ANHARMONIC HELMHOLTZ FREE ENERGY TO $O(\lambda^4)$ IN THE NON-LEADING TERM APPROXIMATION

by

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ABSTRACT

Expressions for the anharmonic Helmholtz free energy contributions up to $O(\lambda^4)$, valid for all temperatures, have been obtained using perturbation theory for a crystal in which every atom is on a site of inversion symmetry. Numerical calculations have been carried out in the high temperature limit and in the non-leading term approximation for a monatomic face-centred cubic crystal with nearest neighbour central-force interactions. The numbers obtained were seen to vary by as much as 47% from those obtained in the leading term approximation, indicating that the latter approximation is not in general very good. The convergence to $O(\lambda^4)$ of the perturbation series in the high temperature limit appears satisfactory.

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1. INTRODUCTION

The harmonic theory of crystal lattices fails in several respects. It incorrectly predicts no thermal expansion, a constant high temperature heat capacity, equal adiabatic and isothermal elastic constants which are temperature and pressure independent, and no phonon-phonon interactions. These failures may be attributed to the neglect of anharmonic interactions in the crystal.

Mie (1) and Gruneisen (2) first allowed for anharmonicity by assuming a temperature-dependent lattice constant in the development of their equation of state. Born and co-workers (3-6) later studied the high temperature dependence of the elastic constants of simple cubic lattices using the quasi-harmonic approximation (volume-dependent vibration frequencies). Born and Brody (7) first investigated the influence of anharmonicity on the caloric equation of state for high temperatures. Later Leibfried (8) employed the perturbation theory of Nakajima (9) and derived expressions for the free energy containing both thermal and caloric equations of state by treating anharmonic effects as perturbations. Peierls (10), Klemens (11), Leibfried (8 and 12) and Schlömann (12) have discussed the anharmonic effect of thermal conduction in insulators.

The traditional perturbation theory approach to the study of anharmonicity is based on the expansion of the crystal hamiltonian in terms of Van Hove's (13) ordering parameter, λ, which is equal in magnitude to a typical atomic displacement divided by the nearest-neighbour distance. The lowest-order anharmonic free energy contribution is then found to be of order λ^2. Previous perturbation studies by Leibfried and Ludwig (14) and Maradudin, Flinn, and Coldwell-Horsfall (15) were carried out only to this lowest order of perturbation. Maradudin et al performed their calculations for a central force nearest neighbour face centrered cubic crystal using the leading term approximation in which only the highest ordered radial derivative of the interatomic potential is retained. Feldman and Horton (16) performed similar calculations in the non-leading term approximation. The specific heat at constant volume was in both cases found to be linear in T at high temperatures but this temperature dependence was found to be inadequate to describe several materials (see ref. 17). For rare gas solids at high temperatures the experimental specific heat rises steadily above the Dulong-Petit value while the theoretical curve drops linearly from it. Recently Shukla and Cowley (18) used a diagrammatic method to calculate the contributions to the Helmholtz free energy up to order λ^4 in the expansion of the anharmonic hamiltonian. Their calculations were restricted however to the leading term approximation for a central force nearest neighbour f.c.c. crystal.

For this thesis the perturbation treatment of Maradudin et al (15) was extended to order λ^4 and all calculations were performed in the high temperature limit without using the leading term approximation. As a result an assessment of the validity of the leading term approximation could be made. It was also desired to determine whether or not there was a contribution linear in T to the high temperature specific heat from terms of order λ^4.

The anharmonic hamiltonian will be introduced first and then used in the expansion of the partition function from which are derived the anharmonic free energy contributions. Details of the numerical evaluations of these contributions are then given and followed by a discussion of the results.

2. THE ANHARMONIC HAMILTONIAN

Consider an infinite non-conducting ideal crystal whose lattice points are defined by

$$\underset{\sim}{x}^{l} = l_1 \underset{\sim}{a}_1 + l_2 \underset{\sim}{a}_2 + l_3 \underset{\sim}{a}_3 \qquad (l_1, l_2, l_3 \text{ integers})$$

where $\underset{\sim}{a}_1$, $\underset{\sim}{a}_2$, $\underset{\sim}{a}_3$ are the primitive translation vectors. The lattice thus consists of an infinite number of cells of the direct lattice which are parallelepipeds having edges $\underset{\sim}{a}_1$, $\underset{\sim}{a}_2$, $\underset{\sim}{a}_3$ and which can be indexed by the sets of integers $l = (l_1, l_2, l_3)$. Denote the equilibrium position vector of the K^{th} atom in the l^{th} cell by

$$\underset{\sim}{x}_K^{l} = \underset{\sim}{x}^{l} + \underset{\sim}{x}_K \tag{1}$$

where $\underset{\sim}{x}_K$ gives the position of the atom K with respect to the cell origin (l_1, l_2, l_3) . At any instant the moving atom K in the l^{th} cell will be displaced from equilibrium by the vector $\underset{\sim}{u}_K^{l}$. The total kinetic energy of the lattice is

$$T = \frac{1}{2} \sum_{lK\alpha} M_K (\dot{u}_{\alpha K}^{l})^2 \tag{2}$$

where M_K is the mass of atom K and α denotes the Cartesian indices x, y and z and the summation over K extends over all n_o atoms in a unit cell. If the total potential energy of the crystal, Φ , is some function of the instantaneous atomic positions, a Taylor's expansion in powers of the displacements yields

$$\Phi = \sum_{n=2}^{\infty} \frac{1}{n!} \sum_{\substack{l_1 K_1 \alpha_1 \\ \vdots \\ l_n K_n \alpha_n}} \Phi_{\alpha_1 \ldots \alpha_n} \begin{pmatrix} l_1 \ldots l_n \\ K_1 \ldots K_n \end{pmatrix} u_{\alpha_1 K_1}^{l_1} \ldots u_{\alpha_n K_n}^{l_n} \tag{3}$$

where

$$\Phi_{\alpha_1,\ldots,\alpha_n}\left(\begin{smallmatrix} l_1,\ldots,l_n \\ \kappa_1,\ldots,\kappa_n\end{smallmatrix}\right) = \left.\frac{\partial^n \Phi}{\partial u_{\alpha_1\kappa_1}^{l_1}\cdots\partial u_{\alpha_n\kappa_n}^{l_n}}\right|_0$$

The subscript zero above denotes that the derivatives are evaluated in the equilibrium configuration of the lattice. In the above expression for Φ the first two terms of the Taylor series have been omitted because the first one is zero if the zero of potential energy is taken to occur for the equilibrium configuration while the second term vanishes because the force on any particle in equilibrium must be zero.

