THE EFFECT OF THE ANHARMONIC POTENTIAL TERMS ON THE ENERGY OF A ONE DIMENSIONAL LATTICE

By

Myles McConnon

Bachelor of Arts, 1941, Oberlin College

Master of Arts, 1946, University of Wisconsin

Submitted to the Graduate School of the University of Pittsburgh in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

Pittsburgh, Pennsylvania

1949

Cp. 3

FOREWORD

The author wishes to express his gratitude to Dr. A. D. Booth, of the University of London, for his indispensable help and stimulation in completing this research. He is also indebted to Dr. J. S. Taylor for his encouragement and guidance and to Dr. E. W. Montroll for the suggestion and initial formulation of the problem. Finally, he gratefully acknowledges the constant inspiration and encouragement of Margaret Burnham McConnon, his wife.

TABLE OF CONTENTS

I INTRODUCTION

The early attempts to calculate thermodynamic properties of crystalline solids by classical statistical mechanics led to results which agreed with the observations of Dulong and Petit at high temperatures. Thus, the total energy of a crystal was found to be 3NkT, and the specific heat, 3Nk. Later, more refined measurements showed that the specific heat actually decreased with decreasing temperature, and the classical theory was entirely unable to account for this behaviour. Since the specific heat could be readily measured, it then became a criterion for the success or failure of any theory of solids.

It was on this basis that Planck's theory of quanta first gained attention by its successful application to a problem different from the theory of radiation for which it was designed. By using Planck's hypothesis of the quantized energy levels of atomic oscillators, Einstein[1] obtained the expression,

$$C_v = 3Nk \frac{\left(\frac{h\nu}{kT}\right)^2 e^{\frac{h\nu}{kT}}}{\left(e^{\frac{h\nu}{kT}} - 1\right)^2}$$

for the specific heat, which agreed qualitatively with the observed results at low temperatures, and which approached the classical results at high temperatures.

The failure of Einstein's treatment to give quantitative agreement at low temperatures was later attributed to his assumption that the oscillators vibrated independently of each other and with the same frequency about their equilibrium positions. Debye[10] assumed that the oscillators were coupled, with a distribution of frequencies among the normal modes. By assuming that the frequencies were densely distributed, Debye treated the crystal as a continuum with a continuous distribution of frequencies, which can be arbitrarily set equal to zero above the maximum or characteristic frequency of the crystal. His expression for the specific heat was,

$$C_v = \frac{\partial}{\partial T}\left\{ 9NkT \frac{T^3}{h\nu_L/k} \int_0^{h\nu_L/kT} \frac{\xi^3}{e^{\xi}-1}\, d\xi \right\}$$

where ν_L is the maximum frequency of the crystal. This formula gave quantitative agreement for the data of the time, and because of its mathematical simplicity, its early success gave Debye's treatment great popularity, to the extent that any discrepancies that were later found tended to be attributed to anomalies of the crystal structure without any reference to the possible limitations of the Debye treatment.

At this same time, Born and Von Karman[7] obtained results for a discreet model, which, while offering a more satisfactory physical picture, introduced mathematical difficulties which caused the theory to be understandably neglected. According to their theory, the crystal was pictured as a periodic lattice structure with atoms vibrating about their equilibrium positions in the lattice with simple harmonic motion. They assumed cyclic boundary conditions in the coordinates and momenta at the surface of the crystal, thus treating the crystal as a four dimensional torus. The analysis of this motion led to a discreet set of frequencies distributed among the normal modes of vibration and obtained as the secular roots of the dynamical equations. Since the set is nearly dense for a large crystal, it can be represented by a continuous distribution function, which was found however to have several infinities which corresponded to peaks in the frequency spectrum. The result was an immediate generalization of Einstein's formula,

$$C_v = k \sum_{i=1}^{3N} \frac{\left(\frac{h\nu_i}{kT}\right)^2 e^{\frac{h\nu_i}{kT}}}{\left(e^{h\nu_i/kT}-1\right)^2}$$

The major difficulty of the method is the problem of determining the large number of determinantal roots, or a distribution of them. Except for highly idealized lattices this has never been done, and a complete solution has only been obtained for the one-dimensional analogue of a crystal.

The next advance was Blackman's[52,54,68] work in extending the methods of Born and Von Karman. For the highly symmetric cases that he studied, Blackman demonstrated that the secular determinant was factorable into three or four ordered determinants, so that the roots were obtainable as solutions of a large number of cubic or quartic equations. To approximate a distribution function, Blackman obtained the roots of a large number of random samples of these equations, and computed the distribution of the samples. To obtain much accuracy, a large number of samples was required, and the work was long and tedious. Moreover, no estimate of error has been obtained. It is also necessary to repeat the work for any change in the lattice parameters, so that it is not easy to evaluate the influence of changes in the parameters on the physical properties of the crystal.

In order to improve this situation, Montroll[95,96,117] suggested an alternative approach to the problem of approximating the distribution function, namely, to represent it by a Fourier expansion. Since this would not require immediate detailed computation, it would be possible to incorporate the lattice parameters. Any orthogonal set of functions, normalized in the range from the lowest to the largest frequency, would of course be suitable, but for the purpose of the proposed technique, a set of polynomials, such as Legendre polynomials, is most convenient. The coefficients of the expansion are then the average values of the polynomials with respect to the required distribution function, or a set of moments of the function. But by well known matrix theorems, the trace of a polynomial in a matrix is the sum of those polynomials in the secular roots, so that an average is obtained by dividing by the order of the matrix. Thus it is possible to obtain the required average directly from the matrix of the dynamical equations and evaluating from them the expression for the distribution function to the desired accuracy.

Throughout this development various secondary considerations have been brought to attention. In particular, the effect of the assumption of cyclic coordinates has caused a great deal of discussion by Born[86,116], Raman[51], Ledermann[90] and others. The problem of obtaining dynamical results independent of the assumption of central forces has been given some attention by Eisenschitz[97,122]. Some general treatment has also been given to the anharmonic vibrations in the lattice by Born[21] and Peierls[38].

The problem that we wish to consider in this paper has, however, been quite generally postponed. This is, to calculate the magnitude of the effect of anharmonic vibration at high temperatures, or to put it the other way, to evaluate the temperature at which discrepancies due to anharmonicity become evident. While crystal forces are extremely large and thus restrict the vibrations to harmonic form over the greater part of the temperature range of the crystal, it is apparent that at some temperature short of the melting point the vibrations will not remain small and should lead to discrepancies in the specific heat. It is also possible that considerable variation in this range may exist among different crystals.

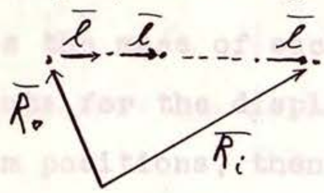
In order to retain a fairly simple treatment and still expose the general trend of the results, we shall consider here only a one-dimensional lattice. While this will have no direct relationship with any real crystal, we may expect that it will give a fair indication of the method of attack desirable for the three-dimensional problem and also some idea of the results to be expected.

In part II we begin with the dynamical analysis based on the Born-Karman model assuming harmonic vibrations. The normal coordinates are first obtained, and then the quantum mechanical solution and the energy eigenvalues, which will be necessary to begin the general treatment in the following section, are found. Since we are primarily interested in the system at high energy, it might be asked why it is necessary to express the solution in quantum mechanical language. But, aside from the fact that we do obtain more valid general results in this way, the purpose here is mainly to simplify the problem, that is, in particular, to allow the use of perturbation methods in the treatment of the next section. While the results in this section are not new, the use of matric methods throughout is not usual in this problem and yet has appeal as being a very natural way to express these transformations.

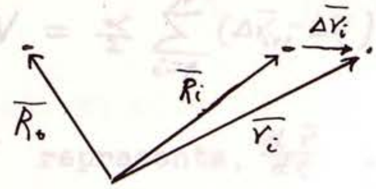
In part III, we begin by carrying out the transformation to the normal coordinates (with respect to harmonic vibration) on the kinetic energy and on the general series for the potential energy. We take one higher term from this series and form its first order perturbation expression as a first correction for anharmonicity to the previously obtained total energy term. This perturbation term is then shown to be reducible at high temperature to a fairly simple expression which can be compared easily with the unperturbed energy term. We next obtain an expression for the unperturbed energy in terms of the temperature by classical statistical methods so that the final effect of anharmonicity can be measured in terms of the temperature.

II DYNAMICS OF A ONE-DIMENSIONAL LATTICE OF HARMONIC OSCILLATORS

The atoms of the lattice are assumed to vibrate with simple harmonic motion about equilibrium points in the lattice which are equally spaced. The atoms are all assumed to be identical. The reference system can be constructed with vectors, where we shall indicate the lattice of zero energy, that is, the lattice with all the atoms in their equilibrium positions, by the diagram,



In the more general situation the atoms are displaced from their equilibrium positions by an amount designated by ,



that is, the equilibrium position and the instantaneous position of each atom are designated by,

$$\begin{cases} \bar{R}_i = \bar{R}_0 + i\bar{\ell} \\ \bar{r}_i = \bar{R}_i + \Delta\bar{r}_i \end{cases}$$

so that the displacement of the atom from its equilibrium position is,

$$\Delta\bar{r}_i = \bar{r}_i - \bar{R}_i$$

We wish to use the Born-Karman[7,9] model for the crystal so that we must assume, that for a large number of atoms, the nature of the vibrations is independent of the conditions imposed on the boundaries. Following Born we assume, for convenience, that the boundary conditions are cyclic, that is,

$$\begin{cases} \overline{R}_{i+N} = \overline{R}_i \\ \overline{r}_{i+N} = \overline{r}_i \end{cases}$$

It then follows that the displacements are also cyclic,

$$1) \quad \Delta \overline{r}_{i+N} = \overline{r}_{i+N} - \overline{R}_{i+N} = \overline{r}_i - \overline{R}_i = \Delta \overline{r}_i$$

If m is the mass of each atom and $\alpha, \beta, \gamma,$ etc. are the force constants for the displacement of the atoms from their equilibrium positions, then the kinetic and potential energies for the lattice are

$$2) \quad \begin{cases} T = \frac{m}{2} \sum_{i=1}^{N} \dot{\overline{r}}_i^{\,2} \\ V = \frac{\alpha}{2} \sum_{i=1}^{N} (\Delta\overline{r}_{i+1} - \Delta\overline{r}_i)^2 + \beta \sum_{i=1}^{N} (\Delta\overline{r}_{i+1} - \Delta\overline{r}_i)^3 + \gamma \sum_{i=1}^{N} (\Delta\overline{r}_{i+1} - \Delta\overline{r}_i)^4 + \cdots \end{cases}$$

Here $\dot{\overline{r}}$ represents, $\frac{d\overline{r}}{dt}$. The first two terms of the potential series are missing in accordance with the assumption that the force and potential energy are zero for an atom in its equilibrium position. If now we introduce coordinates to represent the displacements,

$$\begin{cases} u_i = \Delta \overline{r}_i \\ \dot{u}_i = \dot{\overline{r}}_i = \Delta \dot{\overline{r}}_i \end{cases}$$

and restrict V to its quadratic term so that we then treat the atoms as harmonic oscillators, the energy expressions become,

$$3) \quad \begin{cases} T = \frac{m}{2} \sum_{i=1}^{N} \dot{u}_i^2 \\ V = \frac{\alpha}{2} \sum_{i=1}^{N} (u_{i+1} - u_i)^2 \end{cases}$$

In order to obtain a dynamical solution it is necessary to find a transformation of coordinates which converts T and V simultaneously to canonical form. We shall do this by means of matrix methods, so that we must consider the coordinates, u_i, as components of the position vector, u, in the space of (u_i). For convenience we now introduce the auxilliary matrix,

