obtained after including triple-dipole interaction and they differ significantly from the first set except for C\textsubscript{12}. However, we do not wish to emphasise the absolute values of the elastic constants since the theoretical values depend significantly on the pair potential used. But the dimensionless quantity B should be relatively insensitive to the pair potential used and hence indicate the effect of the triple-dipole interaction. Indeed it may be observed that for all the elements except neon the effect of the triple-dipole interaction is to alter B from a positive to a negative quantity. It should be possible to perform experiments to measure B and thus confirm or deny the presence of three body forces in inert gas crystals. B for neon remains positive (although reduced by the three-body term) since its zero point energy is relatively larger compared with its lattice energy than any of the other elements considered and thus B is larger. Further the triple-dipole lattice energy of neon compared with its total lattice energy, Table 1, Chapter 3, is relatively smaller than for the other elements and hence its effect on reducing B is much less. Calculations made of B at T = 0\textdegree K at elevated pressures show (Figure 1) that the absolute value of B in all cases is reduced as the pressure is increased but it does not appear to have a limiting value at high pressures. However, since at elevated pressures the atoms are much closer together the short-range triplet exchange interactions would be expected to play a more important role, and agreement with experiment
in these regions can only be considered fortuitous. Since
the short-range interactions appear to be of the same sign
and have a similar angular dependency to the triple-dipole
interactions it might be expected that they would reduce the
value of $B$ further and perhaps make $B$ zero or even negative
at high pressures for neon.

Values of $\Theta^0$ calculated with set (a) of the potential
parameters agree excellently with those calculated by Barron
and Klein (1965a) and agree reasonably well with experiment.
However, the effect of the triple-dipole interaction is
to reduce $\Theta^0$ as calculated from (2.8) considerably and agree­
ment with experiment is now not so good. The bulk modulus,
$K$, evaluated with parameters (a) is in fair agreement with
experiment although for the lighter elements agreement is
not so good. For these the anharmonic vibrational energy
might be expected to be important and the disagreement is
not surprising [Brown and Horton (1967) have shown how its
inclusion removes the discrepancy for neon and argon.]
Using parameters (b) and including the triple-dipole inter­
action in the calculations makes very little difference to
the value of $K$, in agreement with Zucker's (1968) isotherm
calculations. Of course the values of $\Theta^0$ and $K$ are absol­
ute and results will depend significantly on the pair pot­
ential.

In conclusion we believe the presence or otherwise of
the long-range three-body forces in the inert gas crystals
can be determined experimentally by measurement of the elas­
tic constants at $T = 0^\circ K$ and hence determining the dimension­
less parameter $B$. It might be argued that $B$ will also be
affected by the presence of other many-body forces and thus an experimental positive value of $B$ for the heavier elements would not conclusively rule out the presence of three-body forces. Against this is the fact that the short-range three-body forces would appear, because of their similar sign and angular dependency to the triple-dipole interaction, to decrease the value of $B$ even more. Other many-body effects such as the dipole-dipole quadrupole interaction order (Ayres and Tredgold, 1956) one would expect to be of higher and not have an appreciable effect. However, negative experimental values of $B$ would clearly demonstrate the existence and importance of three-body forces. It might be further argued that the effects of many body forces have already been included in the two-body potential function through the potential parameters $\xi$ and $\sigma$. While the results of Zucker (1968) for theoretical isotherms would lend support to this argument for isotropic crystal properties, the results of this chapter on the elastic constants clearly demonstrate that this is not the case for anisotropic properties.

APPENDIX  Elastic Constants by the Method of Homogeneous Deformations

Figure 2.
Let $\phi^3(R_m, R_{mn}, R_n)$ be the triple-dipole interaction function between three atoms, $\ell$, $m$ and $n$ whose position vectors in the undistorted crystal with respect to an arbitrary lattice site, $C$, as origin are $\ell$, $m$ and $n$ respectively (Figure 2).

$$\ell = (\ell_1a, \ell_2a, \ell_3a), \quad m = (m_1a, m_2a, m_3a), \quad n = (n_1a, n_2a, n_3a)$$

where the $\ell_i$'s, $m_i$'s and $n_i$'s are integers characterising the lattice. The total interaction energy of an undistorted crystal of $N$ atoms is

$$E(3L) = \frac{1}{6} \sum_{\ell \neq m \neq n} \phi^3(|\ell-m|, |m-n|, |n-\ell|) \quad (A.1)$$

After a homogeneous deformation the interaction energy becomes

$$E^D(3L) = \frac{1}{6} \sum_{\ell \neq m \neq n} \phi^3\left(\left[|\ell-m|^2 + 2\rho_{\ell m}\right]^{\frac{1}{2}}, \left[|m-n|^2 + 2\rho_{mn}\right]^{\frac{1}{2}}, \left[|n-\ell|^2 + 2\rho_{n\ell}\right]^{\frac{1}{2}}\right) \quad (A.2)$$

where $2\rho_{\ell m}$ represents the change in the square of the separation of two atoms $\ell$ and $m$ after deformation and

$$\rho_{\ell m} = a^2 \sum_{i=1}^3 \sum_{j=1}^3 (\ell_i - m_i)(\ell_j - m_j)x_{ij}.$$ 

The $x_{ij}$ are elements of the Lagrangian strain tensor and are given by

$$x_{ij} = \frac{1}{2}(\ell_i \cdot a_j - a_2^2 \ell_{ij})/a^2$$

where the $a_i$ are new elementary lattice vectors formed when a cube is deformed into a parallelepiped. $a^3 = bv$.
where $v$ is the volume per molecule and $b$ is equal to 1, 1/4 and 1/2 for a simple cubic, body-centred cubic and face-centred cubic lattice respectively. Expanding (A.2) in a Taylor series in $\rho$ about the undistorted lattice positions

$$E(3L) = E(3L) + \frac{1}{6} \sum_{\ell \neq m \neq n} \left\{ \frac{3}{2} \sum_{i=1}^{3} (\rho_i D_i + \frac{1}{2} \sum_{j=1}^{3} \rho_i \rho_j D_i D_j + \ldots) \phi^{(3)} \right\}$$

where the suffix $\ell m$ has been abbreviated to 1, mn to 2 and nl to 3, and the operator $D_{\ell m}$ is $\frac{1}{|x_{\ell m}|} \frac{\partial}{\partial |x_{\ell m}|}$.

In summing over all triplets in the lattice the sum containing $\rho_i D_i$ is equal to that containing $\rho_j D_j$ and that containing $\rho_i \rho_j D_i D_j$ to $\rho_k \rho_l D_k D_l$. As any lattice site may be used as an origin in the crystal for convenience we now choose the $\ell$th atom as origin. Therefore $\ell = 0$ and (A.3) becomes

$$E(3L) = E(3L) + \frac{N}{2} \sum_{m \neq n} (\rho_mD_m + \frac{1}{2} \rho_m^2 D_m^2 + \rho_m \rho_n D_mD_n + \ldots) \phi^{(3)}.$$  

(A.4)

Substituting for $\rho$ and using the symmetry properties of cubic lattices we obtain

$$E^D(3L) = E(3L) + \frac{N}{2} \left[ a^2 T_1(x_{11} + x_{22} + x_{33}) + (a^4/2) (T_2 + 2T_3) (x_{11}^2 + x_{22}^2 + x_{33}^2) \right. \\
+ \left. a^4 (T_4 + 2T_5) (x_{11} x_{22} + x_{22} x_{33} + x_{33} x_{11}) \right.$$

$$+ 2a^4 T_4 (x_{12}^2 + x_{23}^2 + x_{31}^2) \phi^{(3)}.$$  

(A.5)

where $$E(3L) = N \phi(3L) = \frac{N}{6} \sum_{m \neq n} \phi^{(3)}$$
Equation (A.5) may be compared directly with the expression for the strained energy density obtained from elasticity theory for cubic lattices,

\[
\frac{E}{Nv} = \frac{3}{v} - P(x_{11} + x_{22} + x_{33}) + (C_{11}/2)(x_{11}^2 + x_{22}^2 + x_{33}^2) \\
+ C_{12}(x_{11}x_{22} + x_{22}x_{33} + x_{33}x_{11}) + 2C_{44}(x_{12}^2 + x_{23}^2 + x_{31}^2) + \ldots
\]  

Thus we have

\[
\Phi(3L) = T_0/3 \\
P(3L) = a^2 T_1/v \\
C_{11}(3L) = a^4 (T_2 + 2T_3)/v \\
C_{12}(3L) = a^4 (T_4 + 2T_5)/v \\
C_{44}(3L) = a^4 T_4/v
\]  

We have numerically evaluated on a computer the sums occurring in (A.6) for the three cubic lattices. Their slow convergence is illustrated by the fact that for the f.c.c. lattice, for example, it was necessary to evaluate
all triplets inside a cube of side 24a (a total of over 30.5x10^6 triplet interactions in all). The sum to infinity was obtained by extrapolation and these values are given in table 2 below together with the estimated error. The final values of the sums in some cases had different signs to their value when only triplets inside a cube of side 2a were considered (this corresponds to only triplets formed by the nearest neighbours for the f.c.c. and b.c.c. lattices and to all triplets formed by atoms out to third neighbours for the s.c. lattice.) To illustrate this these values are also given.

To check the summation two different methods were used to calculate the triplet sums inside a cube of side 4a and the computed nearest-neighbour results were also compared with those obtained by hand calculations for triplets formed by the nearest-neighbours. The sums can be further checked by using the two relations

\[ P^*(3L) = -\left(\frac{\partial^2 f^*(3L)}{\partial V^*}\right) \]

and

\[ K^*(3L) = -V^*\left(\frac{\partial F^*(3L)}{\partial V^*}\right) = \frac{1}{3}\left[2C_{12}^*(3L) + 2C_{12}^*(3L) + P^*(3L)\right] \]

which confirm that the sums are correct to the accuracy stated.
<table>
<thead>
<tr>
<th>Lattice</th>
<th>$T_0 x \frac{a}{\nu}$</th>
<th>$T_{1x} x \frac{a}{\nu}$</th>
<th>$T_{2x} x \frac{a}{\nu}$</th>
<th>$T_{3x} x \frac{a}{\nu}$</th>
<th>$T_{4x} x \frac{a}{\nu}$</th>
<th>$T_{5x} x \frac{a}{\nu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F.C.C. (i)</td>
<td>2.54 ± 0.005</td>
<td>-2.54 ± 0.01</td>
<td>-6.65 ± 0.1</td>
<td>9.6 ± 0.1</td>
<td>-2.57 ± 0.02</td>
<td>5.13 ± 0.02</td>
</tr>
<tr>
<td>(ii)</td>
<td>1.554</td>
<td>-1.055</td>
<td>0.900</td>
<td>-0.225</td>
<td>0.450</td>
<td>0.389</td>
</tr>
<tr>
<td>B.C.C. (i)</td>
<td>0.3160 ± 0.0005</td>
<td>-0.3155 ± 0.0005</td>
<td>-0.765 ± 0.002</td>
<td>1.196 ± 0.002</td>
<td>-0.335 ± 0.001</td>
<td>0.633 ± 0.0002</td>
</tr>
<tr>
<td>(ii)</td>
<td>0.0735</td>
<td>-0.0348</td>
<td>-0.0135</td>
<td>-0.0461</td>
<td>-0.0135</td>
<td>-0.0461</td>
</tr>
<tr>
<td>S.C. (i)</td>
<td>19.85 ± 0.01</td>
<td>-19.84 ± 0.01</td>
<td>-93.5 ± 0.5</td>
<td>94.8 ± 0.2</td>
<td>-14.9 ± 0.2</td>
<td>37.8 ± 0.1</td>
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<tr>
<td>(ii)</td>
<td>18.01</td>
<td>-13.83</td>
<td>-12.84</td>
<td>17.12</td>
<td>5.01</td>
<td>12.29</td>
</tr>
</tbody>
</table>

(i) Extrapolated values of sum to infinity.  (ii) Sum inside a cube of side 2a.

**Table 2**  Triple-Dipole Lattice Sums
1. Introduction

The zero point vibrational energy is known to play an important part in determining the thermodynamic and thermophysical properties of some substances. In particular the cohesive energy, equilibrium volume, bulk modulus and the elastic constants of the lighter inert gas solids depend appreciably not only on the harmonic but also the anharmonic vibrational energy at $0^\circ$K. It is the purpose of this chapter to very briefly review the methods that have been used to calculate the zero point vibrational energy and then develop a new method based on the Bethe approximation which, it will be shown, has certain distinct advantages over other techniques that have been employed.

The Einstein approximation which was discussed in Chapters 2 and 3 has been one of the starting points in the past for the calculation of the zero point energy. Henkel (1955) extended the approximation to include the quartic anharmonic energy which he treated as a perturbation on the harmonic energy. The work of Henkel was further developed by Zucker (1958) who generalised Henkel's results to any central pair-wise additive potential function and any lattice. Later, using a method developed by Coulson and McWeeney (1948), Zucker (1959, 1961, 1964) showed how the quartic and higher order terms could be evaluated to any desired accuracy in the Einstein approximation. Hurst and Levett (1961) also used an anharmonic Einstein theory to calculate the zero
point energy when they extended their cell model of the liquid state (Levelt and Hurst, 1960) to the solid state. The Einstein theory has certain advantages. These are

(i) it is relatively simple,
(ii) it can easily be treated as an all neighbour model,
(iii) higher order anharmonic terms can be included in the calculation and treated to any accuracy,
(iv) it also allows the perturbation expansion to be checked for convergency.

However, it also has certain disadvantages. And these are

(i) the anharmonic terms of odd power in the vibrational displacements give zero contribution to the energy,
(ii) the anharmonic terms of even power give an order of magnitude estimate only of the actual anharmonic energy,
(iii) the theory is poor in describing those properties of solids sensitive to the true frequency spectrum of the crystal.

Domb and Salter (1952) made use of a method developed by Thirring (1913, 1914) for calculating analytically the even frequency moments to evaluate accurately the harmonic zero point energy of the three cubic lattices. For the frequency spectrum they used the results of Montroll (1942, 1943, 1944). Isenberg (1963) developed a method of calculating the higher frequency moments. He evaluated the first 34 moments for the f.c.c. lattice and gave the harmonic energy to an accuracy of seven decimal places for a nearest-
neighbour model. However, such methods are not applicable to calculating the anharmonic properties of solids.

Using a quantum variational technique Bernardes (1960) expressed the zero point energy and other thermodynamical quantities in terms of a power series in Planck's constant at $T = 0^\circ K$. Other variational calculations by Nosanow (1966), Koehler (1967) and Hetherington et al. (1967) have been concerned with the problem of calculating the ground state energy of helium while Gillis et al. (1968) have employed the self-consistent phonon approximation to investigate the properties of the inert gas solids.

Recently, with the advent of high speed computers, an approach to the problem of calculating the anharmonic contributions to the free energy has been developed based on the formal expressions derived by Ludwig (1958) and involving summations over the wave numbers and polarization vectors of the lattice. Thus Maradudin et al. (1961a) developed the computational techniques for performing the necessary sums and applied them to evaluating the zero point energy of a linear chain of atoms. Later Maradudin and Flinn (1963) re-applied the method and calculated the anharmonic contribution to the zero point energy of a f.c.c. lattice. Further calculations of the free energy of crystals at $0^\circ K$ were carried out by Leibfried and Ludwig (1961) and Wallace (1964). More recently Feldman and Horton (1967) have recalculated and improved on the work of Flinn and Maradudin (1963). They extended the calculations to include non-leading terms (that is they did not ignore terms such as $\phi(n-1)/R_0$ compared with $\phi(n)$, where $\phi(n)$ is the $n^{th}$ derivative
of the pair potential function and $R_0$ the nearest neighbour distance. It has been shown by Lloyd (1964a) and Barron and Klein (1965) and reaffirmed by the results of Feldman and Horton that it is necessary to include the non-leading terms as they are of the same order as the effect studied. All the above mentioned authors restricted their calculations to central pair-wise additive potential functions and nearest neighbour interactions.

Goetze and Schmidt (1966) and more recently Chell and Zucker (1967) have investigated the effect of a long-range, three-body, non-central potential of the form given by Axilrod and Teller (1943) on the zero-point harmonic energy using the Einstein approximation. Chell and Zucker found (see also previous chapter) that the non-central force contribution was of the same order as the anharmonic energy and therefore could not justifiably be neglected.

In the present chapter a method based on an approximation first introduced by Bethe (1935) for the Ising model of Ferromagnetism and later adapted by Lloyd (1964a,b) to calculate the high temperature limit of the free energy and the elastic constants is used to determine the zero point energy of the three cubic lattices. The results are applied to the inert gas solids to investigate the following crystal models: (i) central, nearest neighbour interactions only; (ii) central, all-neighbour interactions using a Lennard-Jones ($\alpha, \beta$) potential function; (iii) central, all neighbour and non-central interactions (the latter using the potential function given by Axilrod and Teller). In the calculations the central, nearest neighbour interactions are treated
in the Bethe approximation while the non-nearest neighbour and non-central interactions are treated in the Einstein approximation.

A paper (Chell, 1967) has already been published giving the harmonic and quartic zero point energies calculated using a nearest neighbour model with central interactions. The leading term approximation was then made so that comparison could be made with the results of Flinn and Maradudin (1963). We now include a non-central potential, all neighbour interactions and the non-leading and cubic anharmonic terms. To calculate the latter it was found necessary to extend the theory from a coupled two particle model to the three particle model used in the present chapter.

The main reasons for the development and extension of the Bethe approximation to the present calculations were:

(i) that it presented a simpler approach to the evaluation of the free energy at 0°K than those calculations based on Ludwig's expression,
(ii) that using cubic symmetry analytical expressions could be derived for the zero point energy in terms of the coordination number q and thus the method would be general to all three cubic lattices,
(iii) that the method would give results of greater accuracy than calculations based on the Einstein approximation, particularly the calculated anharmonic energy, while still retaining all the advantages of that method,
(iv) that it might be possible to extend the theory to enable expressions for the free energy at finite temperatures to be derived.