In the above energy expressions the summations over the cell indices "l" extend over the infinite crystal. Suppose now that we subdivide the infinite crystal into "macrocrystals" which are parallelepipeds having edges $L\underset{\sim}{a}_1$, $L\underset{\sim}{a}_2$ and $L\underset{\sim}{a}_3$ and assume the cyclic boundary condition

$$\underset{\sim}{u}_{\kappa}^{l+L} = \underset{\sim}{u}_{\kappa}^{l} \tag{4}$$

where $l+L$ denotes a cell at a position

$$\underset{\sim}{x}^{l} + L(m_1\underset{\sim}{a}_1 + m_2\underset{\sim}{a}_2 + m_3\underset{\sim}{a}_3) \qquad (m_1, m_2, m_3 \text{ integers})$$

Any one of these macrocrystals can be taken to represent the real finite crystal under study with inappreciable error for large L (19) .

We now introduce the following transformation (A) to creation and annihilation operators:

$$u_{\alpha\kappa}^{l} = \left(\frac{\hbar}{2NM_\kappa}\right)^{\frac{1}{2}} \sum_{\underset{\sim}{k}j} \frac{e_\alpha(\kappa|{\underset{\sim}{k}\atop j})}{\sqrt{\omega_{\underset{\sim}{k}j}}}\left(a_{\underset{\sim}{k}j} - a^{+}_{-\underset{\sim}{k}j}\right) e^{2\pi i\underset{\sim}{k}\cdot\underset{\sim}{x}(l)} \tag{5}$$

$$\dot{u}^{l}_{\alpha\kappa} = i\left(\frac{\hbar}{2NM_\kappa}\right)^{\frac{1}{2}} \sum_{\underset{\sim}{k}j} e_\alpha(\kappa|{}^{\underset{\sim}{k}}_{j}) \sqrt{\omega_{\underset{\sim}{k}j}}\,(a_{\underset{\sim}{k}j} + a^{+}_{-\underset{\sim}{k}j})\, e^{2\pi i \underset{\sim}{k}\cdot\underset{\sim}{x}(l)}$$

The allowed values of the wave vector $\underset{\sim}{k}$ are determined by the cyclic condition of Eq. (4) and are uniformly distributed throughout one unit cell of the reciprocal lattice. They are given by

$$\underset{\sim}{k} = \frac{h_1}{L}\underset{\sim}{b}_1 + \frac{h_2}{L}\underset{\sim}{b}_2 + \frac{h_3}{L}\underset{\sim}{b}_3 \qquad (h_1, h_2, h_3 = 1, 2, \ldots, L) \tag{6}$$

where the primitive translation vectors $\underset{\sim}{b}_1, \underset{\sim}{b}_2, \underset{\sim}{b}_3$ of the reciprocal lattice are defined by

$$\underset{\sim}{a}_i \cdot \underset{\sim}{b}_j = \delta_{ij}$$

and a reciprocal lattice vector is

$$\underset{\sim}{\tau}(h) = h_1\underset{\sim}{b}_1 + h_2\underset{\sim}{b}_2 + h_3\underset{\sim}{b}_3 \qquad (h_1, h_2, h_3 \text{ integers}) \tag{7}$$

The eigenvectors $e_\alpha(\kappa|{}^{\underset{\sim}{k}}_{j})$ and eigenvalues $\omega_{\underset{\sim}{k}j}$ satisfy the equation

$$\sum_{\kappa'\beta} D_{\alpha\beta}\left({}^{\;\underset{\sim}{k}}_{\kappa\kappa'}\right) e_\beta(\kappa'|{}^{\underset{\sim}{k}}_{j}) = \omega^2_{\underset{\sim}{k}j}\, e_\alpha(\kappa|{}^{\underset{\sim}{k}}_{j}) \tag{8}$$

where we define the dynamical matrix by its elements

$$D_{\alpha\beta}\left({}^{\;\underset{\sim}{k}}_{\kappa\kappa'}\right) = \frac{1}{(M_\kappa M_{\kappa'})^{1/2}} \sum_{\bar{l}} \Phi_{\alpha\beta}\left({}^{\;\bar{l}}_{\kappa\kappa'}\right) e^{-2\pi i \underset{\sim}{k}\cdot\underset{\sim}{x}(\bar{l})} \tag{9}$$

The periodic boundary conditions were used to obtain the result

$$\Phi_{\alpha\beta}\begin{pmatrix} \ell & \ell' \\ \kappa & \kappa' \end{pmatrix} = \Phi_{\alpha\beta}\begin{pmatrix} \ell-\ell' & 0 \\ \kappa & \kappa' \end{pmatrix} = \Phi_{\alpha\beta}\begin{pmatrix} \bar{\ell} \\ \kappa\kappa' \end{pmatrix} \qquad (\bar{\ell} = \ell - \ell')$$

The number of units cells in the crystal is assumed to be N $(= L^3)$. The branch index j takes on the values 1,2,...,$3n_0$ where each integer labels a particular solution of Eq. (8).

The operator $a_{\underset{\sim}{k}j}$ and its Hermitean conjugate $a^+_{\underset{\sim}{k}j}$ obey the following commutation relations:

$$[a_{\underset{\sim}{k}j}, a^+_{\underset{\sim}{k}'j'}] = \Delta(\underset{\sim}{k}'-\underset{\sim}{k})\,\delta_{jj'}$$
$$[a_{\underset{\sim}{k}j}, a_{\underset{\sim}{k}'j'}] = [a^+_{\underset{\sim}{k}j}, a^+_{\underset{\sim}{k}'j'}] = 0 \qquad (10)$$

where $\delta_{jj'}$ is a Kronecker delta while

$$\Delta(\underset{\sim}{k}) = 1 \quad \text{for } \underset{\sim}{k} = \underset{\sim}{0} \text{ or a reciprocal lattice vector}$$
$$= 0 \text{ otherwise}$$

When these operators are applied to the "$3n_0N$ particle" orthonormal eigenstates $|n\rangle$ of the operator $a^+_{\underset{\sim}{k}j}a_{\underset{\sim}{k}j}$ specified by the $3n_0N$ quantum numbers $\{n_{\underset{\sim}{k}j}\}$ where $n_{\underset{\sim}{k}j}$ is either zero or a positive integer we get

$$a^+_{\underset{\sim}{k}j}|\ldots, n_{\underset{\sim}{k}j}, \ldots\rangle = \sqrt{n_{\underset{\sim}{k}j}+1}\,|\ldots, n_{\underset{\sim}{k}j}+1, \ldots\rangle$$
$$a_{\underset{\sim}{k}j}|\ldots, n_{\underset{\sim}{k}j}, \ldots\rangle = \sqrt{n_{\underset{\sim}{k}j}}\,|\ldots, n_{\underset{\sim}{k}j}-1, \ldots\rangle \qquad (11)$$