4) $$S = \left[\delta^N_{i+1,j}\right]$$

where we imply the following δ convention,

$$\begin{cases} \delta^N_{ij} = 1, & \text{if } i \equiv j \text{ modulo } (N) \\ \delta^N_{ij} = 0, & \text{if } i \not\equiv j \text{ modulo } (N) \end{cases}$$

We now observe the following properties of S,

$$\begin{aligned} SM &= \left[\delta^N_{i+1,j}\right]\left[m_{ij}\right] \\ &= \left[m_{i+1,j}\right] \end{aligned}$$

Applying this result successively,

5) $$S^n M = \left[m_{i+n,j}\right]$$

from which we obtain the result,

$$\begin{aligned} S^N &= \left[\delta^N_{i+N,j}\right] = \left[\delta^N_{i,j}\right] \\ &= I \end{aligned}$$

applying 5) to this result we obtain the inverse,

$$S^{-1} = S^{-1} S^N = S^{N-1}$$

and applying 5) to S^T, we show that S is orthogonal,

$$\begin{aligned} SS^T &= S\left[\delta^N_{i,j+1}\right] = \left[\delta^N_{i+1,j+1}\right] \\ &= I \end{aligned}$$

or,

$$S^T = S^{-1}$$

we can now use S and u to build up the energy terms in 3),

$$\begin{cases} u = [u_i] \\ Su = [u_{i+1}] \\ (S-I)u = [u_{i+1} - u_i] \end{cases}$$

applying this result to 3) we obtain,

$$6) \begin{cases} T = \frac{m}{2}\dot{u}^2 \\ V = \frac{\alpha}{2} u(S^T - I)(S-I)u = \alpha u\left(I - \frac{S+S^{-1}}{2}\right)u \end{cases}$$

Substituting 6) into Lagrange's equation,

$$\begin{cases} \frac{\partial T}{\partial \dot{u}} = \frac{m}{2}(I)\dot{u} + \frac{m}{2}(I)^T\dot{u} = m\dot{u} \\ \frac{\partial V}{\partial u} = \alpha\left(I - \frac{S+S^{-1}}{2}\right)u + \alpha\left(I - \frac{S+S^{-1}}{2}\right)^T u = 2\alpha\left(I - \frac{S+S^{-1}}{2}\right)u \end{cases}$$

the differential equation of motion becomes,

$$7) \quad \ddot{u} + \frac{2\alpha}{m}\left(I - \frac{S+S^{-1}}{2}\right)u = 0$$

In order to solve this equation we procede to diagonalize the coefficients. However, since the coefficients are polynomials in S, it is only necessary to diagonalize S itself in order to accomplish this, because, when a matrix is diagonalized, any polynomial in that matrix will also be diagonalized, that is, if,

$$KuK^{-1} = d \qquad \text{(a diagonal matrix)}$$

and,

$$P(u) = \sum_i a_i u^i$$

then,

$$KP(u)K^{-1} = K\sum_i a_i u^i K^{-1} = \sum_i a_i K u^i K^{-1}$$
$$= \sum_i a_i KuK^{-1}KuK^{-1} - - KuK^{-1}$$
$$= \sum_i a_i d^i = P(d)$$

but, any polynomial in a diagonal matrix is itself a diagonal matrix, which proves the assertion. The diagonal terms of d are, moreover, the characteristic roots of u, and the characteristic roots of P(d) are the characteristic roots of P(u).

In order to diagonalize S, we must first find its characteristic roots. Construct the N-order determinants, $\Omega(N)$, $\phi(N)$ and $\psi(N)$ as follows:

$$\Omega(N) = |\lambda I - S| = \begin{vmatrix} \lambda & -1 & 0 & 0 & \cdots & 0 & 0 \\ 0 & \lambda & -1 & 0 & \cdots & 0 & 0 \\ 0 & 0 & \lambda & -1 & \cdots & 0 & 0 \\ 0 & 0 & 0 & \lambda & \cdots & 0 & 0 \\ \vdots & & & & & & \vdots \\ 0 & 0 & 0 & 0 & \cdots & \lambda & -1 \\ -1 & 0 & 0 & 0 & \cdots & 0 & \lambda \end{vmatrix}_N$$

$$\phi(N) = \begin{vmatrix} \lambda & -1 & 0 & 0 & \cdots & 0 & 0 \\ 0 & \lambda & -1 & 0 & \cdots & 0 & 0 \\ 0 & 0 & \lambda & -1 & \cdots & 0 & 0 \\ 0 & 0 & 0 & \lambda & \cdots & 0 & 0 \\ \vdots & & & & & & \vdots \\ 0 & 0 & 0 & 0 & \cdots & \lambda & -1 \\ 0 & 0 & 0 & 0 & \cdots & 0 & \lambda \end{vmatrix}_N.$$

$$\psi(N) = \begin{vmatrix} 0 & -1 & 0 & 0 & \cdots & 0 & 0 \\ 0 & \lambda & -1 & 0 & \cdots & 0 & 0 \\ 0 & 0 & \lambda & -1 & \cdots & 0 & 0 \\ 0 & 0 & 0 & \lambda & \cdots & 0 & 0 \\ \vdots & & & & & & \vdots \\ 0 & 0 & 0 & 0 & \cdots & \lambda & -1 \\ -1 & 0 & 0 & 0 & \cdots & 0 & \lambda \end{vmatrix}_N$$

Expanding the determinants by cofactors of the first rows,

$$\begin{cases} \Omega(N) = \lambda\,\phi(N-1) + \psi(N-1) \\ \phi(N) = \lambda\,\phi(N-1) = \lambda^N \\ \psi(N) = \psi(N-1) = -1 \end{cases}$$

Solving simultaneously we obtain for $\Omega(N)$,

$$\Omega(N) = \lambda^N - 1$$

so that the secular equation is,

8) $$|\lambda I - S| = \lambda^N - 1 = 0$$

The characteristic roots are,

9) $$\lambda_n = \lambda^n = e^{2\pi \frac{n}{N} \sqrt{-1}}$$

where of course n is reduced modulo N. According to the program for diagonalizing a matrix, we now seek the adjoint of $(\lambda I - S)$. Since the characteristic roots are distinct, the adjoint should be of unit rank. Expressing the inverse in terms of the adjoint,

$$(\lambda I - S)^{-1} = \frac{\text{adj.}\,(\lambda I - S)}{|\lambda I - S|} = \frac{\text{adj.}\,(\lambda I - S)}{\lambda^N - 1}$$

we now solve for the adjoint,

$$\text{adj.}\,(\lambda I - S) = \frac{\lambda^N I - I}{\lambda I - S} = \frac{\lambda^N I - S^N}{\lambda I - S}$$

If we carry out the division formally we obtain,

$$\text{adj.}\,(\lambda I - S) = \sum_{\gamma=1}^{N} \lambda^{N-\gamma} S^{\gamma-1} = \sum_{\gamma=1}^{N} \lambda^{N-\gamma}\left[\delta^N_{i+\gamma-1,\,j}\right]$$

$$= \left[\sum_{\gamma=1}^{N} \lambda^{N-\gamma}\, \delta^N_{i+\gamma-1,\,j}\right]$$

$$= \left[\lambda^{N+i-j-1}\right]$$

For a particular root, λ_n, we can obtain a factored form of the adjoint, in terms of vectors, because of its unit rank.

$$\text{adj.}\,(\lambda I - S) = \left[\lambda_n^{N+i-j-1}\right]$$

$$= \left[\lambda_n^{i-1}\right]\left[\lambda_n^{N-j}\right]$$

We now obtain the modal columns for the required transformation,

$$K_n = \left[\lambda_n^{i-1}\right] = \left[\lambda^{n(i-1)}\right]$$

By arranging the modal columns conveniently we obtain the following modal matrix and its inverse,

10) $$\begin{cases} K = \left[\lambda^{ij}\right] \\ K^{-1} = \frac{1}{N}\left[\lambda^{-ij}\right] \end{cases}$$

In order that the transformation does not change the unit of length in the new coordinates, it is necessary to normalize the matrix K. This means that we require that the determinant of the modal matrix have an absolute value of unity. Observe that,

$$K^2 = N[\delta_{i,-j}]$$

and also,

$$\begin{cases} K^4 = N^2 I \\ |K|^4 = N^{2N} \\ |K| = N^{\frac{1}{2}N} \end{cases}$$

We thus choose the normalized modal matrix and its inverse,

11) $$\begin{cases} K = \frac{1}{\sqrt{N}}[\lambda^{ij}] \\ K^{-1} = \frac{1}{\sqrt{N}}[\lambda^{-ij}] \end{cases}$$

The transformation will involve the following transformations of S and S^{-1},

12) $$\begin{cases} K^{-1}SK = [\lambda^i \delta_{ij}] \\ K^{-1}S^{-1}K = [\lambda^{-i}\delta_{ij}] \end{cases}$$

The normal coordinates of the lattice are obtained from the transformation, K. Let q be the vector of the normal coordinates, then,

13) $$u = Kq$$

By means of 13), 7) can now be expressed in normal coordinates,

$$K\ddot{q} + \frac{2\alpha}{m}\left(I - \frac{S+S^{-1}}{2}\right)Kq = 0$$

multiplying by K^{-1} we obtain,

14) $$\ddot{q} + \frac{2\alpha}{m}\left(I - [\delta_{ij}\cos 2\pi \tfrac{i}{N}]\right)q = 0$$

14) is the differential equation for simple harmonic vibration, with the frequency,

15) $$\begin{cases} \omega_i^2 = (2\pi\nu_i)^2 = \frac{2\alpha}{m}\left(1 - \cos 2\pi\frac{i}{N}\right) = \frac{4\alpha}{m}\sin^2 \pi\frac{i}{N} \\ \Lambda = [\omega_i \delta_{ij}] \end{cases}$$

The equation and its solution become,

$$\text{16)}\quad \begin{aligned} &\ddot{q} + \Lambda^2 q = 0 \\ &q = \cos \Lambda t \; A + \sin \Lambda t \;\; B \end{aligned}$$

A and B are arbitrary constant vectors. We observe that the transformation K is complex, whereas the vector u is real. There must then be some relationship among the elements of q. Thus, from 13),

$$u_i = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} \lambda^{ij} q_j = \frac{1}{2\sqrt{N}} \sum_{j=1}^{N} (\lambda^{ij} q_j + \lambda^{-ij} q_{N-j})$$

a sufficient condition that u is real is readily seen to be,

$$\text{17)}\quad q_r = q^*_{N-r}$$

where, q^* is the complex conjugate of q. A transformation of q to real coordinates, which satisfies 17), is seen to be,

$$\text{18)}\quad \begin{cases} \sqrt{2}\, q_r = \varphi_r + i\,\varphi_{N-r}, & r < \frac{N}{2} \\ q_{\frac{N}{2}} = \varphi_{\frac{N}{2}} \\ \sqrt{2}\, q_r = \varphi_{N-r} - i\,\varphi_r, & r > \frac{N}{2} \\ q_N = \varphi_N \end{cases}$$

A and B in 16) are multiplied by diagonal matrices, and thus their terms differ from those of q only by real multipliers, so that they are subject to conditions similar to 17),

$$\begin{cases} A_r = A^*_{N-r} \\ B_r = B^*_{N-r} \end{cases}$$

and must be transformed to real constants by transformations similar to 18),

$$\text{19)}\quad \begin{cases} \sqrt{2}\, A_r = a_r + i\,a_{N-r}, \; r < \frac{N}{2} \\ A_{\frac{N}{2}} = a_{\frac{N}{2}} \\ \sqrt{2}\, A_r = a_{N-r} - i\,a_r, \; r > \frac{N}{2} \\ A_N = a_N \end{cases} \qquad \begin{cases} \sqrt{2}\, B_r = b_r + i\,b_{N-r}, \; r < \frac{N}{2} \\ B_{\frac{N}{2}} = b_{\frac{N}{2}} \\ \sqrt{2}\, B_r = b_{N-r} - b_r, \; r > \frac{N}{2} \\ B_N = b_N \end{cases}$$

We must now normalize the matrix of transformations 18) and 19).