(v) that a non-central potential function could be included in the calculations of the thermodynamical quantities from the expression for the free energy and thus the effects of such a potential assessed, at least qualitatively if not quantitatively.

2. **Theory**

2.1 **General**

The adaptation of the Bethe approximation as described here and by Lloyd (1964a,b) essentially consists of assuming that the atoms in a crystal move in the mean field produced by all the other atoms. By assuming an effective harmonic potential between nearest neighbours the unknown parameters occurring in it can be determined from two consistency relations. The wave function and eigenfrequencies of the 3 atom system then being determined, the anharmonic terms in the potential expansion can be treated as perturbations. Thus the Bethe approximation can be considered to be the approximation next in order to the Einstein approximation. It is entirely equivalent to considering the lattice to be composed of a series of non-intersecting chains of atoms and will in fact give the identical answer to calculations based on such a lattice (Domb, 1960).

Considering the case of central, nearest neighbour interactions we represent the harmonic potential between
two atoms \( m \) and \( n \) by \( \mathbf{v}^{(2)}(\mathbf{r}_m, \mathbf{r}_n) \) where \( \mathbf{r}_m \) is the displacement vector of the \( m \)th atom from its equilibrium lattice site. The potential representing a coupled three particle system is then written as

\[
\mathcal{W}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \sum_i v_i(\mathbf{r}_1) + v^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + \sum_j ' v_j(\mathbf{r}_2) \\
+ v^{(2)}(\mathbf{r}_2, \mathbf{r}_3) + \sum_k ' v_k(\mathbf{r}_3) \quad (2.1)
\]

where \( v_i(\mathbf{r}_m) \) is the \( i \)th bond of the \( m \)th atom. The single prime indicates that the sum is to be taken over all nearest neighbours excluding the bond \( v^{(2)}(\mathbf{r}_m, \mathbf{r}_n) \) and the double prime that both bonds \( v^{(2)}(\mathbf{r}_m, \mathbf{r}_n) \) and \( v^{(2)}(\mathbf{r}_m, \mathbf{r}_l) \) are to be excluded. Suffix 2 denotes the centre atom of the three atoms labelled 1, 2 and 3 in the coupled system. The consistency relations are then

\[
\int \int \psi^2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \, d^3\mathbf{r}_1 \, d^3\mathbf{r}_2 = \psi^2(\mathbf{r}_2) \quad (2.2)
\]

and

\[
\mathcal{E}_2 = 3\mathcal{E}_1 \quad (2.3)
\]

where \( \mathcal{E}_2 \) is the zero point energy of the three atom system and \( \mathcal{E}_1 \) the energy of a one particle system. \( \psi \) represents the ground state wave function.

In expanding the potential function \( \phi \) about the equilibrium lattice sites in terms of the difference in the displacements of the two atoms \( m \) and \( n \) from these sites we have

\[
v_i = v_i^{(2)} + v_i^{(3)} + v_i^{(4)}
\]

where

\[
v_i^{(2)} = \frac{1}{2}a_1 A^2 + \frac{1}{2}a_2 B,
\]
$$V_1(3) = \frac{1}{6} \gamma_1 A^3 + \frac{1}{6} \gamma_2 AB,$$

$$V_1(4) = \frac{1}{24} \gamma_1 A^4 + \frac{1}{24} \gamma_2 A^2B + \frac{1}{24} \gamma_3 B^2, \quad (2.4)$$

$$A = \mathbf{i} \cdot \Delta \mathbf{r}, \quad B = (\Delta \mathbf{r})^2 - A^2,$$

$$\alpha_1 = \phi(2), \quad \alpha_2 = \phi(1)/R_0,$$

$$\gamma_1 = \phi(3), \quad \gamma_2 = 3\phi(2)/R_0 - 3\phi(1)/R_0^2,$$

$$\delta_1 = \phi(4), \quad \delta_2 = 6\phi(3)/R_0 - 12\phi(2)/R_0^2 + 12\phi(1)/R_0^3,$$

$$\nu_3 = 3\phi(2)/R_0^2 - 3\phi(1)/R_0^3 \quad (2.5)$$

where the derivatives are evaluated at the nearest neighbour distance $R_0$ and $\Delta \mathbf{r} = \mathbf{r}_m - \mathbf{r}_n$. $\mathbf{i}$ is a unit vector in the direction of the $i$th bond.

### 2.2 Harmonic Energy

Taking the three atoms to lie on the x-axis

$$V(2)(\mathbf{r}_m, \mathbf{r}_n) = \frac{1}{2} \alpha_1 (x_m - x_n)^2 + \frac{1}{2} \alpha_2 [(y_m - y_n)^2 + (z_m - z_n)^2], \quad (2.6)$$

we let

$$V_i(\mathbf{r}_m) = \frac{1}{2} \alpha_1 (\mathbf{i} \cdot \mathbf{r}_m)^2 + \frac{1}{2} \alpha_2 |(\mathbf{r}_m)^2 - (\mathbf{i} \cdot \mathbf{r}_m)^2| + \chi_0 \quad (2.7)$$

where $\chi_0$, $\chi_1$, and $\chi_2$ are the unknown parameters to be determined. Then

$$\sum_i V_i(\mathbf{r}_m) = \chi \left[ \frac{1}{2} x_m^2 + y_m^2 + z_m^2 \right] + q\chi_0 \quad (2.8)$$

where

$$\chi = \frac{9}{2}(\chi_1 + 2\chi_2) + k + R$$

and we have included the contribution of non-nearest neigh-
hours and a non-central force in an Einstein approximation by the symbols k and \( \kappa \) respectively. \( q \) is the co-ordination number. Evidently

\[
\sum_i V_1(r_m) = \frac{1}{2}[X-x_1]x_m^2 + \frac{1}{2}[X-x_2][y_m^2 + z_m^2] + (q-1)x_0 \quad (2.9)
\]

and

\[
\sum_i V_2(r_m) = \frac{1}{2}[X-2x_1]x_m^2 + \frac{1}{2}[X-2x_2][y_m^2 + z_m^2] + (q-2)x_0 \quad (2.10)
\]

The expressions (2.6), (2.8), (2.9) and (2.10) were substitute into (2.1) and the three particle Schrödinger equation solved for the potential \( W(r_1, r_2, r_3) \).

The diagonalisation of the dynamical matrix, the normal mode transformation, normal mode frequencies, \( \nu_{ij} \), and the ground state wave function are given in the appendix. The one particle ground state wave function is

\[
\psi(r_m) = (S/\hbar^2)^{3/2} \exp \left\{ -\frac{S^2}{2} \left[ x_m^2 + y_m^2 + z_m^2 \right] \right\} \quad (2.11)
\]

where \( S^4 = m \chi / h^2 \), \( m \) is the atomic mass and \( \hbar = h/2\pi \). \( h \) is Planck's constant. Using the consistency relation (2.2) we find, after performing the necessary integrations and some simplification,

\[
S^2 = a_1 - c_1^2/(2b_1 - d_1) = a_2 - c_2^2/(2b_2 - d_2) \quad (2.12)
\]

from which \( x_1 \) and \( x_2 \) may be determined. \( a_1, b_1 \) and \( c_1 \) are defined in the appendix.

\[
E_1 = \frac{3}{2} \hbar \nu + qx_0
\]

where \( \nu = \hbar S^2 / 2\pi m \), the frequency of the one potential system,
and 

\[ E_3 = \frac{\hbar f}{2} + (3q - 4)x_0 \]

where 

\[ f = \sum_{i=1}^{3} \sum_{j=1}^{3} v_{ij}. \]

Hence, using the consistency relation (2.3),

\[ x_0 = \frac{\hbar}{8}(f - 9v) \]  

(2.13)

and 

\[ E_1 = \frac{3\hbar v}{2}(1 - \frac{3q}{4}) + \frac{\alpha \hbar f}{8}. \]  

(2.14)

2.3 Anharmonic Energy

The quartic anharmonic energy is determined from first order perturbation theory

\[ E^{(4)} = \frac{9}{4} < 0 | V^{(4)}(r_1, r_2) + V^{(4)}(r_2, r_3) | 0 > \]  

(2.15)

Substituting for \( V^{(4)}(r_m, r_n) \) from (2.4), remembering that the three atoms lie on the x-axis and taking the expectation value using the normal mode transformation we find

\[ E^{(4)} = \frac{9}{4} \left( \frac{\hbar}{2\pi \alpha} \right)^2 \left\{ \frac{1}{16} q_1 + \frac{1}{24} q_2 (q_1 + 4q_2) \right\} \]  

(2.16)

where \( q_i = \sum_{j=1}^{3} a_{ij}, \; a_{ij} = P_{ij}^{2/v_{ij}} \)

and the \( p_{ij} \) are defined in the appendix.

Similarly the cubic anharmonic energy is given by second order perturbation theory

\[ E^{(3)} = \frac{9}{4} \sum_{m \neq 0} | < n | V^{(3)}(r_1, r_2) + V^{(3)}(r_1, r_3) | 0 > |^2 / (E_0 - E_m) \]  

(2.17)

where again \( V^{(3)}(r_m, r_n) \) is given by (2.4). Hence
\[ E(3) = \frac{q}{4} \left[ \frac{1}{(2\pi)^2} \right] \left\{ \frac{\gamma_1}{4!} q_{11}^2 \left[ \frac{1}{2v_{11}} + \frac{q_{12}}{v_{11} + 2v_{12}} + \frac{q_{13}}{v_{11} + 2v_{13}} \right] \ight. \\
+ \frac{\gamma_2}{8!} q_{11}^2 \left[ \frac{q_{21}}{v_{11} + 2v_{21}} + \frac{q_{22}}{v_{11} + 2v_{22}} + \frac{q_{23}}{v_{11} + 2v_{23}} \right] \
+ \frac{q_{22}q_{23}}{(v_{11} + v_{22} + v_{33})} \
+ 2q_{21} \left[ \frac{q_{12}q_{22}}{v_{12} + v_{21} + v_{22}} \right] \\
+ \frac{q_{12}q_{23}}{(v_{12} + v_{21} + v_{23})} + \frac{q_{13}q_{22}}{(v_{13} + v_{21} + v_{22})} + \frac{q_{13}q_{23}}{(v_{13} + v_{21} + v_{23})} \right\} \]

(2.18)

In calculating the anharmonic energy we have used the fact that the Bethe approximation gives the same answer as a lattice of non-intersecting chains of atoms.

3. Calculations

3.1 Nearest Neighbour Model with Central Forces Only

For this model \( \alpha_2 = \kappa_2 = 0 \),
\( R = k = 0 \).

The equations (2.16) and (2.18) simplify slightly to give

\[ E(4) = \frac{q}{4} \left[ \frac{1}{(2\pi)^2} \right] \left\{ \frac{\gamma_1}{4!} \left[ \frac{6}{16} q_{11}^2 \left[ \frac{1}{12v} Q_1 + \frac{2}{3} \frac{V^2}{v^2} \right] \right] \right\} \]

(3.1)

and

\[ E(3) = \frac{q}{4} \left[ \frac{1}{(2\pi)^2} \right] \left\{ \frac{\gamma_1}{4!} q_{11}^2 \left[ \frac{1}{2v_{11}} + \frac{q_{12}}{v_{11} + 2v_{12}} + \frac{q_{13}}{v_{11} + 2v_{13}} \right] \ight. \\
+ \frac{\gamma_2}{8} \left[ \frac{4q_{11}}{(v_{11} + 2v)} + \frac{3q_{12}}{(v_{12} + 2v)} + \frac{3q_{13}}{(v_{13} + 2v)} \right] \right\} \]

(3.2)

In Table 1 below are displayed the parameter \( \kappa_1 \), the harmonic and anharmonic energies calculated using the Bethe approximation, and also given wherever possible are the
<table>
<thead>
<tr>
<th>Lattice</th>
<th>$x_1/\alpha_1$</th>
<th>Harmonic Energy*</th>
<th>Cubic Energy**</th>
<th>Quartic Energy**</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.C.</td>
<td>0.3883</td>
<td>1.2249</td>
<td>$N_1$ 0.03882</td>
<td>$N_2$ 0.7769</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.9099a</td>
<td>$N_2$ 0.02611a</td>
<td>$N_3$ 0.1520a</td>
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<tr>
<td>B.C.C.</td>
<td>0.6057</td>
<td>2.3006</td>
<td>$N_1$ 0.02992</td>
<td>$N_2$ 0.3272</td>
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<td></td>
<td></td>
<td>2.2992b</td>
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<tr>
<td>F.C.C.</td>
<td>0.7687</td>
<td>2.8901</td>
<td>$N_1$ 0.02015</td>
<td>$N_2$ 0.1586</td>
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<tr>
<td></td>
<td></td>
<td>2.8925c</td>
<td>$N_1$ 0.01575d</td>
<td>$N_2$ 0.00396d</td>
</tr>
</tbody>
</table>

a, Maradudin et al. (1961); b, Domb and Salter (1952); c, Isenberg (1963); d, Fel'man and Horton (1967). The unlettered numbers refer to calculations in the present work. The results of other authors are given to the same accuracy as the present calculations.

* The harmonic energy is given in units of $\hbar(\phi^{(2)}/m)^{1/2}$.

** The cubic and quartic anharmonic energies characterized by the numbers $N_1, M_1$ are given by

$$-\frac{n^2}{m\phi(2)^2}\left\{N_1(\phi(3))^2 + N_2\left(\frac{\phi(3)\phi(2)}{R_0}\right) + N_3\left(\frac{\phi(2)}{R_0}\right)^2\right\}, \quad \frac{n^2}{m\phi(2)^2}\left\{M_1\phi(4) + M_2\frac{\phi(3)}{R_0} + M_3\frac{\phi(2)}{R_0^2}\right\}$$

Table 1. Zero Point Energy with Central, Nearest Neighbour Interactions
latest values obtained by others. It may be seen that the
harmonic and the leading terms of the quartic anharmonic
energies are in good agreement with the results obtained by
others using standard lattice dynamical methods. However
the cubic anharmonic energies appear to be considerably
overestimated. The discrepancy is thought to be due to
the unsuitability of the method for second order perturbation
calculations involving strong coupling. (The non-leading
terms also appear to have been affected for a similar reason).
It was found that a method similar to that used by Lloyd
(1964a) to overcome a similar problem in his classical ap­
proach to high temperature limit of the cubic anharmonic
energy was not applicable to the quantum mechanical second
order perturbation method needed to calculate the cubic an­
harmonic energy at 0°K. Extension of the approximation
to a three coupled particle system greatly improved the
accuracy of the method relative to the two coupled particle
model. However, further improvements could only be implemen­
ted at the expense of simplicity.

3.2 All Neighbour Model with Central Forces.  R=0.

To illustrate this model a Lennard-Jones (12,6) potential
function was chosen of the form

$$\phi(r) = 4\epsilon \left[ (\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6 \right] \quad (3.3)$$

where $\epsilon$ is the depth of the potential at the minimum and $\sigma$
the distance at which $\phi(r)$ equals zero. The theory was
applied in evaluating the zero point energies of the inert
gas solids Ne, Ar, Kr and Xe which crystallise into a f.c.c.
structure. In the calculations two sets of parameters were used. Those given by Zucker (1968) when the three-body lattice energy was neglected [parameters (a)] and those when the three-body lattice energy was included in the free energy at $T = 0^\circ \text{K}$ [parameters (b)] (See Chapter 3 Table 2). The experimental nearest neighbour distance $R_0$ was obtained from Pollack (1964).

It can easily be shown that for the above potential

$$\frac{\alpha_2}{\alpha_1} = \frac{[-12(\sigma/R_0)^{12} + 6(\sigma/R_0)^6]}{\alpha}$$

and

$$k/\alpha_1 = \frac{[132(\sigma/R_0)^{12}(c_{14} - 12) - 30(\sigma/R_0)^6(c_8 - 12)]}{3\alpha}$$

where

$$\alpha = 156(\sigma/R_0)^{12} - 42(\sigma/R_0)^6$$

and the $C_n$'s are lattice sums given by Hirschfelder et al. (1954). Using these quantities $x_1$ and $x_2$ were calculated from (2.13) and hence the zero point energies evaluated. The results are given in Table 2, together with the results obtained from the nearest neighbour model using parameters (a).

It may be seen that the zero point energy of Ne is least affected and that of Xe most affected by the inclusion of all neighbours. The harmonic contribution of Ne is reduced by 1.6% and 3.9% and that of Xe by 4.6% and 9% for parameters (a) and (b) respectively. The effect of the non-nearest neighbours on the anharmonic energy was assessed through the change in the harmonic eigenfrequencies $v_{ij}$ only that is the non-nearest neighbour interactions were neglected. These would anyway only change the anharmonic energy by a few
<table>
<thead>
<tr>
<th>Model</th>
<th>$\alpha_1/\alpha_1$</th>
<th>$\alpha_2/\alpha_1$</th>
<th>Harmonic Energy</th>
<th>Anharmonic Energy</th>
<th>Central, nearest neighbour interactions only with parameters (a)</th>
<th>Central, all neighbour interactions with parameters (a)</th>
<th>Central, all neighbour interactions with parameters (b)</th>
<th>Central and three-body non-central interactions with parameters (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>0.7687</td>
<td>1.003</td>
<td>127.4</td>
<td>19.92</td>
<td>4.90</td>
<td>-4.90</td>
<td>24.83</td>
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<tr>
<td>(ii)</td>
<td>0.7579</td>
<td>0.9925</td>
<td>125.3</td>
<td>20.34</td>
<td>5.27</td>
<td>25.61</td>
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<tr>
<td>(iii)</td>
<td>0.7610</td>
<td>0.9928</td>
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<td>20.75</td>
<td>5.39</td>
<td>26.14</td>
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<tr>
<td>(iv)</td>
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<td>1.003</td>
<td>120.9</td>
<td>21.03</td>
<td>5.68</td>
<td>26.71</td>
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<tr>
<td>A</td>
<td>0.7687</td>
<td></td>
<td>180.9</td>
<td>6.04</td>
<td>-1.36</td>
<td>7.40</td>
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<tr>
<td>(ii)</td>
<td>0.7401</td>
<td>1.005</td>
<td>173.6</td>
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<td>(iii)</td>
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<td>(iv)</td>
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<tr>
<td>Kr</td>
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<tr>
<td>(ii)</td>
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<tr>
<td>(iii)</td>
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<td>-0.43</td>
<td>1.85</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Units: Calories per gm. mole.