Also, since the dynamical matrix is Hermitean and hence $\omega^2_{\underset{\sim}{k}j}$ is real, we can consistently satisfy the requirement that $u^{l}_{\alpha\kappa}$ be Hermitean by assuming that

$$e_\alpha(\kappa|{}^{\underset{\sim}{k}}_{j}) = -\,e^{*}_{\alpha}(\kappa|{}^{-\underset{\sim}{k}}_{j}) \tag{12}$$

Using the transformations of Eq. (5) and retaining only the first five terms of the expansion for Φ the hamiltonian of the anharmonic lattice becomes

$$H = H_o + \sum_{n=3}^{6} \lambda^{n-2} H_n \tag{13}$$

where the harmonic hamiltonian is given by

$$H_o = \sum_{\underset{\sim}{k}j} \hbar\omega_{\underset{\sim}{k}j}\left(a^{+}_{\underset{\sim}{k}j}\, a_{\underset{\sim}{k}j} + \tfrac{1}{2}\right) \tag{14}$$

and

$$H_n = \sum_{\lambda_1\cdots\lambda_n} V(\lambda_1\cdots\lambda_n)\, A_{\lambda_1}\cdots A_{\lambda_n}$$

$$V(\lambda_1\cdots\lambda_n) = \frac{1}{n!} N^{1-\frac{n}{2}} \Delta(\underset{\sim}{k}_1+\cdots+\underset{\sim}{k}_n)\left[\hbar^n/2^n\,\omega_{\lambda_1}\cdots\omega_{\lambda_n}\right]^{\frac{1}{2}} \times \Phi(\lambda_1\cdots\lambda_n) \tag{15}$$

$$\Phi(\lambda_1\cdots\lambda_n) = \sum_{\substack{l_1\kappa_1\alpha_1\\ \vdots \\ l_n\kappa_n\alpha_n}} \frac{1}{\sqrt{M_{\kappa_1}\cdots M_{\kappa_n}}}\, \Phi_{\alpha_1\cdots\alpha_n}\begin{pmatrix} l_1\cdots l_n\\ \kappa_1\cdots\kappa_n\end{pmatrix} \times e_{\alpha_1}(\kappa_1|\lambda_1)\cdots e_{\alpha_n}(\kappa_n|\lambda_n)\exp\left(2\pi i\left[\underset{\sim}{k}_1\cdot \underset{\sim}{x}(l_1)+\cdots+\underset{\sim}{k}_n\cdot\underset{\sim}{x}(l_n)\right]\right) \tag{16}$$

$$A_{\lambda_i} = a_{\lambda_i} - a^{+}_{-\lambda_i}, \; e_{\alpha_i}(\kappa_i|\lambda_i) = e_{\alpha_i}(\kappa_i|{\underset{\sim}{k}_i \atop j_i}),$$

$$\omega_{\lambda_i} = \omega_{\underset{\sim}{k}_i j_i}, \; a_{-\lambda_i} = a_{-\underset{\sim}{k}_i j_i}, \quad i = 1, 2, \ldots, n$$

In the above, use has been made of the result

$$\sum_{\ell}^{N} e^{2\pi i \underset{\sim}{k} \cdot \underset{\sim}{x}(\ell)} = N\Delta(\underset{\sim}{k}) \tag{17}$$

the summation being over the N cells in the "macrocrystal".
The order of magnitude relations

$$\Phi_{\alpha\beta}\begin{pmatrix} \ell_1 & \ell_2 \\ \kappa_1 & \kappa_2 \end{pmatrix} \sim a_0 \Phi_{\alpha\beta\gamma}\begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ \kappa_1 & \kappa_2 & \kappa_3 \end{pmatrix} \sim a_0^2 \Phi_{\alpha\beta\gamma\delta}\begin{pmatrix} \ell_1 & \ell_2 & \ell_3 & \ell_4 \\ \kappa_1 & \kappa_2 & \kappa_3 & \kappa_4 \end{pmatrix} \sim \cdots$$

where a_0 is the lattice paramater, suggested the use of an order parameter λ in Eq. (11) to indicate the number of factors $\frac{1}{a_0}$ contained in the H_n relative to H_o. At the end of the calculation λ can be set equal to unity.

3. ANHARMONIC FREE ENERGY

The anharmonic Helmholtz free energy is obtained from the partition function defined by

$$Z = \mathrm{Tr}\, e^{-\beta H}, \quad \beta = \frac{1}{k_B T} \tag{18}$$

where the anharmonic hamiltonian H will be defined by Eq. (13). If we work in the diagonal representation of H_o, we will need to express the exponential in some form containing $e^{-\beta H_o}$ as a factor. This is done in Appendix A, where the exponential is expanded in powers of λ using an iteration procedure (20). Having retained terms in the hamiltonian (EQ.13) only up to order λ^4, to be consistent we must do the same with the expanded partition function. The result is

$$Z = Z_o + \lambda^2 (Z_1 + Z_2) + \lambda^4 (Z_3 + Z_4 + \ldots + Z_{10}) \tag{19}$$

where

$$Z_o = \mathrm{Tr}\, e^{-\beta H_o} \tag{20}$$

$$Z_1 = -\beta\, \mathrm{Tr}\, e^{-\beta H_o} \int_0^1 ds_1\, e^{s_1 \beta H_o} H_4\, e^{-s_1 \beta H_o}$$

$$Z_2 = \beta^2 \, Tr\, e^{-\beta H_0} \int_0^1 ds_1 \int_0^{s_1} ds_2\, e^{s_1 \beta H_0} H_3\, e^{(s_2 - s_1)\beta H_0} H_3\, e^{-s_2 \beta H_0}$$

$$Z_3 = -\beta\, Tr\, e^{-\beta H_0} \int_0^1 ds_1\, e^{s_1 \beta H_0} H_6\, e^{-s_1 \beta H_0}$$

$$Z_4 = \beta^2 \, Tr\, e^{-\beta H_0} \int_0^1 ds_1 \int_0^{s_1} ds_2\, e^{s_1 \beta H_0} H_3\, e^{(s_2 - s_1)\beta H_0} H_5\, e^{-s_2 \beta H_0}$$