This matrix is, explicitly,

$$
\begin{array}{c}
1 \\ 2 \\ 3 \\ \vdots \\ r \\ \vdots \\ \frac{N}{2} \\ \vdots \\ N-r \\ \vdots \\ N-3 \\ N-2 \\ N-1 \\ N
\end{array}
\begin{pmatrix}
\frac{1}{\sqrt2} & 0 & 0 & \cdots & 0 & \cdots & 0 & \cdots & 0 & \cdots & 0 & 0 & \frac{i}{\sqrt2} & 0 \\
0 & \frac{1}{\sqrt2} & 0 & \cdots & 0 & \cdots & 0 & \cdots & 0 & \cdots & 0 & \frac{i}{\sqrt2} & 0 & 0 \\
0 & 0 & \frac{1}{\sqrt2} & \cdots & 0 & \cdots & 0 & \cdots & 0 & \cdots & \frac{i}{\sqrt2} & 0 & 0 & 0 \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
0 & 0 & 0 & \cdots & \frac{1}{\sqrt2} & \cdots & 0 & \cdots & \frac{i}{\sqrt2} & \cdots & 0 & 0 & 0 & 0 \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
0 & 0 & 0 & \cdots & 0 & \cdots & 1 & \cdots & 0 & \cdots & 0 & 0 & 0 & 0 \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
0 & 0 & 0 & \cdots & \frac{1}{\sqrt2} & \cdots & 0 & \cdots & \frac{-i}{\sqrt2} & \cdots & 0 & 0 & 0 & 0 \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
0 & 0 & \frac{1}{\sqrt2} & \cdots & 0 & \cdots & 0 & \cdots & 0 & \cdots & \frac{-i}{\sqrt2} & 0 & 0 & 0 \\
0 & \frac{1}{\sqrt2} & 0 & \cdots & 0 & \cdots & 0 & \cdots & 0 & \cdots & 0 & \frac{-i}{\sqrt2} & 0 & 0 \\
\frac{1}{\sqrt2} & 0 & 0 & \cdots & 0 & \cdots & 0 & \cdots & 0 & \cdots & 0 & 0 & \frac{-i}{\sqrt2} & 0 \\
0 & 0 & 0 & \cdots & 0 & \cdots & 0 & \cdots & 0 & \cdots & 0 & 0 & 0 & 1
\end{pmatrix}
$$

If we add the (N- r)th row to the rth row, the matrix becomes,

$$
\begin{pmatrix}
\frac{2}{\sqrt2} & 0 & & 0 & 0 & 0 \\
0 & \frac{2}{\sqrt2} & & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 \\
0 & \frac{1}{\sqrt2} & & \frac{-i}{\sqrt2} & 0 & 0 \\
\frac{1}{\sqrt2} & 0 & & 0 & \frac{-i}{\sqrt2} & 0 \\
0 & 0 & & 0 & 0 & 1
\end{pmatrix}
$$

The matrix is now triangularized so that its determinant is equal to the product of the diagonal elements, which has the absolute value of unity, so that we see that the transformations 18) and 19) are already normalized. We can now obtain a real solution of the dynamical problem by combining 13), 16) and 19). In explicit form the solution is,

$$
20)\quad u_i = \frac{1}{\sqrt2}\sum_{r=1}^{N}\Big\{\Big[a_r \cos 2\pi\frac{ir}{N} - a_{N-r}\sin 2\pi\frac{ir}{N}\Big]\cos\frac{2\alpha}{m}\Big(1-\cos 2\pi\frac{r}{N}\Big)t + \Big[b_r\cos 2\pi\frac{ir}{N} - b_{N-r}\sin 2\pi\frac{ir}{N}\Big]\sin\frac{2\alpha}{m}\Big(1-\cos 2\pi\frac{r}{N}\Big)t\Big\}
$$

20) can be simplified by shifting terms and employing trigonometric substitution. 20) then becomes

$$21) \quad U_i = \sum_{r=1}^{N} (a_r \cos \omega_r^2 t + b_r \sin \omega_r^2 t) \sin(2\pi \frac{ir}{N} + \frac{\pi}{4})$$

We now wish to obtain the energy expressions 6) in terms of the new coordinates. To do this we note the results,

$$22) \quad \begin{cases} K = K^T \\ K^2 = [\delta_{i,-j}] \\ KSK = [\lambda^j \delta_{i,-j}] \\ KS^{-1}K = [\lambda^{-j} \delta_{i,-j}] \end{cases}$$

Then applying 22) and 13) to 6) we get the result,

$$23) \quad \begin{cases} T = \frac{m}{2} \dot{q} [\delta_{i,-j}] \dot{q} = \frac{m}{2} \sum_{r=1}^{N} \dot{q}_r \dot{q}_{N-r} \\ V = \alpha q [(1-\cos 2\pi \frac{j}{N}) \delta_{i,-j}] q = \alpha \sum_{r=1}^{N} (1-\cos 2\pi \frac{r}{N}) q_r q_{N-r} \\ \quad = \frac{m}{2} \sum_{r=1}^{N} \omega_r^2 q_r q_{N-r} \end{cases}$$

Applying the transformation 18) to 23),

$$24) \quad \begin{cases} T = \frac{m}{2} \sum_{r=1}^{N} \dot{\Phi}_r^2 \\ V = \frac{m}{2} \sum_{r=1}^{N} \omega_r^2 \Phi_r^2 \end{cases}$$

The energy expressions, 24), are now in normal coordinates, so that we can immediately express the state of the system in quantum mechanical language. From 24) we now get the quantum mechanical Hamiltonian,

$$25) \quad H = -\frac{\hbar^2}{2m} \sum_{r=1}^{N} \frac{\partial^2}{\partial \Phi_r^2} + \frac{m}{2} \sum_{r=1}^{N} \omega_r^2 \Phi_r^2$$

using 25), the Schroedinger equation for the system is,

$$26) \quad -\frac{\hbar^2}{2m} \sum_{r=1}^{N} \frac{\partial^2 \psi(\Phi)}{\partial \Phi_r^2} + \frac{m}{2} \sum_{r=1}^{N} \omega_r^2 \Phi_r^2 \psi(\Phi) = E \psi(\Phi)$$

We see at once that the variables are separable on the assumption,

$$27) \quad \begin{cases} \psi(\Phi) = \prod_{r=1}^{N} \chi_r(\Phi_r) \\ E = \sum_{r=1}^{N} E_r \end{cases}$$

Substituting 27) into 28), we can then separate variables and obtain N equations of the form,

28) $$\frac{d^2\chi_r(\Phi_r)}{d\Phi_r^2} + \left[\frac{2mE_r}{\hbar^2} - \left(\frac{m\omega_r \Phi_r}{\hbar}\right)^2\right]\chi_r(\Phi_r) = 0$$

We can simplify 28) by the following substitution,

29) $$\begin{cases} \lambda = \dfrac{2mE_r}{\hbar^2} \\ \alpha^2 = \dfrac{m\omega_r}{\hbar} \end{cases}$$

and obtain the solution for the r th normal mode,

30) $$\begin{cases} \chi_r(\Phi_r) = C_r e^{-\frac{\alpha_r}{2}\Phi_r^2} H_{n_r}(\sqrt{\alpha_r}\,\Phi_r) \\ \lambda = (2n_r+1)\alpha_r \\ C_r^2 = \left(\frac{\alpha_r}{\pi}\right)^{\frac{1}{2}}(n_r!\,2^{n_r})^{-1} \end{cases}$$

We obtain from 30) the energy eigenvalues,

31) $$E_r = (n_r + \tfrac{1}{2})\omega_r\hbar = (n_r+\tfrac{1}{2})h\nu_r$$

Combining the solutions 30) according to 27), the solution for the lattice becomes,

32) $$\begin{aligned} \psi(\Phi) &= \prod_{r=1}^{N}\left(\frac{\alpha_r}{\pi}\right)^{\frac{1}{4}}(n_r!\,2^{n_r})^{-\frac{1}{2}} e^{-\frac{\alpha_r}{2}\Phi_r^2} H_{n_r}(\sqrt{\alpha_r}\,\Phi_r) \\ E_n &= \sum_{r=1}^{N}\omega_r\hbar\,(n_r+\tfrac{1}{2}) \end{aligned}$$

Here, $H_n(x)$ is the nth Hermite polynomial in x. Equations 32) will be useful in the next section when we wish to obtain a perturbation of E_n corresponding to the addition of a higher term of 2) to the Hamiltonian, 25). We shall also need a more explicit form for the transformation to normal coordinates. Writing 13) out, we have,

$$\begin{aligned} u_i &= \frac{1}{\sqrt{N}}\sum_{r=1}^{N}\lambda^{ir}q_r = \frac{1}{2\sqrt{N}}\sum_{r=1}^{N}(\lambda^{ir}q_r + \lambda^{-ir}q_{N-r}) \\ &= \frac{1}{2\sqrt{N}}\sum_{r=1}^{N}\Big\{\left(\cos 2\pi\tfrac{ir}{N} + \sqrt{-1}\,\sin 2\pi\tfrac{ir}{N}\right)(\Phi_r + \sqrt{-1}\,\Phi_{N-r}) \\ &\qquad + \left(\cos 2\pi\tfrac{ir}{N} - \sqrt{-1}\,\sin 2\pi\tfrac{ir}{N}\right)(\Phi_r - \sqrt{-1}\,\Phi_{N-r}) \end{aligned}$$

$$u_i = \frac{1}{\sqrt{N}} \sum_{r=1}^{N} \left[\cos 2\pi \frac{ir}{N} + \sin 2\pi \frac{ir}{N}\right] \phi_r$$

By using a trigonometric identity, we obtain from this result,

33) $$u_i = \frac{2}{\sqrt{2N}} \sum_{r=1}^{N} \phi_r \sin\left(2\pi \frac{ir}{N} + \frac{\pi}{4}\right)$$

If we now designate the transforming matrix by,

34) $$L = \left[\frac{2}{\sqrt{2N}} \sin\left(2\pi \frac{ir}{N} + \frac{\pi}{4}\right)\right]$$

the transformation which reduces the energy terms to simple quadratic forms is,

35) $$u = L\phi$$

III EVALUATION OF THE ANHARMONIC ENERGY TERMS

In part II the normal coordinates of the lattice were obtained. That means that a coordinate system was chosen such that, in it, the kinetic and potential energy expressions were found to be linear combinations of the squares of the momenta and coordinates in that system. If we apply this transformation to the higher degree terms of the potential energy they will not, in general, be similarly reduced to simple powers, so that a complete solution of the dynamical equations is not generally feasible. We must instead treat the additional terms as perturbations of the Hamiltonian of the system.