Table 2. Harmonic and Anharmonic Zero Point Energies
per cent, a change which would be negligible in a quantity which is itself only about 10% of the harmonic energy for all the inert gases considered except Ne. The anharmonic energy is increased for Ne by 2.1% and 4.2% and for Xe by 5.3% and 8.7% for parameters (a) and (b) respectively.

3.3 All Neighbour Model with Central and Non-Central Forces

The non-central potential function considered was the long-range three-body potential first derived by Axilrod (1943) and which has already been described and used in calculating the zero point harmonic energy in Chapter 3. For the same reasons as those given in that chapter we neglect the short-range exchange interactions between triplets of atoms.

The expression derived in Chapter 3 for the three-body potential contribution to the zero point harmonic energy in the Einstein approximation was

\[ R = -1134\nu / 3R_C. \]

Parameters (b) were used in the calculations and again the non-nearest neighbour and non-central anharmonic effects were considered only through the change in the harmonic eigenfrequencies \( \nu_{ij} \). The results are shown in Table 2.

The effect of the three-body potential is to further decrease the harmonic and increase the anharmonic energies. With respect to the nearest neighbour results the harmonic energy of Ne is decreased by 5.1% whilst the anharmonic energy is increased by 4.2%, the values for Xe are 11.5% and 15.3% respectively. Gotze and Schmidt (1966) and Chell and Zucker (1967) also found that the three-body
potential decreased the harmonic energy. Comparing cases (iii) and (iv) in Table 2 gives the magnitude of the non-central contribution which is similar to that calculated in Chapter 3 but slightly larger. As pointed out there it is of opposite sign and of the same order as the anharmonic energy for A, Kr and Xe.

4. Discussion and Summary

The harmonic and cubic and quartic anharmonic energies have been calculated from an expression for the zero point energy of the three cubic lattices derived using the Bethe approximation. The approximation has been shown to give results for a central nearest neighbour model in good agreement with methods based on normal lattice dynamics for the harmonic and leading term of the quartic anharmonic energy. For non-leading terms and the cubic anharmonic energy the agreement is generally not so good. The assumption of central, nearest neighbour interactions between atoms in a crystal has been investigated for the inert gas solids by taking into account (1) central non-nearest neighbour interactions and (2) non-nearest neighbours with a central and a three-body non-central interaction using the Einstein approximation. It was found that effects (1) and (2) decreased the harmonic energy and increased the anharmonic energy, Ne being least and Xe being most affected.

The contribution of the three-body potential to the harmonic zero point energy was $-1.5$, $-3.5$, $-3.3$, $-3.2$ cals/gm.mole for Ne, A Kr and Xe respectively. For the latter three this is of the same order, but opposite in sign to, the anharmonic energy and therefore when working to this order cannot
justifiably be neglected. In the case of Ne, because of its relatively large anharmonic energy and the smallness of the coefficient $v$, the three-body potential has little effect.

The total effect of non-nearest neighbour and non-central interactions in Xe is to change the nearest neighbour model harmonic energy by 11.5% and the anharmonic energy by 15.3%. For Ne the change is smaller but still appreciable. It has been shown in Chapter 3 that the contribution of the three-body potential to the harmonic zero point energy must be considered as an all neighbour interaction and that a nearest neighbour model would be in serious error for this potential.

The harmonic energy of the central, non-nearest neighbour interactions model differs from that of the nearest neighbour model by 1.6% for Ne and 4.6% for Xe. When parameters (b) are used the central, all neighbour interactions change the harmonic energy by 3.9% and 9% for Ne and Xe respectively. Clearly a large part of the three-body contribution comes through the modification of the parameters used in the central potential.

Results have also been obtained for Lennard-Jones $(m,6)$ potential functions and for values of $m$ ranging from 10 to 14. These will not be given here but they indicate that the smaller the value of $m$ the smaller the zero point energy is and that the greater the effects described above.

In the next chapter we demonstrate how the consistency relation (2.3) used in the previous calculation appears from the more general theory used to calculate the free energy at finite temperatures.
APPENDIX

In matrix form the harmonic potential \( W(x_1, x_2, x_3) \) can be written as

\[
\frac{1}{2}(x \ y \ z) \begin{pmatrix} A & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & C \end{pmatrix} \begin{pmatrix} x^t \\ y^t \\ z^t \end{pmatrix}
\]

where \( x, y \) and \( z \) are the row vectors \((x_1 \ x_2 \ x_3), (y_1 \ y_2 \ y_3) \) and \((z_1 \ z_2 \ z_3) \) respectively. Superscript \( t \) indicates the transpose and

\[
A = \begin{pmatrix} A_{11} & -\alpha_1 & 0 \\ -\alpha_1 & A_{11} + \beta_1 & -\alpha_1 \\ 0 & -\alpha_1 & A_{11} \end{pmatrix}, \quad B = C = \begin{pmatrix} A_{21} & -\alpha_2 & 0 \\ -\alpha_2 & A_{21} + \beta_2 & -\alpha_2 \\ 0 & -\alpha_2 & A_{21} \end{pmatrix}
\]

with \( \beta_1 = \alpha_1 - \lambda_1 \) and \( A_{11} = \lambda_1 + \beta_1 \).

When \( W(x_1, x_2, x_3) \) is substituted into the Schrodinger equation and putting \( \psi(x, y, z) = \psi_1(x)\psi_2(y)\psi_3(z) \) the variables can be separated and we obtain three independent equations in \( x, y \) and \( z \). All three equations are similar in form and can be solved in the same manner by transforming to normal coordinates.

The simultaneous diagonalisation of the kinetic energy and potential energy matrices is dealt with in most text books on physical applications of matrices and therefore will not be presented here in any great detail. The latent roots of the matrices \( A \) and \( B \) are \( A_{11}, A_{12} \) and \( A_{13} \) where \( i \) is 1 or 2 respectively and

\[
A_{12} = A_{11} + \frac{\xi_1}{2}, \quad A_{13} = A_{11} + \frac{\lambda_1}{2}
\]
where
\[ \xi_1 = \beta_1 - (\beta_1^2 + 8\alpha_1^2)^{\frac{1}{2}}, \quad \eta_1 = \beta_1 + (\beta_1^2 + 8\alpha_1^2)^{\frac{1}{2}}. \]

After forming three orthonormal vectors in the usual manner we finally arrive at the transformation to normal coordinates given by

\[ X_1 = \frac{1}{2\xi}(x_1 + x_3), \quad X_2 = \frac{1}{n_1}[\alpha_1 x_1 - \xi_1 x_2 + \alpha_1 x_3], \]
\[ X_3 = \frac{1}{m_1}[\alpha_1 x_1 - \xi_1 x_2 + \alpha_1 x_3], \]
\[ Y_1 = \frac{1}{2\eta}(y_1 + y_3), \quad Y_2 = \frac{1}{n_2}[\alpha_2 y_1 - \eta_2 y_2 + \alpha_2 y_3], \]
\[ Y_3 = \frac{1}{m_2}[\alpha_2 y_1 - \eta_2 y_2 + \alpha_2 y_3], \]

and a similar transformation for the z's.

\[ n_1 = 4\alpha_1^2 + \beta_1 \xi_1 / 2, \quad m_1 = 4\alpha_1^2 + \beta_1 \eta_1 / 2. \]

We also have the useful relations

\[ x_2 - x_1 = p_{11} X_1 + p_{12} X_2 - p_{13} X_3, \]
\[ x_3 - x_2 = p_{11} X_1 + p_{12} X_2 + p_{13} X_3, \]
\[ y_2 - y_1 = p_{21} Y_1 + p_{22} Y_2 - p_{23} Y_3, \]
\[ y_3 - y_2 = p_{21} Y_1 - p_{22} Y_2 + p_{23} Y_3, \]

and similar equations for z₁-z₃.

\[ p_{11} = \frac{1}{2\xi}, \quad p_{12} = n_1^{\frac{1}{2}}(2\alpha_1 - \eta_1 / 2)/\alpha_1 (\eta_1 - \xi_1), \]
\[ p_{13} = m_1^{\frac{1}{2}}(2\alpha_1 - \eta_1 / 2)/\alpha_1 (\eta_1 - \xi_1). \]
In the new coordinates the potential becomes

\[ \dot{\psi}(X, Y, Z) \begin{pmatrix} D & 0 & 0 \\ 0 & E & 0 \\ 0 & 0 & F \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} \]

where

\[ D = \begin{pmatrix} A_{11} & 0 & 0 \\ 0 & A_{12} & 0 \\ 0 & 0 & A_{13} \end{pmatrix}, \quad E = F = \begin{pmatrix} A_{21} & 0 & 0 \\ 0 & A_{22} & 0 \\ 0 & 0 & A_{23} \end{pmatrix} \]

and the normalised ground state wavefunction is

\[ \psi(X, Y, Z) = \frac{1}{\sqrt{\pi^{3/2}}} \exp \left\{ -\frac{1}{2} \sum_{i=1}^{3} S_{ii} X_i^2 \right\} \]

\[ \times \frac{1}{\sqrt{\pi^{3/2}}} \exp \left\{ -\frac{1}{2} \sum_{i=1}^{3} S_{2i} (Y_i^2 + Z_i^2) \right\} \]

where \( S_{ij} = m A_{ij} / \hbar^2 \).

The normal mode frequencies, \( \nu_{ij} \), are given by

\[ \nu_{ij} = \frac{\hbar S_{ij}}{2\pi m} \quad (i = 1, 2 \text{ and } j = 1, 2 \text{ or } 3) \]

The first suffix refers to the mode, \( i = 1 \) to the X mode, \( i = 2 \) to the Y and Z modes, the second suffix labels the mode coordinate. The frequencies corresponding to the Y and Z modes are equal. In the text the Z mode frequencies are sometimes labelled \( \nu_{3j} \) to simplify the notation.

In the original coordinates the ground state wavefunction is given by
\[\psi(r_1, r_2, r_3) = \left(\frac{S_{11} S_{12} S_{13}}{\pi^{3/2}}\right)^{1/2} \exp\left\{-\frac{1}{2} [a_1 x_2^2 + b_1 (x_1^2 + x_3^2) - c_1 (x_1 x_2 + x_2 x_3) - d_1 x_1 x_3]\right\} \times \left(\frac{S_{22} S_{23}}{\pi^{3/2}}\right) \exp\left\{-\frac{1}{2} [a_2 (y_2^2 + z_2^2) + b_2 (y_1^2 + y_3^2 + z_1^2 + z_3^2) - c_2 (y_1 y_2 + y_2 y_3 + z_1 z_2 + z_2 z_3) - d_2 (y_1 y_3 + z_1 z_3)]\right\}\]

where
\[a_1 = \frac{1}{4} (S_{12} z_1^2/n_1 + S_{13} z_1^2/m_1),\]
\[b_1 = S_{11} z_1^2/2 + (S_{12} z_1^2/n_1 + S_{13} z_1^2/m_1) a_1^2,\]
\[c_1 = (S_{12} z_1^2/n_1 + S_{13} z_1^2/m_1) a_1,\]
\[d_1 = S_{11} z_1^2 - 2 a_1^2 (S_{12} z_1^2/n_1 + S_{13} z_1^2/m_1).\]
CHAPTER 6

THE FREE ENERGY OF CUBIC CRYSTALS AT FINITE TEMPERATURES

1. Introduction

In order to calculate further thermodynamic and thermoelastic properties of the inert gas solids it is necessary to obtain an expression for the free energy. From this expression it is then theoretically possible to derive the temperature, volume and pressure dependence of many quantities. We will in this chapter initially give a very brief review of attempts that have been made in the past to obtain such an expression and later show how the free energy at finite temperatures may be derived using the Bethe approximation.

The theory of lattice dynamics in the harmonic approximation has been reviewed by Maradudin et al (1963). In the inert gas solids neon and argon the anharmonic terms play an important role in determining the crystal properties, especially at high temperatures. For the heavier elements krypton and xenon the so-called quasi-harmonic approximation appears adequate for the calculation of thermal data, e.g. compressibility (Liebfried and Ludwig, 1961, Barron, 1965), but even for these gases an anharmonic theory must be employed in the determination of caloric data e.g. specific heats.

Dugdale and MacDonald (1954) investigated the anharmonicity in a linear chain of atoms. Zucker (1958) used a Henkel (1955) model based on the Einstein approximation to
study anharmonic effects in solid argon. He found that theoretically calculated quantities determined from this model gave better agreement with experiment at high temperatures than those predicted by the Debye continuum theory. Other calculations at high temperatures were made by Stern (1958). Ludwig (1958) derived formal expressions for the free energy at any temperature including both cubic and quartic anharmonic terms. However these are not very useful as they stand since they involve complicated sums over wave and polarisation vectors for each temperature considered. Maradudin et al. (1961) made the leading term approximation and evaluated the anharmonic contributions to the vibrational free energy. By adopting an approximation introduced by Bethe (1935), Lloyd (1964a) derived expressions for the cubic and quartic free energy terms in the classical high temperature limit. Further work in the high temperature limit was carried out by Wallace (1963) who made certain approximations to simplify the expressions derived by Ludwig (1958). He then calculated the thermal expansion, specific heat and other anharmonic properties of crystals (Wallace, 1965). Feldman and Horton (1967) have re-performed the computer calculations of Maradudin et al (1961) for the high temperature limit of the free energy without making the leading term approximation. Both Maradudin et al. and Feldman and Horton used a nearest neighbour model. Recently Overton (1967) has suggested approximations which can be applied to the formal expressions of Ludwig (1958) in order to simplify the computations involved.

In the present chapter we derive expressions for the free energy of cubic crystals at finite temperatures.
Thus expression is then compared with the results of others by assuming central, nearest neighbour interactions only and taking the limiting form for high temperatures. This procedure together with the results obtained in the previous chapter then allow one to assess the accuracy of the method at the two extremes of temperature to which the free energy expressions will be applied.

2. Theory

2.1 General

The adaptation of the Bethe approximation to enable the free energy at finite temperatures to be determined follows from writing the consistency relation (2.3) of Chapter 5 in a more general manner. The consistency relation for the free energy consists of a temperature independent part and a temperature dependent part. Equating the harmonic temperature independent expressions gives rise to equation (2.3) of Chapter 5. The harmonic temperature dependent part enables an unknown parameter to be determined and hence the free energy at finite temperatures to be calculated. Expressions are then derived for the temperature dependence of the cubic and quartic anharmonic terms occurring in the potential expansion by treating them as perturbations on the harmonic energy. Unless otherwise stated the symbols occurring in the present chapter have the same meaning and definition as those in Chapter 5.

2.2 Harmonic Energy

We assume that for a one particle system the free energy, $F_1$, per particle can be written as
\[ -\beta z_1 = \log z_1 x^q = \log Z_1 + q \log x \quad (2.1) \]

where \( x \) is an unknown parameter to be determined. \( \beta = 1/kT \)
where \( k \) is Boltzmann's constant and \( T \) the absolute temperature. \( Z_1 \) is the one particle partition function. For a coupled three particle system the free energy, \( F_3 \), is given by

\[ -\beta F_3 = \log Z_3 + (3q-4) \log x \quad (2.2) \]

where \( Z_3 \) is the three particle partition function.

The consistency relation (2.3) of Chapter 5 now becomes

\[ F_3 = 3F_1 \quad (2.3) \]

and hence from (2.1) and (2.2)

\[ x = (Z_3/Z_1^3)^{1/4} \quad (2.4) \]

In the harmonic approximation

\[ Z_1 = \sum_{\{n_i\} = 0}^{\infty} \exp(-[n_1+n_2+n_3+3/2]\gamma) \]

\[ = (1-e^{-\gamma})^{-3} e^{-3\gamma/2} \quad (2.5) \]

where \( \gamma = \hbar v \beta \) and the set of three quantum numbers \( \{n_i\} \) characterise the state of the system.

\[ Z_3 = \sum_{\{n_{ij}\} = 0}^{\infty} \exp(-\frac{3}{2} \sum_{i=1}^{3} \sum_{j=1}^{3} [n_{ij} + \frac{1}{2}] Y_{ij}) \]

\[ = \prod_{ij} (1-e^{-Y_{ij}})^{-1} e^{-Y_{ij}/2} \quad (2.6) \]
where $\gamma_{ij} = \hbar \omega_{ij} \beta$ and the nine quantum numbers $\{n_{ij}\}$ characterise the state of the three atom system. Therefore

$$\kappa = \left[\frac{(1-e^{-\gamma_{ij}})^{9/2}}{(1-e^{-\gamma_{ij}})^{1/2}}\right]^{1/4}$$  \hspace{1cm} (2.7)

and

$$\beta F_1 = \beta E_1 + 3 \log \left\{(1-e^{-\gamma}) P^{q/12}\right\}$$  \hspace{1cm} (2.8)

where

$$E_1 = \frac{3h}{2}(1-3\zeta/4) + qHF/8$$  \hspace{1cm} (2.9)

and

$$P = \frac{\prod_{ij} (1-e^{-\gamma_{ij}})^{9}}{(1-e^{-\gamma})^{9}}$$

Equation (2.9) was also derived in Chapter 5.