$$Z_5 = \beta^2 \, Tr\, e^{-\beta H_0} \int_0^1 ds_1 \int_0^{s_1} ds_2\, e^{s_1 \beta H_0} H_4\, e^{(s_2 - s_1)\beta H_0} H_4\, e^{-s_2 \beta H_0}$$

$$Z_6 = \beta^2 \, Tr\, e^{-\beta H_0} \int_0^1 ds_1 \int_0^{s_1} ds_2\, e^{s_1 \beta H_0} H_5\, e^{(s_2 - s_1)\beta H_0} H_3\, e^{-s_2 \beta H_0}$$

$$Z_7 = -\beta^3 \, Tr\, e^{-\beta H_0} \int_0^1 ds_1 \int_0^{s_1} ds_2 \int_0^{s_2} ds_3\, e^{s_1 \beta H_0} H_3\, e^{(s_2 - s_1)\beta H_0} H_3\, e^{(s_3 - s_2)\beta H_0} H_4\, e^{-s_3 \beta H_0}$$

$$Z_8 = -\beta^3 \, Tr\, e^{-\beta H_0} \int_0^1 ds_1 \int_0^{s_1} ds_2 \int_0^{s_2} ds_3\, e^{s_1 \beta H_0} H_3\, e^{(s_2 - s_1)\beta H_0} H_4\, e^{(s_3 - s_2)\beta H_0} H_3\, e^{-s_3 \beta H_0}$$

$$Z_9 = -\beta^3 \, Tr\, e^{-\beta H_0} \int_0^1 ds_1 \int_0^{s_1} ds_2 \int_0^{s_2} ds_3\, e^{s_1 \beta H_0} H_4\, e^{(s_2 - s_1)\beta H_0} H_3\, e^{(s_3 - s_2)\beta H_0} H_3\, e^{-s_3 \beta H_0}$$

$$Z_{10} = \beta^4 \, Tr\, e^{-\beta H_0} \int_0^1 ds_1 \int_0^{s_1} ds_2 \int_0^{s_2} ds_3 \int_0^{s_3} ds_4\, e^{s_1 \beta H_0} H_3\, e^{(s_2 - s_1)\beta H_0} H_3\, e^{(s_3 - s_2)\beta H_0}$$

$$\times\; H_3\, e^{(s_4 - s_3)\beta H_0} H_3\, e^{-s_4 \beta H_0}$$

Terms of order λ and λ^3 make no contribution to the partition function (see p.21). We now use the eigenvalue equation

$$H_o|n\rangle = \Big\{\sum_{\underset{\sim}{k}j} \hbar\omega_{\underset{\sim}{k}j}(n_{\underset{\sim}{k}j}+\tfrac{1}{2})\Big\}|n\rangle = E_n|n\rangle \tag{21}$$

which follows from Eqs. (11) and (14).

From Eq. (21) we get

$$e^{-\beta H_o}|n\rangle = e^{-\beta E_n}|n\rangle \tag{22}$$

and the adjoint equation

$$\langle n|e^{-\beta H_o} = \langle n|e^{-\beta E_n} \tag{23}$$

With the aid of the cyclic theorem for traces, an inversion of the orders of integration, and Eqs. (22) and (23) (see APPENDIX B) we get

$$Z_o = \sum_n e^{-\beta E_n} \tag{24}$$

$$Z_1 = -\beta\sum_n e^{-\beta E_n}\langle n|H_4|n\rangle$$

$$Z_2 = \beta \sum_{m,n} e^{-\beta E_n} \frac{\langle n|H_3|m\rangle\langle m|H_3|n\rangle}{E_m - E_n} \{1 + Z'\}$$

$$Z_3 = -\beta \sum_{n} e^{-\beta E_n} \langle n|H_6|n\rangle$$

$$Z_4 = \beta \sum_{m,n} e^{-\beta E_n} \frac{\langle n|H_3|m\rangle\langle m|H_5|n\rangle}{E_m - E_n} \{1 + Z'\}$$

$$Z_5 = \beta \sum_{m,n} e^{-\beta E_n} \frac{\langle n|H_4|m\rangle\langle m|H_4|n\rangle}{E_m - E_n} \{1 + Z'\}$$

$$Z_6 = \beta \sum_{m,n} e^{-\beta E_n} \frac{\langle n|H_5|m\rangle\langle m|H_3|n\rangle}{E_m - E_n} \{1 + Z'\}$$

$$Z_7 = -\beta \sum_{n,m,p} e^{-\beta E_n} \frac{\langle n|H_3|m\rangle\langle m|H_3|p\rangle\langle p|H_4|n\rangle}{(E_p - E_n)(E_m - E_n)} \{1 + Z''\}$$

$$Z_8 = -\beta \sum_{n,m,p} e^{-\beta E_n} \frac{\langle n|H_3|m\rangle\langle m|H_4|p\rangle\langle p|H_3|n\rangle}{(E_p - E_n)(E_m - E_n)} \{1 + Z''\}$$

$$Z_9 = -\beta \sum_{n,m,p} e^{-\beta E_n} \frac{\langle n|H_4|m\rangle\langle m|H_3|p\rangle\langle p|H_3|n\rangle}{(E_p - E_n)(E_m - E_n)} \{1 + Z''\}$$

$$Z_{10} = \beta \sum_{n,m,p,q} e^{-\beta E_n} \frac{\langle n|H_3|m\rangle\langle m|H_3|p\rangle\langle p|H_3|q\rangle\langle q|H_3|n\rangle}{(E_q - E_n)(E_p - E_n)(E_m - E_n)} \{1 + Z'''\}$$

$$Z' = \frac{e^{-\beta(E_m - E_n)} - 1}{\beta\,(E_m - E_n)}$$

$$Z'' = Z' - \frac{E_m - E_n}{\beta(E_m - E_p)(E_n - E_p)} \left[e^{\beta(E_n - E_p)} - 1 \right] - \frac{e^{\beta(E_n - E_m)} - 1}{\beta\,(E_m - E_p)}$$

$$Z''' = \frac{1}{\beta}(E_p-E_n)(E_m-E_n)\left\{ \frac{e^{-\beta(E_m-E_n)}-1}{(E_p-E_n)(E_m-E_n)^2} + \frac{e^{-\beta(E_p-E_n)}-1}{(E_m-E_p)(E_n-E_p)^2} \right.$$

$$+ \frac{e^{-\beta(E_q-E_n)}-1}{(E_p-E_q)(E_m-E_q)(E_n-E_q)} + \frac{e^{-\beta(E_m-E_n)}-1}{(E_p-E_n)(E_m-E_p)(E_n-E_m)} + \frac{e^{-\beta(E_m-E_n)}-1}{(E_p-E_q)(E_m-E_q)(E_n-E_m)}$$

$$\left. + \frac{e^{-\beta(E_p-E_n)}-1}{(E_m-E_p)(E_n-E_p)(E_p-E_q)} + \frac{e^{-\beta(E_m-E_n)}-1}{(E_p-E_q)(E_m-E_p)(E_m-E_n)} \right\}$$