The general expression in normal coordinates is obtained by applying the transformation 35) to 2). Thus, 35) written explicitly yields,

$$36)\begin{cases} u_i = \frac{2}{\sqrt{2N}} \sum_r \phi_r \sin\left(2\pi \frac{ir}{N} + \frac{\pi}{4}\right) \\ u_{i+1} - u_i = \frac{2}{\sqrt{2N}} \sum_r \left[\sin\left(2\pi \frac{(i+1)r}{N} + \frac{\pi}{4}\right) - \sin\left(2\pi\frac{ir}{N} + \frac{\pi}{4}\right)\right]\phi_r \\ \qquad = 2\sqrt{\frac{2}{N}} \sum_r \phi_r \sin \pi \frac{r}{N} \cos\left(2\pi \frac{(i+\frac{1}{2})r}{N} + \frac{\pi}{4}\right) \end{cases}$$

The summations will now be understood to run from one to N. We can simplify 36) by making the substitution,

$$37)\quad \sigma_{ir} = 2\sqrt{\frac{2}{N}} \sin \pi \frac{r}{N} \cos\left(2\pi \frac{(i+\frac{1}{2})r}{N} + \frac{\pi}{4}\right)$$

Applying these to equations 2), we obtain,

$$38)\begin{cases} T = \frac{m}{2} \sum_r \dot{\phi}_r^2 \\ V = \frac{m}{2} \sum_r \omega_r^2 \phi_r^2 + \sum_i \left[\beta\left(\sum_r \sigma_{ir}\phi_r\right)^3 + \gamma\left(\sum_r \sigma_{ir}\phi_r\right)^4 + \cdots\right] \end{cases}$$

Our purpose now is to apply the cubic terms of the potential energy series as perturbation on the result 32). The change in the Hamiltonian is,

39) $$\Delta H = \Delta V = \beta \sum_i \left(\sum_r \sigma_{ir} \varphi_r\right)^3$$

and the first order perturbation of the energy is then,

$$\Delta E_n = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \beta \sum_i \left(\sum_r \sigma_{ir} \varphi_r\right)^3 \psi_n^2(\varphi)\, d\tau$$

40) $$= \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \beta \sum_i \left(\sum_r \sigma_{ir} \varphi_r\right)^3 \prod_r \left(\frac{\alpha_r}{\pi}\right)^{\frac{1}{2}} (n_r!\, 2^{n_r})^{-1} e^{-\alpha_r \varphi_r^2} H_{n_r}^2(\sqrt{\alpha_r}\, \varphi_r)\, d\varphi_r$$

We observe that on expanding 40) the integrand becomes odd in each φ_r, and since the integrals converge, they must all be zero, thus causing ΔE_n to vanish. We can see, moreover, that no odd powered term of 38) will contribute to the first order perturbation of the energy. We now consider the fourth powered terms to be the first contributing to the perturbation and observe that the only terms of $\gamma \sum_i \left(\sum_r \sigma_{ir} \varphi_r\right)^4$ which contribute are,

41) $$\Delta H = \gamma \sum_i \left[\sum_r \sigma_{ir}^4 \varphi_r^4 + 6 \sum_{r>s} \sigma_{ir}^2 \sigma_{is}^2 \varphi_r^2 \varphi_s^2\right]$$

Applying 41) as a perturbation on 32) we now obtain,

42) $$\Delta E_n = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \gamma \sum_i \left[\sum_i \sigma_{ir}^4 \varphi_r^4 + 6 \sum_{r>s} \sigma_{ir}^2 \sigma_{is}^2 \varphi_r^2 \varphi_s^2\right] \prod_t \sqrt{\frac{\alpha_t}{\pi}} (n_t!\, 2^{n_t})^{-1} \times e^{-\alpha_t \varphi_t^2} H_{n_t}^2(\sqrt{\alpha_t}\, \varphi_t)\, d\varphi_t$$

We now separate the variables in 42),

43) $$\Delta E_n = \gamma \sum_r \left[\sqrt{\frac{\alpha_r}{\pi}} (n_r!\, 2^{n_r})^{-1} \sum_i \sigma_{ir}^4\right] \int_{-\infty}^{\infty} \varphi_r^4 e^{-\alpha_r \varphi_r^2} H_{n_r}^2(\sqrt{\alpha_r}\, \varphi_r)\, d\varphi_r \times \prod_{t \neq r} \sqrt{\frac{\alpha_t}{\pi}} (n_t!\, 2^{n_t})^{-1} \int_{-\infty}^{\infty} e^{-\alpha_t \varphi_t^2} H_{n_t}^2(\sqrt{\alpha_t}\, \varphi_t)\, d\varphi_t$$
$$+ 6\gamma \sum_{r=s} \left[\sqrt{\frac{\alpha_r \alpha_s}{\pi^2}} (M_r!\, M_s!\, 2^{M_r + M_s})^{-1} \sum_i \sigma_{ir}^2 \sigma_{is}^2\right] \int_{-\infty}^{\infty} \varphi_r^2 e^{-\alpha \varphi_r^2} H_{n_r}^2 (\sqrt{\alpha_r}\, \varphi_r)\, d\varphi_r \int_{-\infty}^{\infty} \varphi_s^2 e^{-\alpha_s \varphi_s^2} H_{n_s}^2(\sqrt{\alpha_s}\, \varphi_s)\, d\varphi_s \times \prod_{t \neq r,s} \sqrt{\frac{\alpha_t}{\pi}} (n_t!\, 2^{n_t})^{-1} \int_{-\infty}^{\infty} e^{-\alpha_t \varphi_t^2} H_{n_t}^2(\sqrt{\alpha_t}\, \varphi_t)\, d\varphi_t$$

These integrals will be put in a more usual form if we make the substitution,

44) $$\xi_r = \sqrt{\alpha_r}\, \varphi_r$$

43) then becomes,

$$45)\ \Delta E_m = \gamma \sum_r \left[(\sqrt{\pi}\alpha_r m_r! 2^{m_r})^{-1} \sum_i \sigma_{ir}^4 \right] \int_{-\infty}^{\infty} \xi_r^4 e^{-\xi_r^2} H_{m_r}^2(\xi_r)\, d\xi_r \times \prod_{t\neq r} (\sqrt{\pi} m_t! 2^{m_t})^{-1} \int_{-\infty}^{\infty} e^{-\xi_t^2} H_{m_t}^2(\xi_t)\, d\xi_t$$

$$+ 6\gamma \sum_{r>s} \left[(\pi \alpha_r \alpha_s m_r! m_s!)^{-1} \sum_i \sigma_{ir}^2 \sigma_{is}^2 \right] \int_{-\infty}^{\infty} \xi_r^2 e^{-\xi_r^2} H_{m_r}^2(\xi_r)\, d\xi_r \times \int_{-\infty}^{\infty} \xi_s^2 e^{-\xi_s^2} H_{m_s}^2(\xi_s)\, d\xi_s \prod_{t\neq r,s} (\sqrt{\pi} m_t! 2^{m_t})^{-1} \int_{-\infty}^{\infty} e^{-\xi_t^2} H_{m_t}^2(\xi_t)\, d\xi_t$$

We are now ready to insert the values of the moments of the Hermite polynomials in place of these integrals. These moments are computed in Appendix I where we find for the zero th moment,

$$46)\ \int_{-\infty}^{\infty} e^{-\xi_t^2} H_{m_t}^2(\xi_t)\, d\xi_t = \sqrt{\pi}\, m_t!\, 2^{m_t}$$

Applying 46) to 45) we note that the extended products reduce to unity. If we now insert the values for the second and fourth moments,

$$47)\ \int_{-\infty}^{\infty} \xi_r^2 H_{m_r}^2(\xi_r) e^{-\xi_r^2} d\xi_r = \sqrt{\pi}\, m_r!^2\, 2^{m_r} \sum_{i=0}^{1,m_r} \frac{2^{i-1}}{(m_r-i)!}$$

$$48)\ \int_{-\infty}^{\infty} \xi_r^4 H_{m_r}^2(\xi_r) e^{-\xi_r^2} d\xi_r = \frac{3}{2}\sqrt{\pi}\, m_r!^2\, 2^{m_r} \sum_{i=0}^{2,m_r} \frac{2^i}{i!^2 (2-i)!(m_r-i)!}$$

45) now reduces to,

$$49)\ \Delta E_m = \frac{3\gamma}{2} \sum_r \frac{\sum_i \sigma_{ir}^4}{\alpha_r^2} \sum_{i=0}^{2,m_r} \frac{2^i m_r!}{i!^2(2-i)!(m_r-i)!} + \frac{3\gamma}{2} \sum_{r>s} \frac{\sum_i \sigma_{ir}^2 \sigma_{is}^2}{\alpha_r \alpha_s} \sum_{i,j=0}^{1,m_r,m_s} \frac{m_r! m_s! 2^{i+j}}{(m_r-i)!(m_s-j)!}$$

There now remains the summation of σ's to be determined. We first obtain σ_{ir}^4 by applying appropriate trigonometric transformations to 37),

$$50)\ \sigma_{ir}^4 = \frac{8}{N^2} \sin^4 \pi\frac{r}{N} \left\{ 3 + \cos\left[\frac{4ri}{N} + \left(\frac{2r}{N} + \frac{1}{2}\right)\right]2\pi + 4\cos\left[\frac{2ri}{N} + \left(\frac{r}{N} + \frac{1}{4}\right)\right]2\pi \right\}$$

With the aid of Appendix II we now sum σ_{ir}^4 to obtain,

$$51)\ \sum_{i=1}^{N} \sigma_{ir}^4 = \frac{8}{N} \sin^4 \pi\frac{r}{N} \left\{ 3 + \cos\left(\frac{2r}{N} + \frac{1}{2}\right)2\pi\, \delta_{4r,0}^{N} \right\}$$

The same process applied to $\sigma_{ir}^2 \sigma_{is}^2$ yields, first,

$$\sigma_{ir}\sigma_{is} = \frac{4}{N} \sin\pi\frac{r}{N} \sin\pi\frac{s}{N} \left\{ \cos\left[\frac{(r+s)i}{N} + \left(\frac{r+s}{2N} + \frac{1}{4}\right)\right]2\pi + \cos\left[\frac{(r-s)i}{N}\right]2\pi \right\}$$

or,

52) $\sigma_{ir}^2\sigma_{is}^2 = \frac{8}{N^2}\sin^2\pi\frac{r}{N}\sin^2\pi\frac{s}{N}\Big\{2+2\cos\left[\frac{2ri}{N}+\left(\frac{r+s}{N}+\frac{1}{4}\right)\right]2\pi+2\cos\left[\frac{2si}{N}+\left(\frac{r+s}{N}+\frac{1}{4}\right)\right]2\pi$
$+\cos\left[\frac{2(r+s)i}{N}+\left(\frac{r+s}{N}+\frac{1}{2}\right)\right]2\pi+\cos\left[\frac{2(r-s)i}{N}\right]2\pi\Big\}.$

Summing, this becomes,

53) $\sum_{i=1}^{N}\sigma_{ir}^2\sigma_{is}^2 = \frac{8}{N}\sin^2\pi\frac{r}{N}\sin^2\pi\frac{s}{N}\Big\{2+2\cos\left(\frac{r+s}{2N}+\frac{1}{4}\right)2\pi\,\delta^N_{2r,0}+2\cos\left(\frac{r+s}{N}+\frac{1}{4}\right)2\pi\,\delta^N_{2s,0}$
$+\cos\left(\frac{r+s}{N}+\frac{1}{2}\right)2\pi\,\delta^N_{2(r+s),0}+\delta^N_{2r,2s}\Big\}$

Before using these results we need to consider a method of simplification. We observe that if N is odd, all of the δ terms vanish. On physical grounds we can see that this should have negligible effect on the energy for large N, and in fact, we can see that inasmuch as the δ's reduce these to very occasional terms, it is reasonable to suppose that the effect would be slight for large N. We can consider that the energy correction due to these terms would actually be an approximate measure of the change in energy of a lattice in passing from an even to an odd number of atoms. We shall neglect this energy by considering here only an odd number of atoms. For N odd we obtain, by applying 15) and 29) and 50) -53) to 49),