The temperature dependent part of the free energy is therefore given by

$$F_1(T) = 3kT \log (1-e^{-\gamma}) P^{q/12}$$  \hspace{1cm} (2.10)

2.3 Anharmonic Energy

As in Chapter 5 we treat the quartic and cubic anharmonic terms occurring in the potential expansion as perturbations on the harmonic energy. The partition function can be expanded in a perturbation series (Maradudin et al., 1961) to give for the free energy

$$-\beta F = -\beta F_0 + (Z_q + Z_c)/Z_0$$  \hspace{1cm} (2.11)

where $F_0$ is the unperturbed harmonic free energy and $Z_q$ and $Z_c$ the quartic and cubic anharmonic perturbations on the unperturbed partition function $Z_0$. 
where $|n\rangle$ stands for the $n^{\text{th}}$ state specified by the $3N$ quantum numbers $\{n\}$ for the $N^{\text{th}}$ particle system. The prime indicates that the term $\{n\} = \{n'\}$ in the summation is to be excluded.

The equations (2.12) and (2.13) have been evaluated in the appendix. The temperature dependent quartic and cubic anharmonic energies are

$$F^{(4)}(T) = \frac{g}{4} \left( \frac{\hbar}{2\pi m} \right)^2 \frac{1}{2} \delta_1 / 8 (F_1 + 2 [G(1,1,1,2) + G(1,1,1,3) + G(1,2,1,3)])$$

$$+ \frac{\delta_2}{12} G_{12} + \frac{\delta_3}{4} (F_2 + 2 [G(2,1,2,2) + G(2,1,2,3) + G(2,2,2,3)])$$

$$+ 2/3 G_{23} F(3q-4)/12$$

(2.14)

$$F^{(3)}(T) = \frac{g^2}{4} \frac{\hbar^2}{(2\pi)^4 m^2} \left\{ \frac{\gamma_1^2}{6} \right\} \left\{ 5f(1,1) + 3 [g(1,1,1,2) + g(1,1,1,3)] \right\}$$

$$+ \frac{\gamma_2^2}{18} \sum_{i=1}^{3} g(1,1,2,1) + 2 [h(1,1,2,2,3) + h(1,2,1,2,3)]$$

$$+ \sum_{i=2}^{3} \sum_{j=2}^{3} h(1,1,2,1,2,3) \right\} \times p^{(3q-4)/12} .$$

(2.15)

The symbols are explained and derivation of (2.14) and (2.15) indicated in the appendix.
Recently Feldman and Horton (1967) have calculated the anharmonic contributions to the free energy of a f.c.c. lattice at the high temperature limit. They used a model based on the assumption of central, nearest-neighbour interactions only and extended the calculations of Maradudin et al. (1961) by including non-leading terms. Feldman and Horton also compared their results with those obtained by other workers who had used different models. Amongst the latter was one based on an approximation first introduced by Bethe (1935) for the Ising model of Ferromagnetism and which has been adapted by Lloyd (1964) for calculating the high temperature limit of the free energy of cubic lattices. The method employed by Lloyd is theoretically applicable to all three cubic lattices and there is good agreement with the results obtained by Feldman and Horton.

It is quite easy to obtain the high temperature limit of the free energy in expression (2.10), (2.14) and (2.15) by letting $T \to \infty$ and expanding the exponentials to the first term in $1/T$. The above formulae then simplify to give

$$F_1(T) = \frac{3}{2\beta} \log \left[ (\beta \nu)^2 q^2 / 6 \right]$$

(2.16)

$$F(4)(T) = \frac{a}{4} (\frac{\nu}{2\pi \epsilon \beta})^{\frac{1}{6}} \left[ \frac{\beta_1 R_1^2}{4} + \frac{\beta_2 R_2^2}{6} + \frac{\beta_3 R_3^2}{6} \right] Q(3q-4)/12$$

(2.17)

$$F(3)(T) = -\frac{a}{4} \frac{\nu^2}{(2\pi)^4 \epsilon^2 \beta^2} \left[ \frac{\gamma_1^2}{6} + 3(\nu_{12}^2 + \nu_{13}^2) \right]$$

$$+ \frac{\gamma_2^2}{2} \left[ \nu_{11} (\nu_{21}^2 + \nu_{22}^2 + \nu_{23}^2 + 4 \nu_{22} \nu_{23}) + 4 \nu_{21} (\nu_{12}^2 + \nu_{13}^2) (\nu_{22}^2 + \nu_{23}^2) \right]$$

$$x \frac{Q(3q-4)}{12}$$

(2.18)
The equation (2.10) was derived using the Bethe approxima-
tions and central, non-nearest neighbour and a-
mation for central, nearest-neighbour/ non-central, all
neighbour interaction was taken into account using the Ein-
stein approximation (c.f. Chapter 5). However non-nearest
neighbour and non-central interactions were included in the
anharmonic energy through the modifications they made to the
harmonic eigenfrequencies $v_{ij}$ only; that is central non-
nearest neighbour anharmonic and non-central anharmonic
interactions were neglected.

2.5 Nearest-Neighbour Interactions

If we make the approximation of central, nearest-neigh-
bour interactions only then the above equations reduce to
a form, displayed in the Table 1 below, which allows comparison
with the results of the other workers.

It can be seen from Table 1 that for the f.c.c. lattice
the harmonic and quartic anharmonic energies are in reason-
ably good agreement with those of Feldman and Horton (1967)
and Lloyd (1964a). However the discrepancy in the cubic
anharmonic terms is disappointing and is considered to be
due to the approximation made to the coupling not being
very good for second order perturbation calculations.

Similar techniques to those used by Lloyd (1964a) for calcu-
lating the cubic anharmonic terms in his classical approach
to the high temperature limit were found not applicable to
the quantum mechanical approach which must be adopted
| Lattice | Harmonic Energy $\frac{3}{2b} \log (\beta^2 \Delta \phi^2 (2) N/m)$ | Quartic Anharmonic Energy $\frac{1}{[\beta^2 \phi^2 (2)]^2} \left[ M_1 \phi^{(4)}(3) + M_2 \phi^{(3)} + M_3 \phi^{(2)}(2) \right]$ | Cubic Anharmonic Energy $\frac{1}{\beta^2 [\phi^2 (2)]^3} \left[ L_1 \phi^{(3)} + L_2 \phi^{(2)} ight]$ |
|---------|-------------------------------------------------|---------------------------------|---------------------------------|
| F.C.C.  | 3.3904                                          | 0.1874                         | 1.0410                          | 1.5327                          | 0.03387                         | 0.6924 |
|         | 3.385\(^a\)                                    | 0.1875\(^a\)                  | 0.9660\(^a\)                   | 0.5910\(^a\)                   | 0.0576\(^a\)                   | 0.399\(^a\) |
|         | 3.375\(^b\)                                    | 0.1875\(^b\)                  | 1.125\(^b\)                   | 1.125\(^b\)                   | 0.0577\(^b\)                   | 0.703\(^b\) |
| B.C.C.  | 1.9738                                          | 0.2942                         | 2.1534                         | 5.5428                         | 0.08645                         | 2.827 |
|         | 2.034\(^b\)                                    | 0.2494\(^b\)                  | 2.124\(^b\)                   | 4.7973\(^b\)                   | 0.1141\(^b\)                   | 2.996\(^b\) |
| S.C.    | 1.1782                                          | 0.4513                         | 5.4048                         | 29.64                          | 0.1947                         | 11.926 |
|         | 1.4142\(^c\)                                    | 0.375\(^c\)                   |                                 |                               | 0.2500\(^c\)                   |         |


The energies are characterised by the numbers $L_1$, $M_1$ and $N$ and the derivatives are to be evaluated at the nearest-neighbour distance $R_v$.

Table 1. The Free Energy of the Three Cubic Lattices at the High Temperature Limit Assuming Central, Nearest-Neighbour Interactions Only
for finite temperatures.

No results are given for the $\mathcal{C}_c$ lattice calculated using the classical approach of Lloyd because that method fails to give a realistic answer for this lattice. Thus in the equation given by Lloyd (1964a) for determining the effective force constant $x_1$, if we assume central, nearest-neighbour interactions and put $\alpha_2=0$, $q=6$ we find $x_1=0$. A physically unrealistic and unacceptable result. We also wish to point out that the number $N$ given by Lloyd for the b.c.c. lattice as 2.46 should in fact be 2.034 as in Table 1.

2.6 Summary

To summarise, we have developed the Bethe approximation to enable the zero point energy and the free energy at finite temperatures to be calculated. Results have been given for and comparisons made with those of other authors for the zero point energy (Chapter 5) and in the present chapter for the high temperature limit. In both cases the harmonic and quartic anharmonic energies are in good agreement with calculations made using standard lattice dynamics. However, the accuracy of the cubic anharmonic energy is not so good.

APPENDIX

We substitute for $v^{(4)}$ and $v^{(3)}$ from equation (2.4) of Chapter 5 into equations (2.12) and (2.13) respectively. For the harmonic oscillator with eigenfrequency $\nu_1$

$$|\ell> = (\frac{\alpha_1}{2^{\ell+1}\sqrt{\pi}})^{\frac{\ell}{2}} e^{-\frac{\alpha_2}{2}\nu_1^2x^2} H_\ell(\alpha_1x), \quad \alpha_2 = 2\pi m v / \hbar.$$
We can write down the following useful relations

\[ <\ell | x^4 | \ell> = \frac{3}{4}\alpha_1^4(2\ell^2+2\ell+1) \]  
(A.1)

\[ <\ell_m | x^2y^2 | \ell_m> = (\alpha_1\alpha_2)^{-2}(\ell+\frac{1}{2})(m+\frac{1}{2}) \]  
(A.2)

\[ \sum_{\ell\neq\ell'} \frac{<\ell | x^3 | \ell'> <\ell' | x^3 | \ell>}{(E_\ell,E_{\ell'})} = \frac{1}{8}(30\ell^2+30\ell+11)(\alpha_1\alpha_2)^{-1} \]  
(A.3)

\[ \sum_{\ell\neq\ell',\ m\neq\ell\ m'} <\ell_m | x^2y | \ell_m>n' > <\ell_m'n | x^2y | \ell_m> \]  

\[ = -\frac{\alpha_1^{-4}\alpha_2^{-2}}{(4\nu_1^2-\nu_2^2)\hbar} \left[ 4\nu_1(2\ell m+\ell m+\frac{1}{2})-\nu_2(\ell^2+\ell+1) \right] \]  
(A.4)

\[ \sum_{\ell\neq\ell', m\neq\ell\ m'} <\ell mn | xyz | \ell_m'n'n'> <\ell_m'n'n | xyz | \ell mn> \]  

\[ = -\alpha_1^{-2}\alpha_2^{-2}\alpha_3^{-2} \left[ \frac{1}{(v_1+v_2+v_3)\hbar} + \frac{(\ell_1 m+n-n-\ell m)}{(v_1-v_2+v_3)^{\hbar}} \right] \]  
+ \frac{(\ell_1 m+n-n-\ell m)}{(v_1-v_2+v_3)\hbar} \]  
(A.5)

Also

\[ \sum_{\{n_{ij}\}} e^{-M} = N \]  
(A.6)

\[ \sum_{\{n_{ij}\}} n_{k\ell} e^{-M} = e^{-Y_{k\ell}(1-e^{-Y_{k\ell}})-1}N \]  
(A.7)

\[ \sum_{\{n_{ij}\}} n_{k\ell}^2 e^{-M} = e^{-Y_{k\ell}(1-e^{-Y_{k\ell}})-1}(1+2e^{-Y_{k\ell}(1-e^{-Y_{k\ell}})}) \]  
\times N \]  
(A.8)

where \( M = \sum_{ij} n_{ij} Y_{ij} \), \( N = \prod_{ij} (1-e^{-Y_{ij}})^{-1} \)

and \( n_{k\ell} \) is one of the set of quantum numbers \( \{n_{ij}\} \). To obtain the one particle free energy we have to evaluate such terms as \( Z_q/Z_0 \) (equation 2.11).
For the three particle system we recognise that

$$Z_0(3\text{-part}) = Z_0^{3\kappa}(3q-4) = N^{(3q-4)/4}. $$

Therefore

$$Z_0(1\text{-part}) = \sqrt[3]{N^{(3q-4)/4}}. $$

Now $Z_0(3\text{-part})$ involves terms such as $A.6$, $A.7$ and $A.8$. To reduce it to a one-particle partition function it is necessary to reduce $N$ from a term associated with the three particle system to a one particle term. This procedure is done by cube rooting it. Thus the anharmonic free energy will contain terms such as

$$e^{-\gamma_{k\ell}(1-e^{-\gamma_{k\ell}}) - \frac{1}{N^{1/3}}(3q-4)/12}.$$ 

Using the above equations combined with equations (2.11), (2.12) and (2.13) we finally arrive after some manipulations with equations (2.14) and (2.15) where we have defined the functions

$$f(i,j) = \frac{q_{i,j}^3}{\gamma_{i,j}}(v_{i,j} +w_{i,j}),$$

$$g(i,j,k,\ell) = \frac{q_{i,j}q_{k\ell}^2}{(4\gamma_{k\ell} + \gamma_{i,j})^2} \left[ 4\gamma_{k\ell}(2v_{i,j}v_{k\ell} + w_{i,j} + w_{k\ell}) - w_{i,j}(v_{k\ell} + w_{k\ell}) \right],$$

$$h(i,j,k,\ell,m,n) = q_{i,j}q_{k\ell}q_{m,n} \left[ (v_{i,j} + w_{i,j} + w_{k\ell} + v_{k\ell} + v_{m,n} + w_{i,j} + w_{k\ell} + w_{m,n}) \right],$$

$$+ \frac{(v_{i,j} + w_{i,j} + w_{k\ell} + v_{k\ell} + v_{m,n} + w_{i,j} + w_{k\ell} + w_{m,n})}{(v_{i,j} + v_{k\ell} + v_{m,n})},$$

$$+ \frac{(v_{i,j} + w_{i,j} + w_{k\ell} + v_{k\ell} + v_{m,n} + w_{i,j} + w_{k\ell} + w_{m,n})}{(-v_{i,j} + v_{k\ell} + v_{m,n})},$$

$$+ \frac{(v_{i,j} + w_{i,j} + w_{k\ell} + v_{k\ell} + v_{m,n} + w_{i,j} + w_{k\ell} + w_{m,n})}{(-v_{i,j} + v_{k\ell} + v_{m,n})},$$

$$+ \frac{(v_{i,j} + w_{i,j} + w_{k\ell} + v_{k\ell} + v_{m,n} + w_{i,j} + w_{k\ell} + w_{m,n})}{(v_{i,j} + v_{k\ell} + v_{m,n})},$$

$$+ \frac{(v_{i,j} + w_{i,j} + w_{k\ell} + v_{k\ell} + v_{m,n} + w_{i,j} + w_{k\ell} + w_{m,n})}{(-v_{i,j} + v_{k\ell} + v_{m,n})},$$

$$+ \frac{(v_{i,j} + w_{i,j} + w_{k\ell} + v_{k\ell} + v_{m,n} + w_{i,j} + w_{k\ell} + w_{m,n})}{(v_{i,j} + v_{k\ell} + v_{m,n})},$$

$$+ \frac{(v_{i,j} + w_{i,j} + w_{k\ell} + v_{k\ell} + v_{m,n} + w_{i,j} + w_{k\ell} + w_{m,n})}{(-v_{i,j} + v_{k\ell} + v_{m,n})}. $$
\[ F(i,j) = a_{ij}^2(x_{ij} + x_{ij}), \]
\[ G(i,j,k,\ell) = a_{ij}a_{k\ell}(2x_{ij}x_{k\ell} + x_{ij} + x_{k\ell}) \]
and
\[ F_i = \sum_{j=1}^{3} F(i,j), \]
\[ G_{ij} = \sum_{k=1}^{3} \sum_{\ell=1}^{3} G(i,j,k,\ell); \]
also \( x_{ij} = e^{-y_{ij}(1-e^{-y_{ij}})^{-1}}, \)
\( y_{ij} = x_{ij}(1+2x_{ij}). \)

In the high temperature limit, letting \( T \to \infty \), the above functions simplify to give

\[ f(i,j) \xrightarrow{T \to \infty} \frac{2a_{ij}^3}{y_{ij}^2}, \]
\[ g(i,j,k,\ell) \xrightarrow{T \to \infty} \frac{2a_{ij}a_{k\ell}}{y_{k\ell}^2 y_{ij}^2}, \]
\[ h(i,j,k,\ell,m,n) \xrightarrow{T \to \infty} \frac{8a_{ij}a_{k\ell}a_{mn}}{y_{ij}^2 y_{k\ell}^2 y_{mn}^2}, \]
\[ F(i,j) \xrightarrow{T \to \infty} \frac{2a_{ij}^2}{y_{ij}^2}, \]
\[ G(i,j,k,\ell) \xrightarrow{T \to \infty} \frac{2a_{ij}a_{k\ell}}{y_{ij}^2 y_{k\ell}^2}, \]

and after some algebra we have equations (2.17) and (2.18).
CHAPTER 7

CALCULATIONS AT 0°K AND CONCLUSIONS

1. Calculations

It is possible using the expression derived in Chapter 5 for the zero point vibrational energy to calculate the bulk moduli of the inert gas solids at 0°K. The bulk modulus, \( K \), is given by the thermodynamic relation

\[
K = V \left( \frac{\partial^2 F_0}{\partial V^2} \right)_{T=0}
\]

where \( F_0 \) is the total vibrational energy at \( T=0 \) plus the static lattice energy. The right hand side of equation (1.1) was evaluated at the experimental volume determined at 0°K.