The Helmholtz free is defined as

$$F = \frac{1}{\beta} \ln Z$$

Using the definition of Z in Eq.(19) and expanding the logarithm up to terms of order we get

$$F = F_0 + \lambda^2(F_1+F_2) + \lambda^4 \sum_{n=3}^{10} F_n + \frac{1}{2\beta}\lambda^4\left(\frac{Z_1+Z_2}{Z_0}\right)^2 \qquad (25)$$

where

$$F_0 = -\frac{1}{\beta} \ln Z_0$$

$$F_n = -\frac{1}{\beta}\frac{Z_n}{Z_0} \qquad n=1,\dots,10$$

Assume now a monatomic crystal with central force interactions. Write the total potential energy of the lattice as

$$\Phi = \frac{1}{2} \sum_{\ell\ell'}' \phi(r^{\ell\ell'}) \tag{26}$$

where the prime indicates that we do not consider terms for which the indices ℓ, ℓ' refer to the same cell. The factor $\frac{1}{2}$ is included so that the interaction between two atoms is counted only once. The instantaneous separation between two atoms in the cells ℓ and ℓ' is

$$r^{\ell\ell'} = \left[(x_o^{\ell\ell'} + u_x^{\ell\ell'})^2 + (y_o^{\ell\ell'} + u_y^{\ell\ell'})^2 + (z_o^{\ell\ell'} + u_z^{\ell\ell'})^2 \right]^{\frac{1}{2}}$$

where

$$x_o^{\ell\ell'} = x_o^{\ell} - x_o^{\ell'}, \text{ etc.}$$

$$u_x^{\ell\ell'} = u_x^{\ell} - u_x^{\ell'}, \text{ etc.}$$

x_o^{ℓ} is the x-component of the equilibrium position vector of the ℓ th atom of the crystal relative to an origin located at some atom. u_x^{ℓ} has the same meaning as before except that the atomic index κ has now been omitted because there is only one atom per primitive cell.

Put

$$\underset{\sim}{r}_o^{\ell} = \frac{a_o}{2} \langle \ell_1, \ell_2, \ell_3 \rangle$$

where the integers l_1, l_2, l_3 are all odd or all even for a body-centered cubic lattice and whose sum is even for a face-centered cubic lattice. a_o is the lattice parameter. If we now expand the two-body potential $\phi(r^{ll'})$ in powers of $u_\alpha^{ll'}$, $\alpha = x, y, z$ up to terms of degree six we get

$$\Phi = \sum_{n=2}^{6} \left(\frac{1}{2} \sum_{ll'}{}' \sum_{\alpha_1 \ldots \alpha_n} \frac{1}{n!} \phi_{\alpha_1 \ldots \alpha_n}(ll') \, u_{\alpha_1}^{ll'} \ldots u_{\alpha_n}^{ll'} \right) \tag{27}$$

with $\alpha_1, \ldots, \alpha_n$ each running over the cartesian indices x, y, z and

$$\phi_{xy}(ll') = \frac{\partial^2}{\partial x \partial y} \phi(r) \Big|_{r = r_o^{ll'}}$$

$$= \left\{ \frac{xy}{r^2} \left[\phi''(r) - \frac{1}{r} \phi'(r) \right] + \frac{\delta_{xy}}{r} \phi'(r) \right\} \Big|_{r = r_o^{ll'}}$$

$$\phi_{xyz}(ll') = \frac{\partial^3}{\partial x \partial y \partial z} \phi(r) \Big|_{r = r_o^{ll'}}$$

$$= \left\{ \frac{xyz}{r^3} \left[\phi'''(r) - \frac{3}{r} \phi''(r) + \frac{3}{r^2} \phi'(r) \right] \right.$$
$$\left. + \left(\delta_{xy} \frac{z}{r^2} + \delta_{yz} \frac{x}{r^2} + \delta_{xz} \frac{y}{r^2} \right) \left[\phi''(r) - \frac{1}{r} \phi'(r) \right] \right\} \Big|_{r = r_o^{ll'}}$$

$$\phi_{xyzu}(ll') = \frac{\partial^4}{\partial x \partial y \partial z \partial u} \phi(r)\Big|_{r=r_0^{ll'}}$$

$$= \Big\{ \frac{xyzu}{r^4}\Big[\phi^{iv}(r) - \frac{6}{r}\phi'''(r) + \frac{15}{r^2}\phi''(r) - \frac{15}{r^3}\phi'(r)\Big]$$

$$+ (xy\delta_{zu} + yz\delta_{xu} + xz\delta_{yu} + xu\delta_{yz} + yu\delta_{xz} + zu\delta_{xy})$$

$$\times \frac{1}{r^3}\Big[\phi'''(r) - \frac{3}{r}\phi''(r) + \frac{3}{r^2}\phi'(r)\Big] + (\delta_{xy}\delta_{zu} + \delta_{yz}\delta_{xu}$$

$$+ \delta_{xz}\delta_{yu})\frac{1}{r^2}\Big[\phi''(r) - \frac{1}{r}\phi'(r)\Big]\Big\}\Big|_{r=r_0^{ll'}}$$

$$\phi_{xyzuv}(ll') = \frac{\partial^5}{\partial x \partial y \partial z \partial u \partial v} \phi(r)\Big|_{r=r_0^{ll'}}$$

$$= \Big\{ \frac{xyzuv}{r^5}\Big[\phi^{v}(r) - \frac{10}{r}\phi^{iv}(r) + \frac{45}{r^2}\phi'''(r) - \frac{105}{r^3}\phi''(r) + \frac{105}{r^4}\phi'(r)\Big]$$

$$+ (yzu\delta_{vx} + xzu\delta_{vy} + xyu\delta_{vz} + xyz\delta_{uv} + xyv\delta_{zu}$$

$$+ yzv\delta_{xu} + xzv\delta_{uy} + xuv\delta_{yz} + yuv\delta_{xz} + zuv\delta_{xy})$$