54) $\Delta E_n = \frac{3\hbar^2\gamma}{Nm\alpha}\Big\{3\sum_r \sin^2\pi\frac{r}{N}\sum_{i=0}^{2,n_r}\frac{2^i n_r!}{i!^2(2-i)!(n_r-i)!}$
$+2\sum_{r>s}\sin\pi\frac{r}{N}\sin\pi\frac{s}{N}\sum_{i,j=0}^{1,n_r,n_s}\frac{2^{i+j}n_r!\,n_s!}{(n_r-i)!(n_s-j)!}\Big\}$

If we make the additional assumption that no eigenvalue, n, is less than two (which is unimportant at high energy), 54) reduces to,

55) $\Delta E_n = \frac{3\hbar^2\gamma}{2Nm\alpha}\Big\{3\sum_r \sin^2\pi\frac{r}{N}(2n_r^2+2n_r+1)$
$+4\sum_{r>s}\sin\pi\frac{r}{N}\sin\pi\frac{s}{N}(4n_r n_s+2n_r+2n_s+1)\Big\}$

We are now interested in comparing this with the energy for the harmonic potential from 32),

56) $E_n = \hbar\sqrt{\frac{\alpha}{m}}\sum_r \sin\pi\frac{r}{N}(2n_r+1)$

In order to complete the comparison we need to determine some distribution of the eigenvalues among the modes of vibration. For a first comparison we can make the assumption that all the modes of vibration are equally likely and thus take all the eigenvalues to be equal. 55) and 56) can then be summed with the aid of Appendix II and we obtain,

$$57)\ \Delta E_n = \frac{3\hbar^2\gamma}{4\pi^2 m\alpha}\left[3\pi^2(2n^2+2n+1)+16(4n^2+4n+1)N\right]$$

$$58)\ E_n = \frac{4\hbar N}{\pi}\sqrt{\frac{\alpha}{m}}\left(n+\frac{1}{2}\right)$$

Another useful comparison is that for a distribution of eigenvalues which makes 55) a maximum with 56) as a restraint. Using the method of Lagrange multipliers, we set the total differentials of 55) and 56) equal to zero,

$$59)\ 3\sum_r \sin^2\pi\frac{r}{N}(4n_r+2)dn_r + 4\sum_{r>s}\sin\pi\frac{r}{N}\sin\pi\frac{s}{N}\left[(4n_s+2)dn_r+(4n_r+2)dn_s\right]=0$$

Combining terms with like differentials this becomes,

$$\sum_r\left\{3\sin^2\pi\frac{r}{N}(2n_r+1)+4\sum_{s=1}^{r-1}\sin\pi\frac{r}{N}\sin\pi\frac{s}{N}(2n_s+1)\right\}dn_r$$
$$+4\sum_{r=1}^{N}\sum_{s=1}^{r-1}\sin\pi\frac{r}{N}\sin\pi\frac{s}{N}(2n_r+1)dn_s=0$$

In the second term we can interchange the order of summation according to, $\displaystyle\sum_{r=1}^{N}\sum_{s=1}^{r-1}=\sum_{s=1}^{N-1}\sum_{r=s+1}^{N}$

thus isolating the coefficients of the differentials, so that we obtain,

$$60)\ \sum_r\left\{3\sin^2\pi\frac{r}{N}(2n_r+1)+4\sum_{s\neq r}\sin\pi\frac{r}{N}\sin\pi\frac{s}{N}(2n_s+1)\right\}dn_r=0$$

Now differentiating 56) we obtain a second equation corresponding to the restraining condition,

$$61)\ \sum_r \sin\pi\frac{r}{N}\,dn_r=0$$

An arbitrary linear combination of 60) and 61) is,

$$62)\ \sum_r\left\{3\sin^2\pi\frac{r}{N}(2n_r+1)+4\sum_{s\neq r}\sin\pi\frac{r}{N}\sin\pi\frac{s}{N}(2n_s+1)-\lambda\sin\pi\frac{r}{N}\right\}dn_r=0$$

The differentials are, however, arbitrary so that we can set each coefficient equal to zero and solve for λ

$$63)\ \lambda = 3 \sin\pi\tfrac{r}{N}(2n_r+1) + 4\sum_{s\neq r}\sin\pi\tfrac{s}{N}(2n_s+1)$$

$$= \sum_r \sin\pi\tfrac{r}{N}(2n_r+1)(4-\delta_{rs})$$

Since λ is independent of S, we subtract equations for S = S and S = t,

$$\sum_r \sin\pi\tfrac{r}{N}\left\{(2n_r+1)(4-\delta_{rs}) - (2n_r+1)(4-\delta_{rt})\right\} = 0$$

or,

$$\sum_r \sin\pi\tfrac{r}{N}(2n_r+1)(\delta_{rt}-\delta_{rs}) = 0$$

Separating the terms, the summation reduces to two terms,

$$\sin\pi\tfrac{s}{N}(2n_s+1) = \sin\pi\tfrac{t}{N}(2n_t+1)$$

Choosing, t = 1
S = i ,

$$64)\ \sin\pi\tfrac{i}{N}(2n_i+1) = \sin\pi\tfrac{1}{N}(2n_1+1)$$

and solving for n_i,

$$65)\ n_i = -\tfrac{1}{2} + (n_1+\tfrac{1}{2})\frac{\sin\frac{\pi}{N}}{\sin\pi\frac{i}{N}}$$

We now apply the restraint, 56). Substituting for n_i from 65),

$$66)\ E_n = \hbar\sqrt{\tfrac{\alpha}{m}}\sum_r (2n_1+1)\sin\tfrac{\pi}{N}$$

Carrying out the summation and then solving for u_1,

$$67)\ n_1 = -\tfrac{1}{2} + \frac{E}{2\hbar\sqrt{\frac{\alpha}{m}}\,N\sin\pi\frac{1}{N}}$$

we can now evaluate n_i completely by substituting 67) in 65),

$$68)\ n_i = -\tfrac{1}{2} + \frac{E}{2\hbar\sqrt{\frac{\alpha}{m}}\,N\sin\pi\frac{i}{N}}$$

which is the required distribution which produces a maximum

ΔE_n due to its quadratic form with leading coefficients positive. It is now convenient to make the simplification,

$$69)\ \tau = \frac{\pi E}{4\hbar\sqrt{\frac{\alpha}{m}}\,N}$$

then 68) becomes,

$$70)\ n_i = -\tfrac{1}{2} + \frac{2\tau}{\pi\sin\pi\frac{i}{N}}$$

and applying this distribution to 55),

$$71)\ \Delta E = \frac{3\hbar^2\gamma}{4\pi^2 N m\alpha}\left\{3\sum_r\left[\pi^2\sin^2\pi\tfrac{r}{N} + 16\tau^2\right]\right.$$

$$\left. + 8\sum_{r>s}\left[\pi^2\left(\sin\pi\tfrac{r}{N}\sin\pi\tfrac{s}{N} - 1\right) + 16\tau^2\right]\right\}$$

Carrying out the summations we obtain,

$$72)\ \Delta E = \frac{3\hbar^2 \gamma}{8\pi^2 m \alpha}\left\{3\left(\pi^2 + 32\Upsilon^2\right) + 8\left(4 - \pi^2 + 16\Upsilon^2\right)N\right\}$$

and from 70) and 56) we have for E,

$$73)\ E = \frac{4\hbar N}{\pi}\sqrt{\frac{\alpha}{m}}\,\Upsilon$$

We can now regard Υ as a generalized eigenvalue which takes on values determined by the integers m_r according to 56) and 69). We are interested in the ratio $\Delta E/E$, and, for high energy and high N, we can neglect the lower powers of Υ and N. Thus 57) with 58) and 72) with 73) yield,

$$74)\ \frac{\Delta E}{E} = \frac{12 n \hbar \gamma}{4\pi\alpha\sqrt{m\alpha}}$$

$$75)\ \frac{\Delta E}{E} = \frac{12 \Upsilon \hbar \gamma}{4\pi\alpha\sqrt{m\alpha}}$$

which is to say that the distribution of eigenvalues which gives a maximum perturbation at high energy is the same as that for which all eigenvalues are the same.

We need finally to express the energy in terms of the temperature in order to evaluate the effect of the anharmonic potential terms as a function of the temperature. For this we must find the partition function[9,83],

$$76)\qquad \log Z(T) = -N\int_0^{\nu_{max}} g(\nu)\log\left(1 - e^{-h\nu/kT}\right)d\nu$$

such that, $\int_0^{\nu_{max}} g(\nu)\,d\nu = \phi$

where $Ng(\nu)\,d\nu$ is the number of normal modes of vibration in the frequency interval ν to $\nu + d\nu$. From 15) we have an expression for the frequency of the ith mode of vibration,

$$77)\ \nu_i = \frac{1}{\pi}\sqrt{\frac{\alpha}{m}}\sin\pi\frac{i}{N}$$

thus,

$$78)\ \nu_{max} = \frac{1}{\pi}\sqrt{\frac{\alpha}{m}}$$

and if we define,

$$79)\ \begin{cases} \varphi_i = \pi\dfrac{i}{N} \\ f_i = \dfrac{\nu_i}{\nu_{max}} = \dfrac{\nu_i}{\nu_L} \end{cases}$$

77) becomes,

80) $f_i = \sin \varphi_i$

The number of frequencies less than $\nu = f\nu_L$ is given by the sum,

81) $N(f\nu_L) = \sum_{\varphi_i=0}^{\sin^{-1} f_i} 1 \xrightarrow[N\to\infty]{} \int_0^{\sin^{-1} f} d\varphi = \sin^{-1} f$

and the fraction of frequencies less than ν is,

82) $\lim_{N\to\infty} \frac{N(f\nu_L)}{N} = \frac{1}{\pi} \sin^{-1} f$

Where π is the length of the interval, treating the points as being dense. We obtain the desired distribution function by differentiating 82) with respect to ν,

83) $g(\nu) = \frac{1}{\pi}\frac{\partial}{\partial \nu} \sin^{-1} f = \frac{1}{\pi}\frac{\partial}{\partial \nu} \sin^{-1}\frac{\nu}{\nu_L} = \frac{1}{\pi\sqrt{\nu_L^2 - \nu^2}}$

83) is normalized in the interval $\varphi = (0, \pi)$, or, f = (0,1) + (1,0), whereas 74) uses only half that interval, $\varphi = (0, \frac{\pi}{2})$, or, f = (0,1), so that in this interval, the normalized distribution function is,

84) $g(\nu) = \frac{2}{\pi\sqrt{\nu_L^2 - \nu^2}}$

The total energy of the lattice is given in terms of the partition function by,

85) $$E(T) = NkT^2 \frac{\partial \log z}{\partial T}$$
$$= N \int_0^{\nu_L} \frac{h\nu g(\nu)\, d\nu}{e^{h\nu/kT} - 1}$$

Applying 84), this now yields,

86) $$E = \frac{2N}{\pi} \int_0^{\nu_L} \frac{h\nu (\nu_L^2 - \nu^2)^{-\frac{1}{2}}}{e^{h\nu/kT} - 1}\, d\nu$$

we note that, $\lim_{x\to 0} x \div (e^x - 1) = 1$ so that, for large T, we can replace $(e^{h\nu/kT} - 1)$ with $h\nu/kT$. Then 86) becomes, with f as the variable of integration,

87) $$E = \frac{2NkT}{\pi} \int_0^1 \frac{h\nu_L f (\nu_L^2 - \nu^2)^{-\frac{1}{2}}}{h\nu_L f/kT}\, \nu_L\, df$$
$$= \frac{2NkT}{\pi} \int_0^1 \frac{df}{\sqrt{1 - f^2}} = NkT$$

Now substituting 87) in 69), which applies for large T and τ, we obtain,

88) $\Gamma = \frac{\pi k T}{4\hbar\sqrt{\frac{\alpha}{m}}}$

so that 75) finally becomes,

89) $\frac{\Delta E}{E} = \frac{3\gamma k T}{\alpha^2}$

or, replacing E with 85),

90) $\Delta E = \frac{3\gamma N k^2}{\alpha^2} T^2$

This is now an expression which can be used to give us correction terms to thermodynamic quantities. Thus the total energy and the specific heat have the values,

91) $E = NkT + \frac{3\gamma N k^2}{\alpha^2} T^2$

92) $C_v = Nk + \frac{6\gamma N k^2}{\alpha^2} T$

IV CONCLUSION

By carrying out a perturbation procedure corresponding to a deviation from harmonic vibration of the lattice, it has been found that to the first order perturbation, the third degree potential terms do not contribute,nor in fact, that any terms containing a normal mode variable to an odd power contribute to the energy of the lattice. With this conclusion we then considered those members of the fourth degree term which contained only even powered variables. We should, however, consider the effect of this choice. There always arises a question, when considering second order effects, due to competing effects. For example, in considering anharmonicity as a second order effect, we might also consider second or third-neighboring atoms as well as first in constructing the potential energy expression. In this problem, however, we were concerned mainly with the deviation with increase in temperature, and we could then assume that anharmonicity was the first effect to be considered. In choosing to examine the fourth powered potential terms, when the third degree term was seen to vanish for the first order perturbation, however, it would also be significant to examine the second order perturbation due to the third degree term, which presumably would not be zero and which might even have an effect comparable to the perturbation that was considered.