In the calculations a Lennard-Jones (12,6) potential was used to represent the pairwise, additive interactions between atoms. Three sets of calculations were performed for each of the inert gas solids Ne, A, kr., and Xe. As in Chapters 3, 4, and 5 two sets of potential parameters labelled (a) and (b) and given by Zucker (1968) were employed (see table 2, Chapter 3). Parameters (a) were derived neglecting the three-body static lattice energy while parameters (b) were calculated with it included in the free energy at \( T=0°K \).

Using parameters (a) the bulk moduli were determined for a nearest-neighbour and then for an all neighbour model assuming two-body interactions only and using the expressions derived for the zero point energy in Chapter 5. The third calculation was made using an all-neighbour model but this
time parameters (b) were used and the three-body potential function of Axilrod and Teller (1943) was included in the static lattice energy and the harmonic zero point vibrational energy (see Chapter 3 and 5). The theoretical results together with the experimental ones are displayed in table 1 below.

From the table it can be seen that the three-body forces have very little effect on the bulk moduli of the inert gas solids. This is in accord with the calculations made in Chapter 4. Both sets of all neighbour results are in excellent agreement with experiment except for krypton. The inclusion of anharmonicity obviously removes the discrepancy between theory and experiment which was obtained using the quasi-harmonic theory. This result was also observed by Brown and Horton (1967).

2. Conclusion

In the preceding chapters we have investigated the contributions of a long-range non-central three-body force to the static lattice energy, zero point vibrational energy and some thermoelastic properties of the inert gas solids Ne, A, kr and Xe. We have shown that if such a force exists in the inert gas solids then theoretically its effects cannot be ignored, especially in calculating anisotropic crystal properties such as the elastic constants. Further it has been demonstrated that the three-body force must be included in an all neighbour model of a crystal for accurate estimations of its effects.
SUBSTANCE

<table>
<thead>
<tr>
<th>MODEL</th>
<th>NEON</th>
<th>ARGON</th>
<th>KRYPTON</th>
<th>XENON</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) 1.01</td>
<td>2.60</td>
<td>3.20</td>
<td>3.62</td>
<td></td>
</tr>
<tr>
<td>(ii) 1.13</td>
<td>2.67</td>
<td>3.25</td>
<td>3.66</td>
<td></td>
</tr>
<tr>
<td>(iii) 1.15</td>
<td>2.66</td>
<td>3.23</td>
<td>3.62</td>
<td></td>
</tr>
</tbody>
</table>

EXPERIMENTAL 1.12±0.03 2.67±0.04 3.44±0.04 3.6±0.1

(i) Nearest-neighbour model, parameters (a)
(ii) All neighbour model with two-body forces only and parameters (a).
(iii) All neighbour model with two and three-body forces and parameters (b)

The experimental results were obtained from Batchelder et. al. (1967) for neon; Peterson et. al. (1967) for argon; Urvas et. al. (1967) for krypton; Packard and Swenson (1963) for xenon.

units: $10^{10}$ dynes cm$^{-2}$

Table 1. Theoretical and Experimental Bulk Moduli.
We have also shown how the Bethe (1935) approximation as used by Lloyd (1964a) for calculating the high temperature limit of the free energy of cubic crystals may be developed and extended to enable an analytical expression for the free energy at finite temperatures to be derived. Making the approximation of central, nearest neighbour interactions only between atoms the accuracy of the expression has been assessed at 0°k and in the high temperature limit. It has been shown how by using the Einstein approximation to represent central, non-nearest neighbour and non-central, all neighbour interactions these may be included in the theory up to the harmonic energy term explicitly and indirectly, through their effects on the harmonic eigenfrequencies, in the anharmonic energy terms. Thus a theory has been developed which enables non-central forces to be simply included in it.

Several suggestions for the extension of the present work suggest themselves. It is possible to take into account coupling, not only between nearest-neighbours but also between next-nearest and even further neighbour interactions in the quasi-harmonic approximation. This might be achieved using the following procedure. Initially next-nearest neighbours with respect to an origin atom are assumed to be at rest on their lattice sites (i.e. treated in the Einstein approximation) but to interact with the origin atom through unknown effective force constants. The nearest-neighbour atoms are treated as previously and consistency relations are derived involving not only the unknown nearest-neighbour
force constants but also the unknown next nearest-neighbour ones. The next step is to treat a similar system but this time the nearest-neighbour atoms are assumed to be at rest on their lattice sites while the three-coupled particle system is now treated as being composed of the origin atom and two atoms from the shell of next nearest-neighbours. Neighbours beyond the next-nearest are treated in the Einstein approximation and are assumed to interact through known force constants. The second stage then leads to a second set of consistency relations which when combined with the first will enable the unknown force constants to be determined. The theory can be further extended to include a crystal where nearest neighbours have different masses.

The anharmonic perturbing energy of higher order terms occurring in the expression of the potential energy, such as the quartic and sextic terms, might also be determined to provide a check on the convergence of the perturbation expansion. However terms determined using second and higher order perturbation theory must be treated with caution as the theory appears to be less accurate for such calculations.

Calculations of more thermodynamic quantities might be made using the finite temperature expression for the free energy. This would provide a more rigorous test of the crystal model employed. Further an expression for the temperature dependence of the elastic constants might be derived by developing the work of Lloyd (1964b) and using the quantum mechanical methods outlined in this thesis. The energy due to the strain would be treated as a further perturbation on
the unstrained harmonic energy. Using the techniques already employed in the present work a non-central force could be included in the calculations and its effects assessed. Thus the present work reveals many avenues where further research might be continued.
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Anharmonic contributions to the zero-point vibrational energy of cubic lattices

Abstract. The quartic anharmonic zero-point vibrational energies of the three cubic lattices are calculated using an approximation first introduced by Bethe. The results are in good agreement with those obtained by standard lattice dynamical methods.

Several methods have been used to evaluate the zero-point vibrational energy of cubic lattices. Domb and Salter (1952) and Isenberg (1963) employed methods based on the evaluation of the frequency moments to calculate the harmonic contribution only, whereas by performing numerical summations over the wave numbers Maradudin and Flinn (1963) and Maradudin et al. (1961) calculated also the anharmonic contributions to the face-centred and simple cubic† lattices respectively. However, they made the leading term approximation, i.e. neglected terms such as $\phi^{(n-1)}/a$ compared with $\phi^{(n)}$, where $\phi^{(n)}$ is the $n$th derivative of the pair potential function and $a$ the nearest-neighbour

† These are derivable from their linear chain results by multiplication by 3.
distance. Both Lloyd (1964) and Barron and Klein (1965) have shown that this is in error and that the terms neglected are of the order of the effect studied.

We are at present engaged in calculating the anharmonic contribution to the zero-point vibrational energy using an approximation introduced by Bethe (1935) and which was successfully adapted by Lloyd to calculating the high-temperature anharmonic contribution to the free energy of cubic lattices. The method has the advantage not only of simplicity when compared, say, with the calculations of Maradudin and Flinn but also the added advantage in that the leading term approximation need not be made.

If the potential function of the displaced atoms is expanded about the equilibrium positions of the lattice, then the resulting expression for a two-body particle model, with a mean or effective potential replacing the interactions between the two coupled atoms and their nearest neighbours, can be solved for the two-particle Schrödinger equation, in the harmonic approximation, for the two-particle wave function. A consistency relationship then allows the unknown parameters in the effective potentials to be determined (cf. Lloyd 1964) and hence the harmonic zero-point energy of the system to be calculated. Application of perturbation theory then yields the anharmonic zero-point energy of the system.

So far the harmonic and quartic anharmonic contributions have been calculated for the three cubic lattices. Some results are shown (in the table) below with the leading term approximation made so that comparison may be made with the work of Maradudin and Flinn, and Maradudin et al.

### Zero-point vibrational energy

<table>
<thead>
<tr>
<th>Lattice</th>
<th>Harmonic energy $\frac{\hbar (\phi^{(2)})^{1/2}}{m^{1/2}}$</th>
<th>Quartic energy $\frac{\hbar^2 \phi^{(4)}}{m \phi^{(2)}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>simple cubic</td>
<td>1.90986$^a$</td>
<td>1.8238$^a$</td>
</tr>
<tr>
<td></td>
<td>1.9316$^b$</td>
<td>1.8640$^b$</td>
</tr>
<tr>
<td>body-centred cubic</td>
<td>2.2992$^e$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.3013$^b$</td>
<td>1.4902$^b$</td>
</tr>
<tr>
<td>face-centred cubic</td>
<td>2.89249$^d$</td>
<td>1.0458$^c$</td>
</tr>
<tr>
<td></td>
<td>2.89031$^e$</td>
<td>1.0442$^b$</td>
</tr>
</tbody>
</table>

$\phi^{(n)}$ is the $n$th derivative of the potential function $\phi$, $\hbar$ is Planck’s constant divided by $2\pi$ and $m$ the atomic mass.

$^a$, Maradudin et al. 1961; $^b$, Chell, present paper; $^c$, Domb and Salter 1952; $^d$, Isenberg 1963; $^e$, Maradudin and Flinn 1963.

Owing to the nature of the Bethe approximation one would expect the accuracy of the results to increase with the co-ordination number. In fact, the table shows that, while the face-centred cubic harmonic zero-point energy differs from Maradudin and Flinn’s result by approximately 0.8%, for the simple cubic lattice the discrepancy is
just over 1%. The quartic anharmonic contribution calculated agrees nearly exactly with Maradudin and Flinn for the face-centred cubic lattice and still shows remarkable good agreement for the simple cubic lattice.

The cubic anharmonic terms are at present under consideration and we hope to have results for these terms in the near future.

The author wishes to thank Dr. I. J. Zucker for many helpful discussions, and the Science Research Council for a research grant.

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26th January 1967

G. G. Chell
The effect of long-range three-body forces on the zero-point energy of the inert gas solids

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MS. received 18th September 1967

Abstract. The contributions to the zero-point vibrational and static lattice energies from a long-range three-body interaction potential of the form given by Axilrod and Teller are calculated for neon, argon, krypton and xenon. It is shown that for the last three the contribution to the vibrational energy is of the same order as the two-body anharmonic contribution and of opposite sign.

1. The three-body static lattice energy

It has now been recognized (Coulson 1965) that three-body forces are of considerable importance in the solid state of the rare gases. Axilrod and Teller (1943) first gave explicitly an expression for the triple-dipole interaction of a triplet of atoms at the vertices of a triangle of sides \( R_{ij}, R_{jk} \) and \( R_{kj} \) with interior angles \( \theta_i, \theta_j, \theta_k \). Their expression is

\[
V^{(3)} = \frac{\nu (3 \cos \theta_i \cos \theta_j \cos \theta_k + 1)}{R_{ij}^6 R_{jk}^6 R_{ki}^6}
\]

which may be rewritten as

\[
V^{(3)} = \frac{\nu (3 C_{ij} C_{jk} C_{ki} + 8 R_{ij}^2 R_{jk}^2 R_{ki}^2)}{8 R_{ij}^6 R_{jk}^6 R_{ki}^6}
\]

where \( C_{ij} = R_{jk}^2 + R_{ki}^2 - R_{ij}^2 \).

This contribution to the triplet interaction arises from the same sources which produce the long-range two-body van der Waals interactions. Jansen (1964) has made several calculations on the short-range exchange triplet interaction. Recently Swenberg (1967) cast some doubts on the validity of an approximation that Jansen made in his calculations. Owing to the uncertainty still surrounding short-range three-body interactions we shall only consider the long-range interactions. Although higher-order long-range triplet interactions such as the dipole–dipole–quadrupole force have been evaluated (Ayres and Tredgold 1956) we shall also neglect these, considering them to be of a lower order than the triple–dipole force. Hence we shall only consider (1.1) as representing the three-body interaction.

The coefficient \( \nu \) in (1.1) was evaluated by Axilrod (1949) and given as \( 9 I \alpha^2 / 16 \), where \( I \) is the ionization potential and \( \alpha \) the polarizability of the given atom. Bell and Kingston (1966) recently calculated \( \nu \) from first principles with an accuracy said to be of order 10%. Within this limit their values agree with Axilrod's and we use them here. Axilrod (1951) further calculated the contribution to the static lattice energy due to triplet interactions for the face-centred cubic and hexagonal close-packed lattices. He did this by direct summation over all triplet interactions of a given atom out to about four nearest-neighbour distances. His result for the triplet static lattice energy \( \Phi(3L) \) for a face-centred cubic lattice is

\[
\Phi(3L) = \frac{N}{3} \times \nu \times \frac{56.7}{R_0^6}
\]

where \( R_0 \) is the nearest-neighbour distance. He also gave the lattice sum for nearest-neighbour triplets as 14-7113. We have recalculated this and find that the number given is wrong and should be 35-1653. We further extended the summation over all triplet interactions out to about ten nearest-neighbour distances and obtained the result 57-41. From a plot of the partial sums against the reciprocal of the nearest-neighbour distance the sum to
infinity was estimated to be $57.60 \pm 0.05$. It is therefore clear that with the triplet interaction nearest neighbours provide only 60% of the lattice interaction. Thus non-nearest neighbours are just as important and must be included in any calculation.

The contribution to the lattice energy at $T = 0$ due to triplet interactions is easily evaluated from (1.2) using values for $\nu$ given by Bell and Kingston (1966). These are given in table 1 together with the experimental heat of sublimation.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$H_0$ (cal mole$^{-1}$)</th>
<th>$R_0$ ($\AA$)</th>
<th>$\nu$</th>
<th>$\Phi(3L)$ (cal mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>neon</td>
<td>448</td>
<td>3.1563</td>
<td>1.677</td>
<td>14.68</td>
</tr>
<tr>
<td>argon</td>
<td>1846</td>
<td>3.7549</td>
<td>74.48</td>
<td>136.6</td>
</tr>
<tr>
<td>krypton</td>
<td>2666</td>
<td>3.9910</td>
<td>223.7</td>
<td>236.9</td>
</tr>
<tr>
<td>xenon</td>
<td>3828</td>
<td>4.3356</td>
<td>749.0</td>
<td>376.6</td>
</tr>
</tbody>
</table>

$\nu$ is given in erg ($\AA)^9 \times 10^{12}$ and derived from values given by Bell and Kingston (1966).

Experimental values for $H_0$ and $R_0$ obtained from Pollack (1964).

It is apparent from these values that even the long-range triplet interactions are of considerable importance. It is very difficult to measure $\Phi(3L)$ experimentally as it is hard to isolate the two-body lattice energy $\Phi(2L)$. Only one experimental result, obtained by Losee and Simmons (1967) for krypton by measurements of vacancy concentrations, is as yet known. The difficulty of the experiment is illustrated by the result given for the many-body interactions of krypton as $650 \pm 300$ cal mole$^{-1}$. Further the experiment cannot distinguish amongst the various possibilities of the origin of three-body and higher-order forces or give their relative importance. However, it clearly gives evidence of the importance of many-body interactions and it is reasonable to assume that triplet interactions are the most important of these.

2. The zero-point vibrational energy

Goetze and Schmidt (1966) first made a calculation on the effect of triplet interactions on the zero-point energy and other properties of argon. In this section we extend their work and give explicit formulae for the zero-point energy. We also include results for the other inert gas solids. Following Goetze and Schmidt we employ an Einstein model of a crystal and evaluate the harmonic contribution to the zero-point energy. This model is used for the following reasons. Although exact expressions have been given for the harmonic zero-point energy of a face-centred cubic lattice by Domb and Salter (1952) and Isenberg (1963), only nearest-neighbour interactions were considered. This is a reasonable approximation for two-body forces but, as already demonstrated in the static lattice energy calculation, it is a very bad approximation for triplet interactions. With the Einstein model the calculation may be done including all neighbour interactions, and even for two-body forces the error in ignoring non-nearest-neighbour interactions is at least as great as that of the Einstein approximation for the nearest-neighbour interactions.

The Einstein model considers the vibration of one atom of the crystal moving in a potential produced by all the others at rest in their equilibrium positions. In the appendix we calculate the potential energy of a typical atom due to its displacement $\rho$ from its lattice position; up to the quadratic term in $\rho$ this is

$$K = \frac{1}{2}(P_2 + 2T_2)\rho^2$$

where

$$P_2 = \sum_{\text{pairs}} \left( \phi'' \frac{2}{R_{ij}} \phi' \right)$$

$$T_2 = \sum_{\text{triplets}} \left( V''''(\rho) + \frac{2}{R_{ij}} V''(\rho) \right)$$

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G. G. Chell and I. J. Zucker
Long-range three-body forces in inert gas solids

The pair potential, and primes indicate differentiation with respect to \( R_{ij} \). Putting the potential energy \( K \) in the Schrödinger equation for a typical atom the harmonic zero-point energy may be written down immediately:

\[
\Phi^H(2Z + 3Z) = \frac{3}{2} \hbar \left( \frac{P_2 + 2T_2}{3m} \right)^{1/2}. \tag{2.2}
\]

With no three-body forces \( T_2 \) is zero and

\[
\Phi^H(2Z) = \frac{3}{2} \hbar \left( \frac{P_2}{3m} \right)^{1/2}. \tag{2.3}
\]

For the face-centred cubic lattice with only nearest-neighbour interactions and neglecting \( \phi' / R \) compared with \( \phi'' \), \( P_2 = 12\phi'' \) and \( \Phi^H(2Z) = 1.061\hbar(8\phi'' / m)^{1/2} \). The exact result in these circumstances is \( 1.0227\hbar(8\phi'' / m)^{1/2} \), so that the Einstein result is only \( 3.5\% \) different. However, we shall not neglect \( \phi' / R \) and include all neighbour interactions in our calculations.