$$\times \frac{1}{r^4}\Big[\phi^{iv}(r) - \frac{6}{r}\phi'''(r) + \frac{15}{r^2}\phi''(r) - \frac{15}{r^3}\phi'(r)\Big]$$

$$+ \Big[\delta_{zu}(y\delta_{xv} + x\delta_{yv}) + \delta_{xu}(z\delta_{yv} + y\delta_{zv}) + \delta_{yu}(x\delta_{zv} + z\delta_{xv})$$

$$+ \delta_{yz}(u\delta_{xv} + x\delta_{uv}) + \delta_{xz}(u\delta_{yv} + y\delta_{uv}) + \delta_{xy}(u\delta_{zv} + z\delta_{uv})$$

$$+ v(\delta_{xy}\delta_{zu} + \delta_{yz}\delta_{ux} + \delta_{xz}\delta_{yu})\Big]\frac{1}{r^3}\Big[\phi'''(r) - \frac{3}{r}\phi''(r) + \frac{3}{r^2}\phi'(r)\Big]\Big\}\Big|_{r=r_0^{ll'}}$$

$$\phi_{xyzuvw}(ll') = \frac{\partial^6}{\partial x\,\partial y\,\partial z\,\partial u\,\partial v\,\partial w}\,\phi(r)\Big|_{r=r_0^{ll'}}$$

$$= \Big\{ \frac{xyzuvw}{r^6}\Big[\phi^{VI}(r) - \frac{15}{r}\phi^{V}(r) + \frac{105}{r^2}\phi^{IV}(r) - \frac{420}{r^3}\phi'''(r) + \frac{945}{r^4}\phi''(r) - \frac{945}{r^5}\phi'(r)\Big]$$

$$+ (yzwv\,\delta_{xu} + xzwv\,\delta_{yu} + xywv\,\delta_{zu} + xyzv\,\delta_{wu} + xyzw\,\delta_{uv}$$

$$+ uyzw\,\delta_{vx} + uxzw\,\delta_{vy} + uxyw\,\delta_{vz} + uxyz\,\delta_{vw} + uxyv\,\delta_{zw}$$

$$+ uyzv\,\delta_{xw} + uzxv\,\delta_{yw} + uxwv\,\delta_{yz} + uywv\,\delta_{xz} + uzwv\,\delta_{xy})$$

$$\times \frac{1}{r^5}\Big[\phi^{V}(r) - \frac{10}{r}\phi^{IV}(r) + \frac{45}{r^2}\phi'''(r) - \frac{105}{r^3}\phi''(r) + \frac{105}{r^4}\phi'(r)\Big]$$

$$+ \Big[\delta_{vx}(zw\,\delta_{yu} + yw\,\delta_{zu} + yz\,\delta_{wu}) + \delta_{vy}(zw\,\delta_{xu} + xw\,\delta_{zu} + xz\,\delta_{wu})$$

$$+ \delta_{vz}(yw\,\delta_{xu} + xw\,\delta_{yu} + xy\,\delta_{wu}) + \delta_{vw}(yz\,\delta_{xu} + xz\,\delta_{yu} + xy\,\delta_{zu})$$

$$+ \delta_{zw}(yv\,\delta_{xu} + xv\,\delta_{yu} + xy\,\delta_{vu}) + \delta_{xw}(zv\,\delta_{yu} + yv\,\delta_{zu} + yz\,\delta_{vu})$$

$$+ \delta_{yw}(xv\,\delta_{zu} + zv\,\delta_{xu} + xz\,\delta_{vu}) + \delta_{yz}(wv\,\delta_{xu} + xv\,\delta_{wu} + xw\,\delta_{uv})$$

$$+ \delta_{xz}(wv\,\delta_{yu} + yv\,\delta_{wu} + yw\,\delta_{vu}) + \delta_{xy}(wv\,\delta_{zu} + zv\,\delta_{wu} + wz\,\delta_{vu})$$

$$+ u\,\delta_{zw}(y\,\delta_{xv} + x\,\delta_{yv}) + u\,\delta_{xw}(z\,\delta_{yv} + y\,\delta_{zv}) + u\,\delta_{yw}(x\,\delta_{zv} + z\,\delta_{xv})$$

$$+ u\,\delta_{yz}(w\,\delta_{xv} + x\,\delta_{vw}) + u\,\delta_{xz}(w\,\delta_{yv} + y\,\delta_{wv}) + u\,\delta_{xy}(w\,\delta_{zv} + z\,\delta_{wv})$$

$$+ uv(\delta_{xy}\,\delta_{zw} + \delta_{yz}\,\delta_{wx} + \delta_{xz}\,\delta_{yw})\Big]\frac{1}{r^4}\Big[\phi^{IV}(r) - \frac{6}{r}\phi'''(r) + \frac{15}{r^2}\phi''(r) - \frac{15}{r^3}\phi'(r)\Big]\Big\}$$

$$+\Big[\delta_{zw}(\delta_{xv}\delta_{yu}+\delta_{xu}\delta_{yv})+\delta_{xw}(\delta_{zu}\delta_{yv}+\delta_{yu}\delta_{zv})$$
$$+\ \delta_{yw}(\delta_{xu}\delta_{zv}+\delta_{zu}\delta_{xv})+\delta_{yz}(\delta_{wu}\delta_{xv}+\delta_{xu}\delta_{wv})$$
$$+\ \delta_{xz}(\delta_{wu}\delta_{yv}+\delta_{yu}\delta_{wv})+\delta_{xy}(\delta_{wu}\delta_{zv}+\delta_{zu}\delta_{wv})$$
$$+\ \delta_{vu}(\delta_{xy}\delta_{zw}+\delta_{yz}\delta_{xw}+\delta_{xz}\delta_{yw})\Big]\frac{1}{r^3}\left[\phi'''(r)-\frac{3}{r}\phi''(r)+\frac{3}{r^2}\phi'(r)\right]\Big\}\Big|_{r=r_0^{\ell\ell'}}$$

The deltas are Kronecker deltas and each of x,y,z,u,v,w extends over the three Cartesian indices x, y, z. The first two terms in the Taylor's expansion of the potential are zero for the reasons previously stated. The derivatives are evaluated at the equilibrium separation

$$r_0^{\ell\ell'}=\left[(x_0^{\ell\ell'})^2+(y_0^{\ell\ell'})^2+(z_0^{\ell\ell'})^2\right]^{\frac{1}{2}}$$