The next decision that arose was to simplify the expressions 51) and 53) by assuming an odd number of lattice points. Again, the effect of this choice might well be investigated, although, on superficial examination of the terms themselves, as well as on physical or intuitive grounds, we can concede that for a large number of atoms, oddness or evenness should not make a significant difference in the total energy of the lattice. We were then able to arrive at 55) as a fairly general first approximation to the energy due to anharmonicity. We observe, however, that this does not give us a unique result, since, according to the statistical mechanical hypothesis of equipartition of energy, all values of the eigenvalues, and thus a wide variety of values for ΔE, are allowed which are consonant with a given value for the total energy, E, at a given temperature. Here also we have alternative approaches. We could either investigate the range of possible values of ΔE, or else find the distribution function for the proportion of systems (considered statistically) which has a given distribution of eigenvalues from $(E + \Delta E)$ and then compute the average value of the total energy. We chose the first alternative as being the simpler and computed ΔE on the basis that all modes of vibration are equally likely, thus arriving at 57). Then using the Lagrange method of undetermined multipliers, we found the distribution of eigenvalues which made ΔE a maximum, given by 72). We then observed that at high temperatures the two results become equal, and so we concluded that the maximum value is approached asymptotically at high temperatures. Next we found the frequency distribution for the unperturbed energy and from it the value of the energy in terms of the temperature. In doing this it was necessary to make the assumption, at 86), that,

$$\frac{h\nu}{\kappa T} < \frac{h\nu_L}{\kappa T} << 1$$

or, in terms of an actual crystal, using the Debye temperature,

$$\frac{\theta_D}{T} << 1$$

From values of θ_D for several crystals*, it is seen that the

*C. F. Fowler and Guggenheim, "Statistical Thermodynamics," p. 145, table 3.

values are generally less than half the melting point, so that there is some range in which the assumption is valid. With the energy terms expressed in terms of T, we then obtain the expression 89) for the ratio,

$$\frac{\Delta E}{E} = \frac{48\gamma kT}{\alpha^2}$$

From the data for various elements we find from 92) that α is of about the same order as k. Assuming that γ is of about the same order of magnitude as α_1, we conclude that the ratio might be of the order of unity. Thus, while our purpose has not been to obtain physical conclusions, but only to carry through the necessary mathematics, we see that the anharmonic energy term is of a magnitude which requires that it should be examined in each case to determine at what temperature it becomes effective.

APPENDIX I

Determination of the Moments of the Hermite Polynomials.

We wish to evaluate the following integral,

$$P^r_{mn} = \int_{-\infty}^{\infty} \xi^r H_m(\xi) H_n(\xi) e^{-\xi^2} d\xi$$

First set up the generating function H_n

$$\begin{cases} \Gamma(\xi, s) = \sum_m \frac{H_m(\xi)}{m!} s^m = e^{\xi^2 - (s-\xi)^2} \\ T(\xi, t) = \sum_n \frac{H_n(\xi)}{n!} t^n = e^{\xi^2 - (t-\xi)^2} \end{cases}$$

Now form,

$$\begin{aligned} \int_{-\infty}^{\infty} \xi^r \Gamma T e^{-\xi^2} d\xi &= \sum_{m,n} s^m t^n \int_{-\infty}^{\infty} \xi^r \frac{H_m(\xi) H_n(\xi)}{m!\, n!} e^{-\xi^2} d\xi \\ &= \sum_{m,n} \frac{s^m t^n}{m!\, n!} P^r_{mn} \\ &= \int_{-\infty}^{\infty} \xi^r e^{-s^2 - t^2 + 2s\xi + 2t\xi - \xi^2} d\xi \\ &= e^{2st} \int_{-\infty}^{\infty} \xi^r e^{-(\xi - s - t)^2} d\xi \end{aligned}$$

In order to replace (ξ -s -t) with p in the last integral,

form the Taylor's expansion for ξ^r

$$\xi^r = \sum_{i=0} a_i (\xi - s - t)^i = \sum_{i=0}^{r} \frac{r^{[i]}}{i!} (s+t)^{r-i} (\xi - s - t)^i$$

making this substitution we obtain,

$$\sum_{mn} \frac{s^m t^n}{m!\, n!} P^r_{mn} = \sum_{i=0}^{r} \frac{r^{[i]}}{i!} (s+t)^{r-i} e^{2st} \int_{-\infty}^{\infty} (\xi - s - t)^i e^{-(\xi - s - t)^2} d(\xi - s - t)$$

In terms of, $p = \xi - s - t$ this becomes,

$$\sum_{mn} \frac{s^m t^n}{m!\, n!} P^r_{mn} = \sum_{i=0}^{r} \frac{r^{[i]}}{i!} (s+t)^{r-i} e^{2st} \int_{-\infty}^{\infty} p^i e^{-p^2} dp$$

The integrand of $\int_{-\infty}^{\infty} p^i e^{-p^2} dp$ is odd, so that, since the integral always converges, it vanishes unless i is even. Now form the generating integral,

$$\int_{-\infty}^{\infty} e^{-\gamma p^2} dp = \gamma^{-\frac{1}{2}} \int_{-\infty}^{\infty} e^{-p^2} dp = \sqrt{\pi}\, \gamma^{-\frac{1}{2}}$$

Differentiate i/2 times with respect to γ ,

$$(-1)^{i/2} \int_{-\infty}^{\infty} p^i e^{-\gamma p^2} dp = \sqrt{\pi} \left(-\tfrac{1}{2}\right)^{[i/2]} \gamma^{-\frac{1}{2} - \frac{i}{2}}$$

Setting γ = 1 and observing the above remarks, this becomes,

$$(-1)^{i/2} \int_{-\infty}^{\infty} p^i e^{-p^2} dp = \sqrt{\pi} \left(-\tfrac{1}{2}\right)^{[i/2]} \delta^{2}_{i,0}$$

Inserting this in the series, changing i to 2i.

$$\sum_{mn} \frac{s^m t^n}{m!\,n!} P^r_{mn} = \sqrt{\pi} \sum_{i=0}^{r/2} \frac{r^{[2i]} (-\frac{1}{2})^{[i]} (-1)^i}{(2i)!} (s+t)^{r-2i} e^{2st}$$

We can now write the form of the result at once in the usual manner for obtaining the coefficients in a Taylor's series.

$$P^r_{mn} = \sqrt{\pi} \sum_{i=0}^{\frac{r}{2}} \frac{r^{[2i]} (-\frac{1}{2})^{[i]} (-1)^i}{(2i)!} \frac{\partial^{m+n}}{\partial s^m \partial t^n} (s+t)^{r-2i} e^{2st} \Big|_{s=t=0}$$

It will be convenient to expand the terms to be differentiated in a power series, thus,

$$(s+t)^{r-2i} e^{2st} = \sum_{k=0}^{r-2i} \frac{(r-2i)^{[k]}}{k!} s^k t^{r-2i-k} \sum_{l=0}^{\infty} \frac{(2st)^l}{l!}$$

$$= \sum_{k=0}^{r-2i} \sum_{l=0}^{\infty} \frac{(r-2i)^{[k]} 2^l}{k!\,l!} s^{k+l} t^{r+l-2i-k}$$

Differentiating the series, we obtain the required derivatives,

$$\frac{\partial^{m+n}}{\partial s^m \partial t^n} (s+t)^{r-2i} e^{2st} \Big|_{s=t=0} = \sum_{k=0}^{r-2i} \sum_{l=0}^{\infty} \frac{(r-2i)^{[k]} 2^l}{k!\,l!} (k+l)^{[m]} (r+l-2i-k)^{[n]}$$

$$\times s^{k+l-m} t^{r+l-2i-k-n} \Big|_{s=t=0}$$

The series reduces to the terms which become constant after the differentiation, so that the non-vanishing of terms requires the condition,

$$\begin{cases} k+l-m = 0 \\ r+l-2i-k-n = 0 \end{cases}$$

which have the simultaneous solutions,

$$\begin{cases} k = \frac{m-n+r}{2} - i \\ l = \frac{m+n-r}{2} + i \end{cases}$$

Since k and l are integers, these give rise to the additional restrictions,

$$\begin{cases} m+n \equiv r \bmod(2) \\ m-n \equiv r \bmod(2) \end{cases}$$

Which we can see are both satisfied or not satisfied simultaneously so that the non-vanishing term of the series is,

$$\frac{(r-2i)^{\left[\frac{m-n+r}{2}-i\right]} 2^{\left(\frac{m+n-r}{2}+i\right)} m!\,n!}{\left(\frac{m-n+r}{2}-i\right)!\left(\frac{m+n-r}{2}+i\right)!}\delta^2_{r,m-n}$$

And now the limits of the series impose still further conditions on k and l,

$$\begin{cases} 0 \le \frac{m-n+r}{2} - i \le r-2i \\ 0 \le \frac{m+n-r}{2} + i \end{cases}$$

which we can arrange so as to indicate these as conditions on i,

$$\frac{r-(m+n)}{2} \le i \le \frac{r+m-n}{2}$$

$$i \le \frac{r-m+n}{2}$$

or more simply,

$$\frac{r-(m+n)}{2} \le i \le \frac{r-|m-n|}{2}$$

The resulting value for P^r_{mn} is now,

$$P^r_{mn} = \sqrt{\pi}\, m!\,n!\,\delta^2_{r,m-n} \sum_{i=0,\frac{r-(m+n)}{2}}^{\frac{r-|m-n|}{2}} \frac{r^{[2i]}(r-2i)^{\left[\frac{m-n+r}{2}-i\right]}\left(-\frac{1}{2}\right)^{[i]}(-1)^i\, 2^{\left(\frac{m+n-r}{2}+i\right)}}{(2i)!\left(\frac{m-n+r}{2}-i\right)!\left(\frac{m+n-r}{2}+i\right)!}$$

Some simplification is possible,

$$\begin{cases} r^{[2i]}(r-2i)^{\left[\frac{m-n+r}{2}-i\right]} = r^{\left[\frac{m-n+r}{2}+i\right]} \\ \left(-\frac{1}{2}\right)^{[i]} = (-1)^i 2^{-i}\,[1\cdot 3\cdot 5\cdot \cdots \cdot (2i-1)] \\ \qquad = (-1)^i 2^{-i}(2i-1)!! \\ \frac{(2i)!}{(2i-1)!!} = (2i)!! = 2^i\, i! \end{cases}$$