For the two-body potential \( \phi \) we shall assume a Lennard-Jones 12-6 potential as typical. This may be written

\[
\phi(R) = 4\epsilon \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^{6}. \tag{2.4}
\]

The parameter \( \epsilon \) is the depth of the potential at the minimum and \( \sigma \) is the distance at which \( \phi(R) \) equals zero. These parameters have been calculated elsewhere (Zucker 1967), using the experimental heat of sublimation \( H_0 \) and the nearest-neighbour distance, both at \( T = 0 \). These two sets of parameters were calculated for each element: in the first case only two-body interactions are considered and then the free energy at \( T = 0 \), \( F_0 \), is given by

\[
F_0 = -H_0 = \Phi(2L) + \Phi(2Z)
\]

where \( \Phi(2Z) \) is the total zero-point energy, including both harmonic and anharmonic terms: in the second case the static triplet lattice energy is included, that is it is assumed that

\[
F_0 = \Phi(2L) + \Phi(2Z) + \Phi(3L).
\]

It should be noted that \( \Phi(3Z) \) has not been included, as it has a negligible effect on the pair potential parameters. The effect of \( \Phi(3L) \) is, however, considerable and both sets of parameters for each element have been given in table 2.

**Table 2. Parameters of \( 4\epsilon(\sigma/R)^{12} - (\sigma/R)^6 \)**

<table>
<thead>
<tr>
<th>Gas</th>
<th>( \epsilon / k )</th>
<th>( \sigma (\AA) )</th>
<th>( \Lambda^* )</th>
<th>( N_\epsilon ) (cal mole(^{-1}))</th>
<th>( \nu^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>neon</td>
<td>(a) 36.46</td>
<td>2.776</td>
<td>0.5809</td>
<td>72.48</td>
<td>0.03401</td>
</tr>
<tr>
<td></td>
<td>(b) 37.54</td>
<td>2.765</td>
<td>0.5749</td>
<td>74.63</td>
<td>0.03429</td>
</tr>
<tr>
<td>argon</td>
<td>(a) 119.4</td>
<td>3.400</td>
<td>0.1864</td>
<td>237.4</td>
<td>0.07438</td>
</tr>
<tr>
<td></td>
<td>(b) 128.3</td>
<td>3.368</td>
<td>0.1815</td>
<td>255.1</td>
<td>0.07535</td>
</tr>
<tr>
<td>krypton</td>
<td>(a) 164.7</td>
<td>3.635</td>
<td>0.1025</td>
<td>327.4</td>
<td>0.08872</td>
</tr>
<tr>
<td></td>
<td>(b) 179.8</td>
<td>3.595</td>
<td>0.0992</td>
<td>357.4</td>
<td>0.08997</td>
</tr>
<tr>
<td>xenon</td>
<td>(a) 231.5</td>
<td>3.960</td>
<td>0.06340</td>
<td>460.1</td>
<td>0.09791</td>
</tr>
<tr>
<td></td>
<td>(b) 255.3</td>
<td>3.911</td>
<td>0.06113</td>
<td>507.4</td>
<td>0.09934</td>
</tr>
</tbody>
</table>

(a) \( \Phi(3L) \) not included; (b) \( \Phi(3L) \) included.

For the 12-6 potential and a face-centred cubic lattice,

\[
P_2 = 4\epsilon \sum_{i \neq f} \left( 132 \frac{\sigma^{12}}{R_{ij}^{14}} - 30 \frac{\sigma^6}{R_{ij}^8} \right)
\]

\[
= 4\epsilon \left( 1591.9 \frac{\sigma^{12}}{R_0^{14}} - 384 \frac{\sigma^6}{R_0^8} \right). \tag{2.5}
\]
The triplet term $T_2$ may also be found explicitly from

$$T_2 = \nu \sum_{t \neq j \neq k} \left\{ \frac{20}{R_{ij}} \left( \frac{73(C_{ij}C_{jk} + C_{jk}C_{ki} - C_{ki}C_{ij}) + 8R_{jk}^2R_{ki}^2}{R_{ij}^3R_{jk}^5R_{ki}^5} + 3(C_{ij} - C_{jk} - C_{ki}) \right) \right\}$$

which gives

$$T_2 = -567 \frac{\nu}{R_0^{11}}.$$  \hspace{1cm} (2.6)

The importance of non-nearest neighbours in the sum over triplets for $T_2$ is made very clear when it is noted that the nearest-neighbour contribution to the lattice sum of $-567$ is only $-92.5$. Even at five nearest-neighbour distances the triplet sum for $T_2$ is only $-538.4$, and at ten nearest-neighbour distances $-561.9$. Extrapolation as before suggested the sum to infinity to be $-567 \pm 1$.

For the purposes of calculation it was convenient to introduce the reduced notation

$$R^* = \frac{R}{\sigma}, \quad \Lambda^* = \frac{\hbar}{\sigma(\alpha e)^{1/2}}, \quad \Phi^* = \frac{\Phi}{N\varepsilon}, \quad \nu^* = \frac{\nu}{\sigma^2 \varepsilon}.$$ 

In this notation the zero-point energy of a crystal of $N$ atoms becomes

$$\Phi^*_{\text{zh}}(2Z + 3Z) = \frac{3\Lambda^*}{4\pi R_0^7} \left( 2122.56 - 512.08 R_0^6 - 378\nu^* R_0^3 \right)^{1/2}. \hspace{1cm} (2.7)$$

The zero-point energy at $T = 0$ was then calculated both with and without the triplet contribution and for both sets of potential parameters for each gas. These results have been given in table 3 together with the contribution to the zero-point energy due to anharmonicity calculated using only the pair potential with an Einstein model. The latter is incorrect for calculating the anharmonic contribution but for consistency we calculate it this way, and the order of magnitude is correct.

| Gas     | $\Phi^*_{\text{zh}}(2Z)$ | $\Phi^*_{\text{zh}}(2Z + 3Z)$ | $|\Phi^*_{\text{zh}}(3Z)|$ | $\Phi^*_{\text{an}}(2Z)$ |
|---------|--------------------------|-----------------------------|-------------------------|----------------------|
| neon    | 130.6                    | 129.3                      | 1.3                     | 14.4                 |
|         | (a)                      | 127.4                      | 1.2                     | 14.7                 |
|         | (b)                      | 126.2                      | 2.9                     | 4.5                  |
| argon   | 182.3                    | 179.4                      | 3.0                     | 4.7                  |
|         | (a)                      | 174.4                      | 2.9                     | —                    |
|         | (b)                      | 176.4                      | 3.0                     | —                    |
| krypton | 145.9                    | 143.3                      | 2.6                     | 1.9                  |
|         | (a)                      | 138.7                      | 2.7                     | 1.9                  |
|         | (b)                      | 138.7                      | 2.7                     | —                    |
| xenon   | 130.0                    | 127.5                      | 2.7                     | 1.0                  |
|         | (a)                      | 123.1                      | 2.7                     | 1.0                  |
|         | (b)                      | 120.4                      | —                       | —                    |

(a) Calculated from parameters (a) in table 2; (b) calculated from parameters (b) in table 2; (c) calculated for the potential of Guggenheim and McGlashan (1960 a, b).

All values are in cal mole$^{-1}$.

3. Discussion

It is evident that the inclusion of triplet interactions reduces the zero-point energy. This was also found by Goetze and Schmidt (1966) who find that the Einstein frequency is lowered by three-body forces. In the case of neon the change is small and negligible compared with the anharmonic term. This is because the triplet interaction coefficient $\nu$ for neon is relatively smaller than for the other elements, and the anharmonicity of neon is relatively larger. But for Ar, Kr and Xe the effect of the triplet interaction is at least of the same order as the anharmonic term.
The choice of a given pair potential although affecting the absolute value of the total harmonic zero-point energy has very little effect on $|\Phi^0(3Z)|$. This is illustrated by using the pair potential suggested by Guggenheim and McGlashan (1960 a, b) for the inert gases. These authors are opposed to the Lennard-Jones 12–6 potential and give one entirely different. It is not possible to calculate $P_2$ completely for their potential since the part involving non-nearest neighbours is drawn in by hand. However, we have computed the zero-point energy at $T = 0$ for argon and krypton from the formula given for the Einstein frequency obtained from the analytic portion of their potential. This is

$$
\nu_b^2 = \frac{6}{\pi^2 m R_{\text{min}}^2} \left( \frac{1}{3} K(1 + \Delta)^{-1}(1 + 3\Delta) - \alpha \Delta(1 + \Delta)^{-1}(1 + 2\Delta) + 2\beta \Delta^2(1 + \Delta)^{-1}\left( \frac{5}{3} - \frac{5}{12} 0.802(1 + \Delta)^{-\frac{5}{3}} \right) \right)
$$

where

$$
\Delta = \frac{R_o - R_{\text{min}}}{R_{\text{min}}}
$$

$R_{\text{min}}, K, \alpha, \beta$ and $\lambda$ are given parameters and we have used the latest values of McGlashan (1965) for argon. The triplet interaction modifies $\nu_b$ to a new frequency $\nu_b'$ given by

$$
(\nu_b')^2 = \nu_b^2 + \frac{2T_2}{12\pi^2 m}.
$$

The zero-point energy is then given by $3Nh_\nu_b'/2$ and the values calculated from (3.2) both with and without the triplet contribution are also given in table 3. As may be seen $|\Phi^0(3Z)|$ is virtually unchanged.

In conclusion it appears that the effect of triplet interactions on the zero-point vibrational energy is independent of the pair potential. The size of the effect in neon is small but in argon, krypton and xenon it is of the same order as the anharmonic pair potential term but of opposite sign. If other three-body terms are of importance—Jansen (1964) believes the short-range terms to be similar to that of the Axilrod and Teller formula but considerably larger—then not only must the triplet lattice energy be included in any solid state calculation, but also the triplet zero-point contributions as well.

Acknowledgments

One of us (G.G.C.) is indebted to the Science Research Council for a research grant.

Appendix. The potential energy of a particle displaced from its lattice site

Pair interactions

Let us consider a typical lattice point as the origin of a coordinate system (figure 1). Let $\rho$ be the displacement of an atom from this point. The potential energy of the displaced atom with all the others at rest on their lattice points due to pair-wise interactions is

$$
\sum_{i \neq j} \phi(|\mathbf{R}_{ij} - \mathbf{\rho}|).
$$

Expanding as a Taylor series up to $\rho^2$ we have

$$
K \text{(two-body)} = \sum_{i \neq j} \phi(|\mathbf{R}_{ij}|) - \mathbf{\rho} \cdot \mathbf{R}_{ij} \frac{\phi'}{\mathbf{R}_{ij}} + \frac{1}{2} \left[ \mathbf{\rho} \cdot \mathbf{\rho} \frac{\phi''}{\mathbf{R}_{ij}} + (\mathbf{\rho} \cdot \mathbf{R}_{ij})^2 \left( \frac{\phi''}{\mathbf{R}_{ij}^2} - \frac{\phi'}{\mathbf{R}_{ij}^3} \right) \right]. \quad (A1)
$$

The first term is simply the lattice energy, $\mathbf{\rho} \cdot \mathbf{R}_{ij} = \rho R_{ij} \cos \theta$, where $\theta$ is the angle between $\rho$ and $R_{ij}$. Because of symmetry the sum over all lattice points of this term vanishes.
Similarly \((\boldsymbol{p} \cdot \mathbf{R}_{ij})^2 = p^2 R_{ij}^2 \cos^2 \theta\) and it may be shown that the sum of \(\cos^2 \theta\) over all lattice points is exactly \(\frac{1}{4}\). Hence

\[
K(\text{two-body}) = \frac{p^2}{6} \sum_{i \neq j} \left( \phi^{*} + \frac{2 \phi}{R_{ij}} \right) = \frac{p^2}{6} P_2. \tag{A2}
\]

_Triplet interactions_

Let us consider the triplet interaction of the displaced atom with all the others at rest on their lattice sites (figure 2). This is

\[
\sum_{i \neq j \neq k} V^{(3)}(|\mathbf{R}_{ij} - \boldsymbol{p}|, |\mathbf{R}_{ik} - \boldsymbol{p}|, |\mathbf{R}_{jk}|)
\]

and again expanding in a Taylor series we have

\[
K(\text{three-body}) = \sum_{i \neq j \neq k} \left\{ V^{(3)}(|\mathbf{R}_{ij}|, |\mathbf{R}_{ik}|, |\mathbf{R}_{jk}|) - \boldsymbol{p} \cdot \left( \frac{\partial V^{(3)}}{\partial R_{ij}} \frac{\mathbf{R}_{ij}}{R_{ij}} + \frac{\partial V^{(3)}}{\partial R_{ik}} \frac{\mathbf{R}_{ik}}{R_{ik}} \right) \right. \\

+ \frac{1}{2} \boldsymbol{p} \cdot \left( \frac{\partial^2 V^{(3)}}{\partial R_{ij}^2} \frac{1}{R_{ij}} + \frac{\partial^2 V^{(3)}}{\partial R_{ik}^2} \frac{1}{R_{ik}} \right) + (\boldsymbol{p} \cdot \mathbf{R}_{ij})^2 \left( \frac{1}{R_{ij}^2} \frac{\partial V^{(3)}}{\partial R_{ij}} \frac{1}{R_{ij}} + \frac{\partial^2 V^{(3)}}{\partial R_{ij}^2} \frac{1}{R_{ij}^2} \right) \\

+ (\boldsymbol{p} \cdot \mathbf{R}_{ik})^2 \left( \frac{1}{R_{ik}^2} \frac{\partial^2 V^{(3)}}{\partial R_{ik}^2} \frac{1}{R_{ik}} + \frac{\partial^2 V^{(3)}}{\partial R_{ik}^2} \frac{1}{R_{ik}^2} \right) + 2(\boldsymbol{p} \cdot \mathbf{R}_{ij})(\boldsymbol{p} \cdot \mathbf{R}_{ik}) \left( \frac{1}{R_{ij} R_{ik}} \frac{\partial^2 V^{(3)}}{\partial R_{ij} \partial R_{ik}} \right). \tag{A3}
\]
The first term is again simply the lattice energy. The first-order term again vanishes in the summation because of symmetry. Similarly, the mixed second-order term also vanishes so that the second-order term reduces to

$$K(\text{three-body}) = \sum_{i \neq j \neq k} \frac{\rho^2}{6} \left( \frac{\partial^2 V^{(3)}}{\partial R_{ij}^2} + \frac{2}{R_{ij}} \frac{\partial V^{(3)}}{\partial R_{ij}} + \frac{\partial^2 V^{(3)}}{\partial R_{ik}^2} + \frac{2}{R_{ik}} \frac{\partial V^{(3)}}{\partial R_{ik}} \right).$$

(A4)

Again because of symmetry the terms with $R_{ij}$ as variable in the summation are equivalent to those with $R_{ik}$ as variable; hence

$$K(\text{three-body}) = \frac{\rho^2}{6} \sum_{i \neq j \neq k} 2 \left( V^{(3)} + \frac{2}{R_{ij}} V^{(3)} \right) = 2T_2 \frac{\rho^2}{6}$$

(A5)

and also

$$K = K(\text{two-body}) + K(\text{three-body})$$

$$= \frac{\rho^2}{6} (P_2 + 2T_2).$$

(A6)

References


Contributions of a non-central force to the elastic constants of the inert gas solids

Abstract. The elastic constants $C_{11}$, $C_{12}$ and $C_{44}$ of the inert gas solids are calculated including the contributions from a non-central force. It is shown that the quantity $(C_{44} - C_{12})C_{12}^{-1}$ provides a critical test for the importance of non-central forces.

The rare gas elements neon, argon, krypton and xenon condense into face-centred cubic crystals for which there are three independent second-order elastic constants $C_{11}$, $C_{12}$ and $C_{44}$. If only central additive two-body forces are present, then neglecting quantum effects the Cauchy-Poisson relation $C_{12} = C_{44}$ holds. However, if zero-point energy effects are included this equality is destroyed. For example, both Salter (1954) and Barron...
and Klein (1965) have calculated the effect of zero-point energy and shown that for reasonable two-body potentials $C_{44} > C_{12}$.

We have calculated the effect on the Cauchy–Poisson relation due to the three-body interaction derived by Axilrod and Teller (1943), and have found that this alone makes $C_{44} < C_{12}$. The effects of zero-point energy and the three-body interaction thus compete.

Some numerical calculations have been made at $T = 0^\circ K$ and at zero pressure. In the Axilrod and Teller (1943) interaction the potential $W^{(3)}$ is given by

$$W^{(3)} = \nu \frac{3 \cos \theta_1 \cos \theta_2 \cos \theta_3 + 1}{R_{12}^3 R_{23}^3 R_{31}^3},$$

where $R_{12}, R_{23}, R_{31}$ are the sides of a triangle with atoms at the vertices, the interior angles being $\theta_1, \theta_2$ and $\theta_3$. The values of the constant $\nu$ used are those given by Bell and Kingston (1966). The two-body interaction used in the calculations was a Lennard-Jones (12, 6) potential whose parameters were calculated from solid state data by Zucker (1967). Two sets of parameters were employed. The three-body contribution to the lattice energy was neglected in the first of these but included in the second set. The method of Barron and Klein (1965) was used to calculate the effects of zero-point energy on the elastic constants and the significant results are displayed in table 1.