The transformation to normal coordinates in Eq. (5) becomes in this case

$$u_\alpha^\ell=\left(\frac{\hbar}{2NM}\right)^{\frac{1}{2}}\sum_{\underset{\sim}{k}j}\frac{e_\alpha(\underset{\sim}{k}\,j)}{\sqrt{\omega_{\underset{\sim}{k}j}}}\;e^{2\pi i\,\underset{\sim}{k}\cdot\underset{\sim}{r}_0^\ell}\left[a_{\underset{\sim}{k}j}-a^+_{-\underset{\sim}{k}j}\right]$$

Substituting this last expression into Eq. (27) and comparing the resulting expression with the corresponding terms in the hamiltonian of Eq. (13) we get

$$\Phi(\lambda_1\ldots\lambda_n)=\frac{1}{2M^{n/2}}\sum_{\ell}\sum_{\alpha_1\ldots\alpha_n}e_{\alpha_1}(\lambda_1)\ldots e_{\alpha_n}(\lambda_n)\,\phi_{\alpha_1\ldots\alpha_n}(\ell)\,(1-e^{-2\pi i\,\underset{\sim}{k}_1\cdot\underset{\sim}{r}_0^\ell})\ldots \times(1-e^{-2\pi i\,\underset{\sim}{k}_n\cdot\underset{\sim}{r}_0^\ell}) \qquad (28)$$

In the above expression the ℓ - summation extends over only nearest neighbour lattice vectors of a given lattice point. (see DISCUSSION)

We now return to the evaluation of the terms $\frac{Z_n}{Z_0}$, $n=1,\ldots,10$ which contribute to the free energy (Eq. 23). Consider first the term

$$Z_3 = -\beta \sum_n e^{-\beta E_n} \langle n | H_6 | n \rangle \tag{29}$$

Using the definition of H_6 in Eqs. (13-16) get

$$Z_3 = -\beta \frac{\hbar^3}{(8)(6!)N^2} \sum_{\lambda_1 \ldots \lambda_6} \Delta(\underset{\sim}{k}_1 + \underset{\sim}{k}_2 + \cdots + \underset{\sim}{k}_6)\, \Phi(\lambda_1 \lambda_2 \ldots \lambda_6)$$
$$\times \frac{1}{\sqrt{\omega_1 \omega_2 \cdots \omega_6}} \sum_n e^{-\beta E_n} \langle n | A_{\lambda_1} A_{\lambda_2} \cdots A_{\lambda_6} | n \rangle$$

where $\omega_i = \omega_{\lambda_i}$

and as before λ_i denotes the index pair $\underset{\sim}{k}_i j_i$ while $-\lambda_i$ will denote the pair $-\underset{\sim}{k}_i j_i$. If we expand the product $A_{\lambda_1} A_{\lambda_2} A_{\lambda_3} \times A_{\lambda_4} A_{\lambda_5} A_{\lambda_6}$ we get a sum of terms each of which is a product of six creation and annihilation operators a_{λ_i} *and* $a^+_{\lambda_i}$. But because of the results of operating on some eigenstate $|n\rangle$ with these operators (see Eq. (11)) and the orthogonality of different states $|n\rangle$, the only contribution to the matrix element $\langle n|A_{\lambda_1}\cdots A_{\lambda_6}|n\rangle$ comes from those terms containing equal numbers of creation and annihilation operators. Moreover, each creation operator must be paired with an annihilation operator such that the result of all the operations on the state $|n\rangle$ is same numerical factor times the same state $|n\rangle$. A typical contributing term is

$$\langle n|a^{+}_{-\lambda_1} a^{+}_{-\lambda_2} a^{+}_{-\lambda_3} a_{\lambda_4} a_{\lambda_5} a_{\lambda_6}|n\rangle$$

$$= \Delta(\underset{\sim}{k}_1+\underset{\sim}{k}_4)\Delta(\underset{\sim}{k}_2+\underset{\sim}{k}_5)\Delta(\underset{\sim}{k}_3+\underset{\sim}{k}_6)\,\delta_{j_1j_4}\,\delta_{j_2j_5}\,\delta_{j_3j_6}$$

$$\times\ n_1 n_2 n_3 \qquad ,$$

where $n_i = n_{\underset{\sim}{k}_i j_i}$ is the number of phonons in the single-particle state labelled with the index pair $\underset{\sim}{k}_i j_i$.
The number of different ways in which we can pair the indices $\lambda_1,\ldots,\lambda_6$ to give non zero matrix elements is easily seen to be 15. Moreover for each pairing scheme the contribution to Z_3 is identical since we can always interchange the labels λ_i without affecting the summand (note that $\Phi(\lambda_1,\ldots,\lambda_6)$, by its definition, is invariant under permutations of the λ_i)

It should be mentioned here that there are no contributions to Z corresponding to odd powers of λ since in such cases the matrix elements involved contain an odd number of operators A_{λ_i} so that when we pair creation and annihilation operators we are always left with an unpaired operator. Hence all such matrix elements are zero.

The final expression for Z_3 becomes

$$Z_3 = -\beta \frac{\hbar^3}{6!8N^2} \times 15 \times \sum_{\lambda_1\lambda_2\lambda_3} \Phi(\lambda_1 -\lambda_1\, \lambda_2 -\lambda_2\, \lambda_3 -\lambda_3) \frac{1}{\omega_1\omega_2\omega_3} \times \sum_n e^{-\beta E_n}(2n_1+1)(2n_2+1)(2n_3+1)$$

Use has been made of the easily proved property of the normal mode frequencies ω_{k_j} that $\omega_{-k_j} = \omega_{k_j}$. The corresponding contribution to the free energy is

$$F_3 = -\frac{1}{\beta}\frac{Z_3}{Z_0}$$

We thus need to evaluate the quotient

$$\frac{\sum_n e^{-\beta E_n}(2n_1+1)(2n_2+1)(2n_3+1)}{\sum_n e^{-\beta E_n}}$$

This is done in APPENDIX C, the result being

$$(2\bar{n}_1+1)(2\bar{n}_2+1)(2\bar{n}_3+1)$$

where we now define the mean phonon occupation number n_i by

$$\bar{n}_i = \frac{1}{e^{\beta\hbar\omega_i}-1}$$

We get

$$F_3 = \frac{\hbar^3}{6!\,8N^2} \times 15 \times \sum_{\lambda_1\lambda_2\lambda_3} \Phi(\lambda_1 -\lambda_1\, \lambda_2 -\lambda_2\, \lambda_3 -\lambda_3)\, \frac{1}{\omega_1\omega_2\omega_3} \tag{32}$$