Thus,

$$P^r_{mn} = \sqrt{\pi}\, m!\,n!\,\delta^2_{r,m-n} \sum_{i=0,\frac{r-(m+n)}{2}}^{\frac{r-|m-n|}{2}} \frac{r^{\left[\frac{m-n+r}{2}+i\right]} 2^{\left(\frac{m+n-r}{2}\right)}}{(2i)!!\left(\frac{m-n+r}{2}-i\right)!\left(\frac{m+n-r}{2}+i\right)!}$$

We can finally write this result in the form,

$$\int_{-\infty}^{\infty} \xi^r H_m(\xi) H_n(\xi) e^{-\xi^2} d\xi = \sqrt{\pi}\, m!\,n!\,2^{\frac{m+n-r}{2}}\delta^2_{r,m-n}$$

$$\times \sum_{i=0,\frac{r-(m+n)}{2}}^{\frac{r-|m-n|}{2}} \left[2^i\, i!\left(\frac{m-n+r}{2}-i\right)!\left(\frac{n-m+r}{2}-i\right)!\left(\frac{m+n-r}{2}+i\right)!\right]^{-1}$$

A case of special interest is the expression for the diagonal terms, for which we record only the non-zero moments,

$$\int_{-\infty}^{\infty} \xi^{2r} H_n^2(\xi) e^{-\xi^2} d\xi = \sqrt{\pi}\, n!^2\, 2^{n-r} (2r)! \sum_{i=0,r-n}^{r} [2^i\, i!\, (r-i)!^2 (n-r+i)!]^{-1}$$

We can write this in a better form following the change of index,

$$i = r - j$$

The result now is,

$$\int_{-\infty}^{\infty} \xi^{2r} H_n^2(\xi) e^{-\xi^2} d\xi = \sqrt{\pi}\, n!^2 (2r)!\, 2^{n-r} \sum_{j=0}^{r,n} \frac{2^j}{j!^2 (n-j)!(r-j)!}$$

As a special case this yields the norm for the Hermite polynomials,

$$\int_{-\infty}^{\infty} H_n^2(\xi) e^{-\xi^2} d\xi = \sqrt{\pi}\, n!\, 2^n$$

APPENDIX II

Some trigonometric Summation Formulas and their Asymptotic Values.

1) $$\sum_{r=1}^{N} \sin \pi \frac{r}{N} = \frac{\sin \frac{\pi}{N}}{1-\cos\frac{\pi}{N}} \xrightarrow[N\to\infty]{} \frac{2}{\pi} N$$

2) $$\sum_{r=1}^{N} \sin^2 \pi \frac{r}{N} = \frac{1}{2} N$$

3) $$\sum_{r=1}^{N} \sin\left(\frac{kr}{N} + b\right) 2\pi = N \sin 2\pi b\, \delta_{k,0}^{N}, \quad k \text{ is an integer}$$

4) $$\sum_{r=1}^{N} \cos\left(\frac{kr}{N} + b\right) 2\pi = N \cos 2\pi b\, \delta_{k,0}^{N}, \quad k \text{ is an integer}$$

5) $$\sum_{r=1}^{N} \sum_{s=1}^{r-1} \sin \pi \frac{s}{N} = \frac{1}{2} N \frac{\sin \pi/N}{1-\cos \pi/N} \xrightarrow[N\to\infty]{} \frac{1}{\pi} N^2$$

6) $$\sum_{r=1}^{N} \sum_{s=1}^{r-1} \sin \pi \frac{r}{N} = \frac{1}{2(1-\cos \pi/N)^2} \left[N(1-\cos \pi/N)\sin \pi/N - 2\sin \pi/N + \sin 2\pi/N\right] \xrightarrow[N\to\infty]{} \frac{1}{\pi} N^2$$

7) $$\sum_{r=1}^{N} \sum_{s=1}^{r-1} \sin \pi \frac{r}{N} \sin \pi \frac{s}{N} = -\frac{1}{4} N + \frac{1}{2} \frac{\sin^2 \frac{\pi}{N}}{(1-\cos\frac{\pi}{N})^2}$$

8) $$\sum_{r=1}^{N} \sum_{s=1}^{r-1} 1 = \frac{N(N-1)}{2} \xrightarrow[N\to\infty]{} \frac{1}{2} N^2$$

BIBLIOGRAPHY

* 1. Planck's Theory of Radiation and the Theory of Specific Heats -
A. Einstein. Bern. Ann. Physik. 22, 180-90. (1907)

2. The Calculation of Molecular Vibration Frequencies. F. A. Lindemann. Physik. Chem. Inst. Berlin. Physik. ., 11, 609-12. (1910)

3. A Relation between the Elastic Behavior and Specific Heat of Solid Bodies with Monatomic molecules. A. Einstein. Ann. Physik, 34, 170-6. (1911)

4. New Problems in the Theory of Heat. W. Nevst. Sitzb. Akad. Wiss. Berlin, 1911, 65-90.
Application to Specific heat.

5. The Theory of Specific Heats and the Application of the Idea of Energy Units to Physics - Chemical Questions. W. Nevst.
Elektroohem., 17, 265-75. (1911)

6. Thermal Molecular Motion in Solid Bodies. A. Einstein. Ann. Physik, 35, 679-94. (1912)
Sp. Ht. & Ht. Cond.

* 7. Vibrations in Space Gratings (Molecular Frequencies) M. Born & Th. V. Karman. Physik. Z., 13, 297-309. (1912)
dynamics of mols. Einstein and Planck theories.

8. The Distribution of the Proper Periods of a Point Grating. M. Born & Th. V. Karman. Physik Z., 14, 65-71. (1913)
appl. Sp. Ht.

* 9. Theory of Specific Heats. M. Born & Th. V. Karman. Physik. Z., 14, 15-9. (1913)
quant. hyp. sp. Ht.

*10. Theory of Specific Heats. P. Debye. Ann. Physik., 39, 789-839. (1913)
Energy quant. Deg. of freed. vs. atoms.

11. Some Observations of the Thermal Conduction in Crystals. N. Botez & H. Hertenstein. Physik. ., 14, 332-6. (1913)
cond. in various directions.

12. The theory of Space-Grating Vibrations and the Specific Heat of Solid Substances. Hans Thirring. Physik. Z., 14, 867-73 (1913)
app. of Born & Karman Theory.

* References of more direct interest for this paper.

13. Evaluating the Characteristic Vibrations of Solid Bodies. Rudolf Crtvay. Ann. Physik. 42, 745-60. (1914)
Debye form. ext. to rhombic cryst.

14. Space Lattice Vibrations, and Specific Heats of Polyatomic Solids.
H. Thirring. Physik Z., 15, 127-33, 130-5 (1914)
Var. of Elast. Const. with temp. Born & Karman.
Ignores Debye formula.

15. The Method of Singular Vibrations in the Theory of Specific Heats.
M. Born. Physik. Z., 15, 185-91. (1914)

16. Variation of the Specific Heat of Solids with the Temperature. A. H. Compton. Phys. Rev. 6, 377-89 (1915)
Agglomeration vs. quant. hyp. in the solid state.

17. Compton's formula for the temperature variation of the specific heat of solids. F. Schwers. Phys. Rev. 8, 117-27. (1916)
Debye's superior.

18. Ultra-red dispersion of diatomic crystals. W. Dehlinger Physik. Z 15, 276-83. (1914)

19. Characteristic Ultra-red vibrations of diatomic crystals. M. Born. Physik. Z., 19, 539-48. (1918)

20. Specific heat and equation of state of crystals. K. Forsterling. Ann. Physik., 61, 549-76 (1920)
Using Hamilton's princ., Born & Debye methods.

*21. Specific heat of solids at high temperatures. M. Born and E. Brody. Z. Physik., 6, 132-9. (1921)

22. Thermodynamics of the Crystal lattice. M. Born. Z. Physik, 7, 217-48. (1921)

23. The behavior of solids at low temperatures. Walther Meissner. Z Ver dent. Jug. 66, 645-7, 876-8 (1922). (1922)
Nemst, Einstein, Debye sp. ht.
exp., elect. and ht. cond., thermoelect. and magnetism.

24. A quantum theory of the thermal conductivity in non-metallic crystals.
Yositosi. Endo. Sci. Repts., Tohoku Imp. Univ. 11, 183-93 (1922)
No good theory yet developed.

25. Thermodynamics of the crystal lattice II, M. Born and E. Brody. Z Physik 11, 327-52. (1922)

26. Partition functions for temperature radiation and internal energy of a crystalline solid. C. G. Darwin & R. H. Fowler. Proc. Cambridge Phil. Soc., 21, 262-73. (1922)
C. A. The Partition of energy. D. & F.
Phil. Mag. 44,450-79 (1922)

27. Specific heat of solids at high temperatures and the quantizing of oscillations of finite amplitude. E. Schrodinger. Z Ruysik, 11, 170-6. (1922)
Uses Hamilton Princ. vs. quant. hyp.

28. A Note on the theory of specific heats. E. Csaszar. Z Physik. 19, 213-20. (1923)
crit. energy limit. discont. below, cont. above. finite & inf. series.

29. Atomtheove der festen Zustandes; Dynamik der Kristallgitter. M. Born. Reviewed in Phys. Rev. 23, 546. (1924)

30. Note on the two works of Elenar Csaszar on radiation theory and specific heats. Erwin Schrodinger. Z Phýsik, 25, 173-4 (1924)

31. The statistical distribution function in radiation and specific heat theory. E Csaszar. Z Physik, 32, 872-80 (1925)

32. Quantum theory of the thermal conductivity in non-metallic crystals. Yosutoso Endo. Nagroka Anniv. vol. 1925, 67-75; Japan J. Physics 4, 3A.

33. M. Born. Problems of Atomic Dynamics. Pt. 1 The Structure of the Atom. Pt. II. The Lattice Theory of Rigid Bodies. Cambridge, Mass: Mass. Inst. Tech.

34. The Debye Formula. N. Barbulescu. Bul. Tunte fizice soc. Vomana stiinte 29, 9-14 (1926-7) D. form. deduced by assn. tot. rad. of osc. syst. prop. to int. energy.

35. Heat equalization in crystals in the light of quantum mechanism.
Th. V. Karman. Naturwissenschaftem, 17, 385-7. (1929)
Th. of ht. cond. Schrodinger's equat.

36. Lattice energetics of thermal vibrations in solids. R. H. Canfield. Phys. Rev., 33, 294. (1929)

37. Thermodynamic theory of heat conduction. W. Jazyua. Physik Z. 31, 253-64. (1930)
matter energy Fourier th. of ht. cond.

*38. Kinetic theory of heat conduction in crystals. R. Peierls. Ann. Physik (B), 3, 1055-1101. (4,121,1930) (1929)

39. The energy of crystal lattices. H. Jones. Proc. Roy. Sec. (London)
A 127, 689-703. (1930)

40. Theory of Conductivity. R. Peierls. Ann. Physik (5) 5, 244-6. lattice osc. (1930)

41. Theory of electric and thermal conductivity of metals. R. Peierls. Ann. Physik, (5), 4, 121-48. (1930)

42. Coupled vibrations with applications to the specific heat and infrared spectra of crystals. Arthur B. Lewis. Phys. Rev. 36, 368-86. (1930)

43. Some Problems in the conduction of heat. George Green. Phil. Mag. (7), 9, 241-60.
wave train method. (1930)

44. Atomic heat of crystalline substances at constant pressure. Yositosi Endo. Rept. Aeronautical Research Inst. Tokeyo Jap. Univ. 6, 71-82. (1931)

45. The lattice theory of ionic crystals. M. Born and Joseph E. Mayer. Z. Physik. 75, 1-18. (1932)

46. Applicability of the statistical method to ionic lattices. W. Lenz. Z Physik, 77, 713-21.
Thomas - Fermi equat. (1932)

47. The thermal motions of atoms in crystals. B. D. Holbrook. Phys. Rev. 39, 177. (1932)

48. Theory of Thermal Conduction. B. Bruzs. Z Physik, 83, 543-53. Thermodynamics (1933)

49. Heat Conductivity in Crystals. Ach. Papapetru. Physik Z. 35, 527-8. (1934)

50. A note on the spectrum of the frequencies of a polar crystal lattice. M. Born & J. H. C. Thompson. Proc. Roy. Soc. (London) A 147, 594-9 (1934)

51. The dynamic theory of the diamond lattice. Nagendra Math. Proc. Indian Acad. Sci. 1A, 333-45. (1934)

*52. Theory of the specific heat of crystals. M. Blackman. Proc. Roy. Soc. (London). A. 148, (365-83 (1935)
(384-406
148, 324

53. The dynamics of molecular crystal lattices. Neon V. Dietz. J. Franklin Inst. 219, 459-69. (1935)
Apply Morgenar's method, Debye, Born and Karman to Ne. and A.