Table 1. The elastic constants (in units of $10^{10}$ dyn cm$^{-2}$) and percentage breakdown of the Cauchy relation $C_{44} = C_{12}$ for the inert gas solids

<table>
<thead>
<tr>
<th>Substance</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{44}$</th>
<th>$(C_{44} - C_{12})/C_{12} \times 100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>1.37</td>
<td>0.668</td>
<td>0.848</td>
<td>27.0</td>
</tr>
<tr>
<td>(b)</td>
<td>1.36</td>
<td>0.641</td>
<td>0.794</td>
<td>23.9</td>
</tr>
<tr>
<td>A</td>
<td>3.70</td>
<td>2.03</td>
<td>2.16</td>
<td>6.4</td>
</tr>
<tr>
<td>(b)</td>
<td>3.59</td>
<td>1.87</td>
<td>1.85</td>
<td>-1.1</td>
</tr>
<tr>
<td>Kr</td>
<td>4.52</td>
<td>2.53</td>
<td>2.61</td>
<td>3.4</td>
</tr>
<tr>
<td>(b)</td>
<td>4.38</td>
<td>2.31</td>
<td>2.17</td>
<td>-5.9</td>
</tr>
<tr>
<td>Xe</td>
<td>4.71</td>
<td>2.80</td>
<td>2.86</td>
<td>2.1</td>
</tr>
<tr>
<td>(b)</td>
<td>3.90</td>
<td>2.55</td>
<td>2.34</td>
<td>-8.3</td>
</tr>
</tbody>
</table>

(a) Calculated neglecting the three-body potential; (b) calculated with the three-body potential included.

The absolute values of the elastic constants do of course depend on the pair potential used, but the relative values and especially the quantity $B = (C_{44} - C_{12})/C_{12}$ is influenced by the zero-point effects and the many-body contributions. For neon, zero-point effects are much larger than the three-body effect, hence $B$ is positive. For krypton and xenon, the reverse is true, so that $B$ is negative, whilst for argon to a first approximation the effects cancel. The theory thus makes definite predictions concerning the sign of $B$. Here then is a critical test of the importance of three-body forces and an experimental determination of $B$ for the inert gas solids is clearly in principle possible, although results are not as yet available.

Results for the quantities at present being calculated, including the pressure dependence of the elastic constants, will be given later, together with a more detailed account of the procedures used.

The author wishes to thank Dr. I. J. Zucker for suggesting the problem and for helpful discussions, and the Science Research Council for financial support.

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The zero-point vibrational energy of cubic crystals

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Abstract. The zero-point vibrational energies of the three cubic lattices are calculated using the Bethe approximation. The harmonic and the quartic anharmonic energies are in good agreement with the results of standard lattice dynamical methods. However, the cubic and some of the non-leading anharmonic terms appear to be considerably overestimated. The results are applied to the inert gas solids to investigate the following models: (i) central nearest-neighbour interactions only; (ii) central all-neighbour interactions using a Lennard-Jones m-6 potential function; (iii) central all-neighbour and non-central interactions (the latter using the potential function given by Axilrod and Teller). Non-nearest-neighbour and non-central interactions were taken into account by using the Einstein approximation while central nearest-neighbour interactions were calculated using the Bethe approximation. It is found that the approximations (ii) and (iii) decrease the harmonic energy and increase the anharmonic energy with respect to approximation (i). The results indicate that the approximation made in (i) is accurate to approximately 5% for calculating the harmonic and 4% for calculating the anharmonic energies of neon. For xenon the accuracy is approximately 11% and 15% respectively. It is therefore concluded that calculations of the properties of the inert gas solids, especially the heavier gases, should include non-central forces and all-neighbour interactions.

1. Introduction

The zero-point vibrational energy has been calculated for the three cubic lattices in the harmonic approximation with central nearest-neighbour interactions by Domb and Salter (1952) and later to a higher accuracy for the face-centred cubic lattice by Isenberg (1953) using a method based on the evaluation of the frequency moments. The quartic anharmonic energy with all-neighbour interactions has been determined in the Einstein approximation by Zucker (1958, 1964), who extended the work of Henkel (1955) and developed a method of evaluating the quartic and higher-order terms in the Einstein approximation to any desired accuracy. Further evaluations of the cubic and quartic energies have been carried out by Maradudin et al. (1961) and Flinn and Maradudin (1963). More recently Feldman and Horton (1967) have recalculated and improved on the work of Flinn and Maradudin. They extended the calculations to include non-leading terms; that is, they did not ignore terms such as \( \phi^{(n-1)}a \) compared with \( \phi^{(n)} \), where \( \phi^{(n)} \) is the \( n \)th derivative of the pair potential function and \( a \) the nearest-neighbour distance. It has been shown by Lloyd (1964 a) and Barron and Klein (1965) and reaffirmed by the results of Horton and Feldman that it is necessary to include the non-leading terms. All the above-mentioned authors restricted their calculations to central pair-wise additive potential functions.

Götze and Schmidt (1966) and more recently Chell and Zucker (1968) have investigated the effect of a long-range three-body non-central potential of the form given by Axilrod and Teller (1943) on the zero-point harmonic energy using the Einstein approximation. Chell and Zucker found that the non-central force contribution was of the same order as the anharmonic energy and therefore could not justifiably be neglected.

In the present paper a method based on an approximation first introduced by Bethe (1935) for the Ising model of ferromagnetism and later adapted by Lloyd (1964 a, b) to calculate the high-temperature limit of the free energy and the elastic constants is used to determine the zero-point energy of the three cubic lattices. In a previous paper (Chell 1967) preliminary results were published giving the harmonic and quartic zero-point energies calculated using a nearest-neighbour model with central interactions. The leading term approximation was then made so that comparison could be made with the results of Flinn and Maradudin (1963). We now include a non-central potential, all-neighbour interactions and the non-leading and cubic anharmonic terms. To calculate the latter it
was found necessary to extend the theory from a coupled two-particle model to a three-particle model. Even so the method gave for the cubic anharmonic energy results differing somewhat from those of Feldman and Horton (1967). The discrepancy is thought to be due to the unsuitability of the method for second-order perturbation calculations involving strong coupling. The harmonic and quartic energies are in good agreement with those obtained by standard lattice-dynamical methods.

2. Theory

2.1. General

The adaptation of the Bethe approximation as described here and by Lloyd (1964a, b) essentially consists of assuming that the atoms in a crystal move in the mean field produced by all the other atoms. Then by assuming an effective harmonic potential between nearest neighbours the unknown parameters occurring in it can be determined from two consistency relations. The wave function and eigenfrequencies of the three-atom system then being determined, the anharmonic terms in the potential expansion can be treated as perturbations.

Considering the case of central nearest-neighbour interactions we represent the harmonic potential between two atoms \( m \) and \( n \) by \( V^{(2)}(r_m, r_n) \), where \( r_m \) is the displacement of the \( m \)th atom from its equilibrium site. The potential representing the three coupled particle system is then written as

\[
W(r_1, r_2, r_3) = \sum \psi_{i}(r_i) + V^{(2)}(r_1, r_2) + \sum \psi_{j}(r_2) + V^{(3)}(r_1, r_3) + \sum \psi_{k}(r_3)
\]

where \( \psi_{i}(r_m) \) is the \( i \)th bond of the \( m \)th atom. The single prime indicates that the sum is to be taken over all nearest neighbours excluding the bond \( V^{(2)}(r_m, r_n) \) and the double prime that both bonds \( V^{(2)}(r_m, r_n) \) and \( V^{(2)}(r_n, r_m) \) are to be excluded. Suffix 2 denotes the centre atom of the three atoms, labelled 1, 2 and 3, in the coupled system.

The consistency relations are then

\[
\int \int \psi^{2}(r_1, r_2, r_3) d^3 r_1 d^3 r_2 d^3 r_3 = \psi^{3}(r_3)
\]

and

\[
E_3 = 3E_1
\]

where \( E_3 \) is the zero-point energy of the three-atom system and \( E_1 \) the energy of a one-particle system. \( \psi \) represents the ground-state wave function.

In expanding the potential function \( \phi \) about the equilibrium lattice sites in terms of the difference in the displacements of the two atoms \( m \) and \( n \) from these sites we have

\[
V_1 = V^{(2)} + V^{(3)} + V^{(4)}
\]

where

\[
\begin{align*}
V^{(2)} &= \frac{1}{2} \alpha_1 A^2 + \frac{1}{2} \alpha_2 B \\
V^{(3)} &= \frac{1}{6} \gamma_1 A^3 + \frac{1}{2} \gamma_2 AB \\
V^{(4)} &= \frac{1}{2} \delta_1 A^4 + \frac{1}{2} \delta_2 A^2 B + \frac{1}{4} \delta_3 B^2 \\
A &= i \cdot \Delta r, \quad B = (\Delta r)^2 - A^2 \\
\alpha_1 &= \phi^{(2)}, \quad \alpha_2 = \phi^{(1)}/a \\
\gamma_1 &= \phi^{(3)}, \quad \gamma_2 = \frac{3\phi^{(2)}}{a} - \frac{3\phi^{(1)}}{a^2} \\
\delta_1 &= \phi^{(4)}, \quad \delta_2 = \frac{6\phi^{(3)}}{a} - \frac{12\phi^{(2)}}{a^2} + \frac{12\phi^{(1)}}{a^3} \\
\delta_3 &= \frac{3\phi^{(2)}}{a^2} - \frac{3\phi^{(1)}}{a^3}
\end{align*}
\]
The zero-point vibrational energy of cubic crystals

where the derivatives are evaluated at the nearest-neighbour distance \( a \) and \( \Delta \mathbf{r} = \mathbf{r}_m - \mathbf{r}_n \).

\( \mathbf{i} \) is a unit vector in the direction of the \( i \)th bond.

2.2. Harmonic energy

Taking the three atoms to lie on the \( x \) axis

\[
V^{(2)}(\mathbf{r}_m, \mathbf{r}_n) = \frac{\gamma_1}{2}(x_m - x_n)^2 + \frac{\gamma_2}{2}((y_m - y_n)^2 + (z_m - z_n)^2)
\]

we let

\[
\psi_i(\mathbf{r}_m) = \frac{\gamma_1}{2} (\mathbf{i} \cdot \mathbf{r}_m)^2 + \frac{\gamma_2}{2} ((\mathbf{i} \cdot \mathbf{r}_m)^2 - (\mathbf{i} \cdot \mathbf{r}_m)^2) + \eta_0
\]

where \( \eta_0, \eta_1 \) and \( \eta_2 \) are the unknown parameters to be determined. Then

\[
\sum_i \psi_i(\mathbf{r}_m) = \frac{\chi}{2} (x_m^2 + y_m^2 + z_m^2) + q\eta_0
\]

where

\[
\chi = \frac{q}{3}(\eta_1 + 2\eta_2) + k + R
\]

and we have included the contribution of non-nearest neighbours and a non-central force in an Einstein approximation by the symbols \( k \) and \( R \) respectively. \( q \) is the co-ordination number. Evidently

\[
\sum_i \psi_i(\mathbf{r}_m) = \frac{\chi}{2} x_m^2 + \frac{\chi}{2} (y_m^2 + z_m^2) + (q - 1)\eta_0
\]

and

\[
\sum_i \psi_i(\mathbf{r}_m) = \frac{\chi}{2} x_m^2 + \frac{\chi}{2} (y_m^2 + z_m^2) + (q - 2)\eta_0.
\]

The expressions (2.6), (2.8), (2.9) and (2.10) were substituted into (2.1) and the three-particle Schrödinger equation solved for the potential \( W(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) \).

The normal mode transformation, normal mode frequencies \( \nu_{ij} \) and the ground-state wave function are given in the appendix. The one-particle ground-state wave function is

\[
\psi(\mathbf{r}_2) = \left( \frac{S}{\pi^{1/2}} \right)^{3/2} \exp \left\{ - \frac{S^2}{2} (x_2^2 + y_2^2 + z_2^2) \right\}
\]

where \( S^4 = m \chi/\hbar^2 \), \( m \) is the atomic mass and \( \hbar = \hbar/2\pi \). \( \hbar \) is Planck's constant. Using the consistency relations (2.2) and (2.3) we find

\[
S^2 = a_1 - \frac{c_1^2}{2b_1 - d_1} = a_2 - \frac{c_2^2}{2b_2 - d_2}
\]

from which \( \eta_1 \) and \( \eta_2 \) may be determined. \( a_i, b_i \) and \( c_i \) are defined in the appendix.

\[
E_1 = \frac{3\hbar}{2} + q\eta_0
\]

where \( \nu = \hbar S^2/2\pi m \), the frequency of the one-particle system,

\[
E_3 = \frac{\hbar f}{2} + (3q - 4)\eta_0
\]

where

\[
f = \sum_{i=1}^{3} \sum_{j=1}^{3} \nu_{ij},
\]

Hence

\[
\eta_0 = \frac{\hbar}{8}(f - 9\nu)
\]
2.3. Anharmonic energy

The quartic anharmonic energy is determined from first-order perturbation theory:

\[ E^{(4)} = \frac{q}{4} \left\langle 0 \mid \left( \frac{\hbar}{2m} \right)^2 \left( \frac{\delta_1^2}{16} Q_1^2 + \frac{1}{24} Q_2 (\delta_2 Q_1 + 4 \delta_3 Q_2) \right) \right\rangle. \]  

(2.15)

Substituting for \( V^{(4)}(r_m, r_n) \) from (2.4) and taking the expectation value using the normal mode transformation, we find

\[ E^{(4)} = \frac{q}{4} \left\langle 0 \mid \left\langle \frac{\hbar}{2m} \right| \left( \frac{\delta_1^2}{16} Q_1^2 + \frac{1}{24} Q_2 (\delta_2 Q_1 + 4 \delta_3 Q_2) \right) \right\rangle \]

(2.16)

where

\[ Q_i = \sum_{j=1}^{3} q_{ij}, \quad q_{ij} = p_{ij}^2 / \nu_{ij} \]

and the \( p_{ij} \) are defined in the appendix.

Similarly the cubic anharmonic energy is given by second-order perturbation theory:

\[ E^{(3)} = \frac{q}{4} \sum_{m \neq 0} \frac{\left\langle m \mid \left| V^{(3)}(r_1, r_2) + V^{(3)}(r_2, r_0) \right| 0 \right\rangle^2}{E_0 - E_m} \]

(2.17)

where again \( V^{(3)}(r_m, r_n) \) is given by (2.4). Hence

\[ E^{(3)} = -\frac{q}{4} \frac{\hbar^2}{(2\pi)^4 m^3} \left\{ 11 q_{11}^2 \left( \frac{9 q_{11}^2}{\nu_{11} + 2 \nu_{12}} + \frac{9 q_{12}^2}{\nu_{11} + 2 \nu_{12}} + \frac{9 q_{13}^2}{\nu_{11} + 2 \nu_{13}} \right) \right\}
\]

\[ + \frac{\gamma_2^2}{18} q_{11} \left( \frac{q_{21}^2}{\nu_{11} + 2 \nu_{21}} + \frac{q_{22}^2}{\nu_{11} + 2 \nu_{22}} + \frac{q_{23}^2}{\nu_{11} + 2 \nu_{23}} + \frac{2 q_{23} \nu_{23}}{\nu_{11} + 2 \nu_{23} + 2 \nu_{23}} \right) \]

\[ + 2 q_{21} \left( \frac{q_{12} q_{22}}{\nu_{12} + \nu_{21} + \nu_{22}} + \frac{q_{12} \nu_{21}}{\nu_{12} + \nu_{21} + \nu_{22}} + \frac{q_{12} q_{23}}{\nu_{12} + \nu_{21} + \nu_{23}} + \frac{q_{13} q_{23}}{\nu_{13} + \nu_{21} + \nu_{23}} + \frac{q_{13} q_{21} + q_{13} q_{23}}{\nu_{13} + \nu_{21} + \nu_{23}} \right). \]

(2.18)

In calculating the anharmonic energies we have used the fact that the Bethe approximation gives the same answer as calculations made with a lattice of non-intersecting chains of atoms (Domb 1960).

3. Calculations

3.1. Nearest-neighbour model with central forces only

For this model

\[ \varphi_a = \gamma_a = 0 \]

\[ R = k = 0. \]

The equations (2.16) and (2.18) simplify slightly to give

\[ E^{(4)} = \frac{q}{4} \left( \frac{\hbar}{2m} \right)^2 \left( \frac{\delta_1^2}{16} Q_1^2 + \frac{\delta_2}{12 \nu} Q_1 + \frac{2 \delta_3}{3 \nu^2} \right) \]

(3.1)
Table 1. Zero-point energy with central nearest-neighbour interactions

<table>
<thead>
<tr>
<th>Lattice</th>
<th>$\eta_1/\eta_2$</th>
<th>Harmonic energy†</th>
<th>Cubic energy‡</th>
<th>Quartic energy‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>s.c.</td>
<td>0.3883</td>
<td>1.9249</td>
<td>0.03882</td>
<td>0.7769</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.9099*</td>
<td>0.02611*</td>
<td>0.1520*</td>
</tr>
<tr>
<td>b.c.c.</td>
<td>0.6057</td>
<td>2.3006</td>
<td>0.02992</td>
<td>0.3272</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.2992*</td>
<td>0.00396</td>
<td>0.1020*</td>
</tr>
<tr>
<td>f.c.c.</td>
<td>0.7687</td>
<td>2.8901</td>
<td>0.02015</td>
<td>0.1586</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.8925*</td>
<td>0.01575*</td>
<td>0.1024*</td>
</tr>
</tbody>
</table>

a, Maradudin et al. 1961; b, Domb and Salter 1952; c, Isenberg 1963; d, Feldman and Horton 1967. The unlettered numbers refer to calculations in the present paper. The results of other authors are given to the same accuracy as the present calculations.

† The harmonic energy is given in units of $\hbar (\phi^{(2)}/m)^{1/2}$.
‡ The cubic and quartic anharmonic energies, characterized by the numbers $N_i, M_i$, are given by

$$\frac{\hbar^2}{m\phi^{(2)}}\left\{N_1(\phi^{(3)})^2 + N_2 \frac{\phi^{(2)2}^{(2)}}{a} + N_3 \left(\frac{\phi^{(2)4}}{a}\right)\right\}$$

and

$$\frac{\hbar^2}{m\phi^{(2)}}\left(M_1\phi^{(4)} + M_2\phi^{(3)} + M_3\phi^{(3)}\right)$$

respectively.
and

$$E^{(3)} = \frac{q}{4 (2\pi)^4 m^3} \left\{ \frac{\gamma_1^2}{2} \left( \frac{11 q_{11}^2}{\nu_{11} + 2 \nu_{12}} + \frac{9 q_{13}^2}{\nu_{11} + 2 \nu_{13}} \right)
\right. 
+ \left. \frac{\gamma_2^2}{36 \nu_{11}^2} \left( \frac{3 q_{12}^2}{\nu_{12} + 2 \nu_{13}} + \frac{3 q_{13}^2}{\nu_{12} + 2 \nu_{13}} \right) \right\}. \quad (3.2)$$

In table 1 are displayed the parameter $\eta_1$, the harmonic and anharmonic energies calculated using the Bethe approximation, and also given wherever possible are the latest values obtained by others. It may be seen that the harmonic and the leading terms of the quartic anharmonic energies are in good agreement with the results obtained by others using standard lattice-dynamical methods. However, for the reason stated in the introduction, the cubic anharmonic energies appear to be considerably overestimated. It is not yet possible to see a way of increasing the accuracy of the cubic terms without overcomplicating the method by extending it to a greater coupled system, and thus destroying its simplicity. The non-leading terms also appear to have been affected for a similar reason.

3.2. All-neighbour model with central forces: $R = 0$

To illustrate this model a Lennard-Jones 12-6 potential function was chosen of the form

$$\phi(r) = 4\epsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right) \quad (3.3)$$

where $\epsilon$ is the depth of the potential at the minimum and $\sigma$ the distance at which $\phi(r)$ equals zero. The theory was applied in evaluating the zero-point energies of the inert gas solids Ne, Ar, Kr and Xe. In the calculations two sets of parameters were used: those given by Zucker (1967) when the three-body lattice energy was neglected (parameters $(a)$), and those when the three-body lattice energy was included in the free energy at $T = 0$ (parameters $(b)$). The experimental nearest-neighbour distance $a$ was obtained from Pollack (1964).

It can easily be shown that for the above potential

$$\frac{z_2}{z_1} = -12 \left( \frac{\sigma}{a} \right)^{12} + 6 \left( \frac{\sigma}{a} \right)^6 / x \quad (3.4)$$

and

$$\frac{k}{z_1} = \left( \frac{132}{a} \right) (C_{14} - 12) - 30 \left( \frac{\sigma}{a} \right)^6 (C_8 - 12) / 3x \quad (3.5)$$

where

$$x = 156 \left( \frac{\sigma}{a} \right)^{12} - 42 \left( \frac{\sigma}{a} \right)^6$$

and the $C_n$'s are lattice sums given by Hirschfelder et al. (1954). Using these quantities, $\eta_1$ and $\eta_2$ were calculated from (2.13) and hence the zero-point energies evaluated. The results are given in table 2, together with the results obtained from the nearest-neighbour model using parameters $(a)$.

It may be seen that the zero-point energy of Ne is least affected and that of Xe most affected by the inclusion of all neighbours. The harmonic contribution of Ne is reduced by 1.6% and 3.9% and that of Xe by 4.6% and 9% for parameters $(a)$ and $(b)$ respectively. The effect of the non-nearest neighbours on the anharmonic energy was assessed through the change in the harmonic eigenfrequencies $v_{ij}$; only, that is non-nearest-neighbour interactions were neglected. The anharmonic energy is increased for Ne by 2.1% and 4.2% and for Xe by 5.3% and 8.7% for parameters $(a)$ and $(b)$ respectively.

3.3. All-neighbour model with central and non-central forces

The potential considered was the long-range three-body potential function first derived by Axilrod and Teller (1943) and elegantly rederived by Götz and Schmidt (1966). As
Table 2. Harmonic and anharmonic zero-point energies

<table>
<thead>
<tr>
<th>Model</th>
<th>$\eta_1/x_1$</th>
<th>$\eta_2/x_2$</th>
<th>Harmonic energy</th>
<th>Total</th>
<th>Cubic</th>
<th>Quartic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>0.7687</td>
<td>0.9925</td>
<td>127.4</td>
<td>19.92</td>
<td>-4.90</td>
<td>24.85</td>
</tr>
<tr>
<td></td>
<td>0.7579</td>
<td>1.003</td>
<td>125.3</td>
<td>20.34</td>
<td>-5.27</td>
<td>25.61</td>
</tr>
<tr>
<td></td>
<td>0.7610</td>
<td>0.9928</td>
<td>122.4</td>
<td>20.75</td>
<td>-5.39</td>
<td>26.14</td>
</tr>
<tr>
<td></td>
<td>0.7610</td>
<td>1.003</td>
<td>120.9</td>
<td>21.03</td>
<td>-5.68</td>
<td>26.71</td>
</tr>
<tr>
<td>Ar</td>
<td>0.7687</td>
<td>0.9925</td>
<td>180.9</td>
<td>6.04</td>
<td>-1.36</td>
<td>7.40</td>
</tr>
<tr>
<td></td>
<td>0.7401</td>
<td>1.005</td>
<td>173.6</td>
<td>6.35</td>
<td>-1.64</td>
<td>7.99</td>
</tr>
<tr>
<td></td>
<td>0.7452</td>
<td>1.012</td>
<td>167.1</td>
<td>6.65</td>
<td>-1.72</td>
<td>8.37</td>
</tr>
<tr>
<td></td>
<td>0.7280</td>
<td>0.9880</td>
<td>163.6</td>
<td>6.82</td>
<td>-1.90</td>
<td>8.72</td>
</tr>
<tr>
<td>Kr</td>
<td>0.7687</td>
<td>0.9925</td>
<td>146.3</td>
<td>2.52</td>
<td>-0.56</td>
<td>3.08</td>
</tr>
<tr>
<td></td>
<td>0.7374</td>
<td>1.002</td>
<td>139.9</td>
<td>2.66</td>
<td>-0.69</td>
<td>3.35</td>
</tr>
<tr>
<td></td>
<td>0.7429</td>
<td>1.002</td>
<td>132.6</td>
<td>2.70</td>
<td>-0.71</td>
<td>3.41</td>
</tr>
<tr>
<td></td>
<td>0.7723</td>
<td>0.9961</td>
<td>129.3</td>
<td>2.81</td>
<td>-0.80</td>
<td>3.61</td>
</tr>
<tr>
<td>Xe</td>
<td>0.7687</td>
<td>0.9925</td>
<td>129.3</td>
<td>1.32</td>
<td>-0.29</td>
<td>1.61</td>
</tr>
<tr>
<td></td>
<td>0.7360</td>
<td>1.000</td>
<td>123.4</td>
<td>1.39</td>
<td>-0.36</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>0.7423</td>
<td>1.000</td>
<td>117.6</td>
<td>1.47</td>
<td>-0.38</td>
<td>1.85</td>
</tr>
<tr>
<td></td>
<td>0.7719</td>
<td>1.000</td>
<td>114.4</td>
<td>1.52</td>
<td>-0.43</td>
<td>1.95</td>
</tr>
</tbody>
</table>

(i) Central nearest-neighbour interactions only with parameters (a); (ii) central all-neighbour interactions with parameters (a); (iii) central all-neighbour interactions with parameters (b); (iv) central and three-body non-central interactions with parameters (b).

Units: cal mole$^{-1}$.

there is no analytical expression for the short-range three-body potential, and doubts have been cast by Swenberg (1967) on the approximation used by Jansen (1964) when calculating the short-range exchange interaction of triplets of atoms, this effect is not considered here.

The expression given by Axilrod and Teller for the triple-dipole interaction of a triplet of atoms at the vertices of a triangle of sides $R_{ij}$, $R_{jk}$ and $R_{ki}$ and interior angles $\theta_i$, $\theta_j$, and $\theta_k$ is

$$v(3 \cos \theta_i \cos \theta_j \cos \theta_k + 1)$$

$$R_{ij}^3 R_{jk}^3 R_{ki}^3.$$

Bell and Kingston (1966) have recently calculated the coefficient $v$, given by Axilrod (1949) as $9I\alpha^3/16$, where $I$ is the ionization and $\alpha$ the polarizability of a given atom, and their values are used in the following calculations.

An expression for the three-body potential contribution to the zero-point harmonic energy in the Einstein approximation has been derived elsewhere (Chell and Zucker 1968). Using this expression

$$R = -1134v/3\alpha^3.$$

Parameters (b) were used in the calculations and again the non-nearest-neighbour anharmonic effects were considered only through the change in the $v_{ij}$'s. The results are shown in table 2.

The effect of the three-body potential is to decrease further the harmonic and to increase the anharmonic energies. With respect to the nearest-neighbour results the harmonic energy of Ne is decreased by 5.1% whilst the anharmonic energy is increased by 4.2%; the values for Xe are 11.5% and 15.3% respectively. Götte and Schmidt (1966) and Chell and Zucker (1968) also found that the three-body potential decreased the harmonic energy. Comparing cases (iii) and (iv) in the table gives the magnitude of the non-central contribution which is similar to that calculated by the latter authors but slightly larger. As pointed
out previously by Chell and Zucker, it is of opposite sign and of the same order as the anharmonic energy for Ar, Kr and Xe.

4. Discussion

The harmonic and cubic and quartic anharmonic zero-point energies have been calculated for the three cubic lattices using an adaptation of the Bethe approximation. The approximation has been shown to give results for a central nearest-neighbour model in good agreement with methods based on normal lattice dynamics for the harmonic and the leading term of the quartic anharmonic energy. For non-leading terms and the cubic anharmonic energy the agreement is generally not so good. The assumption of central nearest-neighbour interactions between atoms in a crystal has been investigated for the inert gas solids by taking into account (i) central non-nearest-neighbour interactions and (ii) non-nearest neighbours with a central and a three-body non-central interaction using the Einstein approximation. A Lennard-Jones 12-6 potential function has been used to represent the two-body central interaction and a potential derived by Axilrod and Teller (1943) to represent the three-body potential. It was found that effects (i) and (ii) decreased the harmonic energy and increased the anharmonic energy, Ne being least and Xe being most affected.

The contribution of the three-body potential to the harmonic zero-point energy was \(-1.5, -3.5, -3.3, -3.2\) cal mole\(^{-1}\) for Ne, Ar, Kr and Xe respectively. For the latter three this is of the same order as, but opposite in sign to, the anharmonic energy and therefore when working to this order cannot justifiably be neglected. In the case of Ne, because of its relatively large anharmonic energy and the smallness of the coefficient \(v\), the three-body potential has little effect.

The total effect of non-nearest neighbours and non-central interactions on Xe is to change the nearest-neighbour model harmonic energy by 11.5\% and the anharmonic energy by 15.3\%. For Ne the change is smaller but still appreciable. It has been shown elsewhere (Chell and Zucker 1968) that the contribution of the three-body potential to the harmonic zero-point energy must be considered as an all-neighbour interaction and that a nearest-neighbour model would be in serious error for this potential.

The harmonic energy of the central non-nearest-neighbour interactions model differs from that of the nearest-neighbour model by 1.6\% for Ne and 4.6\% for Xe. When parameters \(\theta\) are used the central all-neighbour interactions change the harmonic energy by 3.9\% and 9\% for Ne and Xe respectively. Clearly a large part of the three-body contribution comes through the modification of the parameters used in the central potential.

Results have also been obtained for Lennard-Jones \(m-6\) potential functions and for values of \(m\) ranging from 10 to 14. These indicate that the lower the value of \(m\) the smaller the zero-point energy is and that the greater the effects described above.

In the above calculations the short-range triplet interaction investigated by Jansen (1964) has been neglected. The work of Jansen indicates that this interaction has a similar angular dependency to, and the same sign as, the long-range interaction and would therefore lead to an even greater three-body contribution to the zero-point energy.

It would therefore appear that calculations of the properties of the inert gas solids must include non-central forces and all-neighbour interactions.

The main advantages of the method used in the calculations are that it is relatively simple, it enables the zero-point energy of all three cubic lattices to be calculated, and the effects of non-nearest neighbours and non-central forces can be estimated by treating them in an Einstein approximation.

Work is in progress at present on using the same approximation to evaluate the anharmonic contributions to the free energy of the cubic lattices at finite temperatures, and it is hoped that at temperatures high enough that coupling is less important the accuracy of the cubic and non-leading terms will be improved.

Acknowledgments

The author wishes to thank Dr. I. J. Zucker for helpful discussions and the Science Research Council for a research grant.
Appendix

Let
\[
\beta_i = \alpha_i - \eta_i \\
\epsilon_i = \beta_i - (\beta_i^2 + 8\alpha_i^2)^{1/2}, \quad \kappa_i = \beta_i + (\beta_i^2 + 8\alpha_i^2)^{1/2} \\
\eta_i = \frac{4\alpha_i^2 + \beta_i \epsilon_i}{2}, \quad \kappa_i = \frac{4\alpha_i^2 + \beta_i \kappa_i}{2} \tag{A1}
\]

\[
A_{11} = \chi_i + \frac{1}{2} \beta_i, \quad A_{12} = A_{11} + \frac{\epsilon_i}{2}, \quad A_{13} = A_{11} + \frac{\kappa_i}{2}
\]

\[
S_{ij} = \frac{m A_{ij}}{\hbar^2}.
\]

Then
\[
a_i = \frac{1}{4} \left( \frac{S_{12} \epsilon_i^2}{n_i} + \frac{S_{13} \kappa_i^2}{m_i} \right) \tag{A2}
\]
\[
b_i = \frac{S_{11} \alpha_i^2}{2} + \left( \frac{S_{12} \epsilon_i^2}{n_i} + \frac{S_{13} \kappa_i^2}{m_i} \right) \alpha_i^2 \tag{A3}
\]
\[
c_i = \left( \frac{S_{12} \epsilon_i^2}{n_i} + \frac{S_{13} \kappa_i^2}{m_i} \right) \alpha_i \tag{A4}
\]
\[
d_i = \frac{S_{11} \alpha_i^2}{2} - 2 \alpha_i^2 \left( \frac{S_{13} \kappa_i^2}{n_i} + \frac{S_{13} \kappa_i^2}{m_i} \right) \tag{A5}
\]

where \(i = 1 \text{ or } 2, \ j = 1, 2 \text{ or } 3.

The normal mode transform is given by
\[
X_1 = \frac{1}{2^{1/2}} (-x_1 + x_3), \quad X_2 = \frac{1}{n_1^{1/2}} \left( \alpha_1 x_1 - \frac{\epsilon_1 x_2}{2} + \alpha_1 x_3 \right) \\
X_3 = \frac{1}{m_1^{1/2}} \left( \alpha_1 x_1 - \frac{\kappa_1 x_2}{2} + \alpha_1 x_3 \right) \\
Y_1 = \frac{1}{2^{1/2}} (-y_1 + y_3), \quad Y_2 = \frac{1}{n_2^{1/2}} \left( \alpha_2 y_1 - \frac{\epsilon_2 y_2}{2} + \alpha_2 y_3 \right) \\
Y_3 = \frac{1}{m_2^{1/2}} \left( \alpha_2 y_2 - \frac{\kappa_2 y_2}{2} + \alpha_2 y_3 \right)
\]

and a similar transformation for the \(z\)'s. We have
\[
x_2 - x_1 = p_{11} X_1 + p_{12} X_2 - p_{13} X_3 \\
x_3 - x_2 = p_{11} X_1 - p_{12} X_2 + p_{13} X_3 \\
y_2 - y_1 = p_{21} Y_1 + p_{22} Y_2 - p_{23} Y_3 \\
y_3 - y_2 = p_{21} Y_1 - p_{22} Y_2 + p_{23} Y_3
\]

and similar equations for \(z_i - z_j\).
\[
p_{11} = \frac{1}{2^{1/2}}, \quad p_{12} = \frac{n_1^{1/2}(2x_1 - \kappa_1)/2}{\alpha_i (\kappa_i - \epsilon_i)} \\
p_{13} = \frac{m_1^{1/2}(2x_1 - \epsilon_i)/2}{\alpha_i (\kappa_i - \epsilon_i)} \\
p_{21} = \frac{n_2^{1/2}(2x_2 - \kappa_2)/2}{\alpha_i (\kappa_i - \epsilon_i)} \\
p_{22} = \frac{m_2^{1/2}(2x_2 - \epsilon_i)/2}{\alpha_i (\kappa_i - \epsilon_i)} \\
p_{23} = \frac{n_2^{1/2}(2x_2 - \kappa_2)/2}{\alpha_i (\kappa_i - \epsilon_i)}
\]

The normal mode frequencies \(v_{ij}\) are given by
\[
v_{ij} = \frac{\hbar S_{ij}^{1/2}}{2\pi m} \tag{A6}
\]
The first suffix refers to the mode: \( i = 1 \) to the \( X \) mode, \( i = 2 \) to the \( Y \) and \( Z \) modes; the second suffix labels the mode coordinate. The frequencies corresponding to the \( Y \) and \( Z \) modes are equal. In the text the \( Z \) mode frequencies are labelled \( r_{3f} \) to simplify the notation.

The ground-state wave function was given by

\[
\psi(r_1, r_2, r_3) = \left( \frac{S_{11}S_{12}S_{13}}{\pi^{3/2}} \right)^{1/2} \exp \left[ -\frac{1}{2} \left( a_1 x_1^2 + b_1 (x_1^2 + x_3^2) - c_1 (x_1 x_2 + x_2 x_3) - d_1 x_1 x_3 \right) \right] \\
\times \frac{S_{21}S_{22}S_{23}}{\pi^{3/2}} \exp \left[ -\frac{1}{2} \left( a_2 (y_2^2 + z_2^2) + b_2 (y_1^2 + y_3^2 + z_1^2 + z_3^2) - c_2 (y_1 y_2 + y_2 y_3 + z_1 z_2 + z_2 z_3) - d_2 (y_1 y_3 + z_1 z_3) \right) \right].
\]  

\[ (A7) \]

References