*54. The theory of specific heat. M. Blackman. Proc. Roy. Soc. (London) A 149(117-25 (1935
(126-130

55. The spectrum of the normal frequencies of a polar crystal lattice. J. H. C. Thompson. Proc. Roy. Soc. (London) A 149, 487-505. (1935)

56. Bakerian Lecture - anomalous specific heats of crystals, with special reference to the contribution of molecular rotations. R. H. Fowler. Proc. Roy. Soc. (London) A 151, 1-22. (1935)

57. Atomic forces of solid states. Wen-Po. Phil. Mag. 22, 49-68 Motions in cryst. lattice. eff. radii. (1936)

58. The absorption of polar crystals in the infra-red. M. Blackman. Trans. Roy. Soc. (London). A 236, 103-31. (1936)

59. Thermal Conductivity in relation to crystal structure. W. A. Wooster. Z Krist. 95, 138-49. (1936)

60. Application of the Heaviside-Bromwich Operational method to the solution of a problem in heat conduction. A. Lykov. Phil. Mag. 22, 239-48. (1936)

61. The Thomson-Gibbs equation for crystals. I. N. Strauski & R. Kaishev. Z. Physik chem. B. 35, 427-32. (1937)

62. Pseudo-cubic lattices and the principle of "variate atom equipoints". F. C. Blake. Physical Rev. 49, 418. (1935)

63. Quantum electrodynamics of crystals. W. Shockley. Phys. Rev. 49, 639. (1935)

64. Quantum theoretical treatment of ionic crystals. D. H. Ewing. & F. Seitz. Phys. Rev. 49, 639-40.

65. Solution of the heat conductivity equation. C. Zwikker. Nederland. Tydschr. Naturkunde, 3, 303-12. (1936)

66. Accidental degeneracy in the energy bands of crystals. Conyers Herring. Phys. Rev. 52, 365-73. (1937)

67. Effect of time-reversal symmetry on energy bands of crystals. C. Herring. Phys. Rev. 52, 361-5. (1937)

*68. The vibrational spectrum of a three-dimensional lattice. M. Blackman. Proc. Roy. Soc. (London) A 159, 516-31. (1937)

69. Some properties of the vibrational spectrum of a lattice. M. Blackman. Proc. Cambridge Phil. Soc. 33, 94-103. (1937)

70. Heat Conductivity of crystals at low temperatures. W. J. De Haas & Th. Biermasz. Physica 5, 320-4. (1938)

71. Lattice vibrations in polar crystals. R. H. Lyddane & K. F. Herzfeld. Phys. Rev. 54, 846-61. (1938)

72. Deformation of crystalline matter. A. Pistocchi. Alluminio 7, 3-13. (1938) rev of interat. cryst. forces.

*73. The normal modes of vibration of a body centered cubic lattice. Paul Charles Fine. Phys. Rev. 56, 355-9. (1939)

74. Theory of thermal conduction in dielectric crystals. S. N. Trachenko & Ya. I. Frenkel J. Exptl. Theoret. Phys. (U. S. S. R.) 9, 570-7. (1939)

75. Stability of lattice crystals. M. Born. Proc. Cambridge Phil. Soc. 36(160-72 173-82 (1940)

76. An approximate solution of the Thomas Fermi equation in a crystal. H. Sauvenier, Bull-Soc. Voy. Sci. Liege 8, 313-20. (1939)

77. Theory of hetercpolar crystals. Calculation of the energy of the crystal lattice taking account of Van der Walls interaction of ions. E. E. Verzilov. Sci. Records Gorky State Univ. 7, 118-21 equat. for cryst. lattice derived from that given by Born & Mayer. (1939)

78. Electrostatic and optical potential in crystal space and in Fourier space. P. P. Ewald. Nachr Geo. Wiss. Gottingen, Math. Bys. Klasse. Fachgruppen II (N.F.) 3, 55-64. (1938)

79. Characteristic elastic vibrations of crystals under mixed boundary conditions. H. Wierzejewski. Z. Krist. 101, 94-116. (1939)

80. Thermal Conductivity of dielectics at temperatures higher than the Debye Temperature. I. Pomeranchuk. J. Exptl. Theoret. Phys. (U. S. S. R.)11, 246-54.

81. Thermal Conductivity of the paramagnetic dielectrics at low temperatures. I. Pomeranchuk. J. Exptl. Theoret. Phys. (U.S.S.R.) 4, 357-74. (1941) (in English).

82. The thermal conductivity of dielectrics. I. Pomeranchuk. Phys. Rev. 60, 820-1. (1941) (above)

83. Frequency spectrum of crystalline solids. E. W. Montroll. J. Chem. Phys. 10, 218-29. (1942)

84. The thermal energy of crystalline solids; basic theory. C. V. Raman. Proc. Indian Acad. Sci. 14A, 459-67. (1941)

85. Note on Raman's theory of specific heat of solids. M. Blackman. Proc. Phys. Soc. (London) 54, 377-9. (1942)

86. Raman's theory of specific heat of crystals. M. Blackman & M. Born. Nature 150,55. Adverse criticism. (1942)

87. The relation of Debye theory and the lattice theory of specific heats. M. Blackman. Proc. Roy. Soc. (London). A 181, 58-67. (1942)

88. Dynamics of real crystals. N. S. Nagendra Math. Nature 151, 196 Criticism of Born's theory. (1943)

89. Density of frequencies in lattice dynamics. M. Born. Nature 151, 197.
Discusses Nath's criticism.

90. Density of frequencies in lattice dynamics. W. Ledermann. Nature 151, 197-8. (1943)
Criticizes Nath.

91. Thermal Conductivities of dielectrics at temperatures lower than the Debye temperature. I. Pomeranchuk, J. Exptl. Theoret. Phys. (U. S. S. R.) 12, 245-63. (1942)

*92. The theory of the specific heat of solids. M. Blackman. Repts. Progress Phys. (Pub. by the Physical Society, London) 8, 11-30. (1941-pub. 1942)

93. The thermodynamics of crystal lattices. M. Born. Proc. Cambridge. Phil. Soc. 39, (100-3 (1943)
(104-13
I Discussion of the methods of Calc. II calc. of certain lattice sums occuring in thermodyn.

94. Statistics of two dimensional lattices with four components. J. Ashkin & E. Teller. Phys. Rev. 64, 178-84. (1943)

*95. Frequency spectrum of crystalline solids. II. General theory and applications to simple cubic lattices. E. W. Montroll. J. Chem. Phys. 11, 481-95. (1943)

*96. Frequency spectrum of crystalline solids. II General theory and application to simple cubic lattices. Enatum. E. W. Montroll. J. Chem. Phys. 12, 111 (1944). III Body centered cubic lattices. E. W. Montroll & D. C. Peasles. J. Chem. Phys. 12, 98-106. (1944)

97. Matrix theory of correlations in a lattice. I. R. Eisenschitz. Proc. Roy. Soc. (London). A 182, 244-59. (1944)
Statistical mechanics of crystals.

98. Modes of atomic vibration in the fourteen Bravois lattices. G. N. Ramachandran. Proc. Indian Acad. Sci. 18A, 266-82. (1943)

99. The normal vibrations in some typical cubic crystals. E. V. Chelam. Proc. Indian Acad. Sci. 18A 257-65. (1943)
Based on Raman's superlattice theory.

100. Normal vibrations of crystal lattices; application of group theory. E. V. Chelam. Proc. Indian Acad. Sci. 18A, 283-97. (1943)

101. Character tables for the atomic vibrations in some cubic crystals. E. V. Chelam. Proc. Indian Acad. Sci. 18A, 327-33. (1943)
Applied to some FCC crystals.

102. The frequency spectrum of the diamond lattice. E. V. Chelam. Proc. Indian Acad. Sci. 18A, 334-40. (1943)

103. The equation of state for solids. R. Furth. Proc. Roy. Soc. (London). A. 183, 87-110. (1944)

104. The thermodynamics of crystal lattices. IV the elastic constants of a FCC lattice, with central forces. M. M. Gow. Proc. Cambridge Phil Soc. 40, 151-66. (1944)
Deduce equation of state.

105. Stability of crystal lattices. IX. Covariant theory of lattice deformations and the stability of some hexagonal lattices. M. Born. Proc. Cambridge. Phil. Soc. 40, 262-3. (1944)
Erratum.

106. The evaluation of the specific heat of rock salt by the new crystal dynamics. Biskeshwar Dayal. Proc. Indian Acad. Sci. 19A, 182-7. (1944)

107. The thermodynamics of heat conduction. J. E. Verschaffelt. Bull. Classe. Sci. Acad. Roy. Belg. 28, 436-54. (1942)

108. The elastic properties of lattices. P. S. Epstein. (Calif. Inst. Tech.). Phys. Rev. 70, 915-22. (1946)

109. E. Schroedinger, Handbuch der Physik, X. (1936)

110. S. Bauer, J. Chem. Phys. 6, 403. (1938)
7, 1097. (1939)

111. E. W. Kellermann, Phil. Trans. Roy. Soc. 238, 513. (1940)

112. M. Iona, Phys. Rev. 60, 822. (1941)

113. A. Einstein, Ann. d. Physik, 22, 800 (1907)
34, 590. (1911)

114. C. V. Raman, et. al. Proc. Ind. Acad. Sci. 15A. (1942)

115. M. Born. Rev. Mod. Phys. 17, 245. (1945)

*116. Born etal. Proc. Phys. Soc. 54, 362 (1942)
Lattice Dynamics and x-ray Scattering

117. E. W. Montroll, J. Chem. Phys. 10, 218-229 (1942)

118. E. W. Montroll, J. Chem. Phys. 15, 575-591 (1947)

119. E. W. Montroll, Quart. Apop. Math. V, 2 (1947)

120. Born & Sarginson - Proc. Roy. Soc. A 179,69 (1941)
Effect to thermal vibrations on the scattering of x-rays.

121. Born - Proc. Roy. Soc. A-180, 397 (1941)

*122. Eisenschitz - Proc. Roy. Soc. A 182, 244 (1943)
Matrix Theory of Correlations in a Lattice.

123. Lassetre & Horoe, J. Chem. Phys. 9, 747, 808 (1941)

124. Montroll, J. Chem Phys. 9, 706 (1941)

125. Ledermann. Proc. Roy. Soc. A 182, 362 (1943)
Asymptotic formulae Relating to the Physical Theory of Crystals.

126. Begbie and Born - Proc. Roy. Soc. A 188, 179, 189 (1945)
Thermal Scattering of x-ray Crystals.

127. Born & Bradburn - Proc Roy. Soc. A. 188, 161 (1945)
The theory of the Raman Effect in Crystals, in particular, rock-salt.