$$\times\, (2\bar{n}_1+1)(2\bar{n}_2+1)(2\bar{n}_3+1)$$

Using the definition of $\Phi(\lambda_1 \ldots \lambda_6)$ in Eq. (25) and substituting for $\phi_{xyzuvw}(\ell)$ from Eq. (23) we have

$$\Phi(\lambda_1 -\lambda_1\, \lambda_2 -\lambda_2\, \lambda_3 -\lambda_3) \tag{33}$$

$$= \sum_{\vec{n}} \Big\{ -\frac{1}{16M^3}\left(\frac{a_0}{r_0}\right)^6 F(r_0) \times (\mathbf{n}\cdot\mathbf{e}_1)^2(\mathbf{n}\cdot\mathbf{e}_2)^2(\mathbf{n}\cdot\mathbf{e}_3)^2$$

$$-\frac{1}{4M^3}\frac{a_0^4}{r_0^5}E(r_0) \times \Big[(\mathbf{e}_1\cdot\mathbf{e}_1)(\mathbf{n}\cdot\mathbf{e}_2)^2(\mathbf{n}\cdot\mathbf{e}_3)^2 + (\mathbf{e}_2\cdot\mathbf{e}_2)(\mathbf{n}\cdot\mathbf{e}_1)^2(\mathbf{n}\cdot\mathbf{e}_3)^2$$

$$+ (\mathbf{e}_3\cdot\mathbf{e}_3)(\mathbf{n}\cdot\mathbf{e}_1)^2(\mathbf{n}\cdot\mathbf{e}_2)^2 + 4(\mathbf{e}_1\cdot\mathbf{e}_2)(\mathbf{n}\cdot\mathbf{e}_1)(\mathbf{n}\cdot\mathbf{e}_2)(\mathbf{n}\cdot\mathbf{e}_3)^2$$

$$+ 4(\mathbf{e}_1\cdot\mathbf{e}_3)(\mathbf{n}\cdot\mathbf{e}_1)(\mathbf{n}\cdot\mathbf{e}_2)^2(\mathbf{n}\cdot\mathbf{e}_3) + 4(\mathbf{e}_2\cdot\mathbf{e}_3)(\mathbf{n}\cdot\mathbf{e}_1)^2(\mathbf{n}\cdot\mathbf{e}_2)(\mathbf{n}\cdot\mathbf{e}_3)\Big]$$

$$-\frac{D(r_0)}{M^3}\frac{a_0^2}{r_0^4}\Big[2(\mathbf{e}_1\cdot\mathbf{e}_2)^2(\mathbf{n}\cdot\mathbf{e}_3)^2 + 2(\mathbf{e}_1\cdot\mathbf{e}_2)(\mathbf{e}_1\cdot\mathbf{e}_3)(\mathbf{n}\cdot\mathbf{e}_2)(\mathbf{n}\cdot\mathbf{e}_3)$$

$$+ (\mathbf{e}_2\cdot\mathbf{e}_2)(\mathbf{e}_1\cdot\mathbf{e}_1)(\mathbf{n}\cdot\mathbf{e}_3)^2 + 4(\mathbf{e}_2\cdot\mathbf{e}_2)(\mathbf{e}_1\cdot\mathbf{e}_3)(\mathbf{n}\cdot\mathbf{e}_1)(\mathbf{n}\cdot\mathbf{e}_3)$$

$$+ 4(\underset{\sim}{e}_2\cdot\underset{\sim}{e}_3)(\underset{\sim}{e}_1\cdot\underset{\sim}{e}_1)(\underset{\sim}{n}\cdot\underset{\sim}{e}_2)(\underset{\sim}{n}\cdot\underset{\sim}{e}_3) + 8(\underset{\sim}{e}_2\cdot\underset{\sim}{e}_3)(\underset{\sim}{e}_1\cdot\underset{\sim}{e}_2)(\underset{\sim}{n}\cdot\underset{\sim}{e}_1)(\underset{\sim}{n}\cdot\underset{\sim}{e}_3)$$

$$+ 8(\underset{\sim}{e}_2\cdot\underset{\sim}{e}_3)(\underset{\sim}{e}_1\cdot\underset{\sim}{e}_3)(\underset{\sim}{n}\cdot\underset{\sim}{e}_1)(\underset{\sim}{n}\cdot\underset{\sim}{e}_2) + (\underset{\sim}{e}_3\cdot\underset{\sim}{e}_3)(\underset{\sim}{e}_1\cdot\underset{\sim}{e}_1)(\underset{\sim}{n}\cdot\underset{\sim}{e}_2)^2$$

$$+ 4(\underset{\sim}{e}_3\cdot\underset{\sim}{e}_3)(\underset{\sim}{e}_1\cdot\underset{\sim}{e}_2)(\underset{\sim}{n}\cdot\underset{\sim}{e}_1)(\underset{\sim}{n}\cdot\underset{\sim}{e}_2) + 6(\underset{\sim}{e}_1\cdot\underset{\sim}{e}_3)(\underset{\sim}{e}_1\cdot\underset{\sim}{e}_2)(\underset{\sim}{n}\cdot\underset{\sim}{e}_2)(\underset{\sim}{n}\cdot\underset{\sim}{e}_3)$$

$$+ 2(\underset{\sim}{e}_1\cdot\underset{\sim}{e}_3)^2(\underset{\sim}{n}\cdot\underset{\sim}{e}_2)^2 + (\underset{\sim}{e}_3\cdot\underset{\sim}{e}_3)(\underset{\sim}{e}_2\cdot\underset{\sim}{e}_2)(\underset{\sim}{n}\cdot\underset{\sim}{e}_1)^2$$

$$+ 2(\underset{\sim}{e}_2\cdot\underset{\sim}{e}_3)^2(\underset{\sim}{n}\cdot\underset{\sim}{e}_1)^2\Big] - \frac{4}{M^3}\frac{C(r_0)}{r_0^3}\Big[2(\underset{\sim}{e}_3\cdot\underset{\sim}{e}_3)(\underset{\sim}{e}_1\cdot\underset{\sim}{e}_2)^2$$

$$+ (\underset{\sim}{e}_1\cdot\underset{\sim}{e}_1)(\underset{\sim}{e}_2\cdot\underset{\sim}{e}_2)(\underset{\sim}{e}_3\cdot\underset{\sim}{e}_3) + 2(\underset{\sim}{e}_2\cdot\underset{\sim}{e}_2)(\underset{\sim}{e}_1\cdot\underset{\sim}{e}_3)^2$$

$$+ 8(\underset{\sim}{e}_1\cdot\underset{\sim}{e}_2)(\underset{\sim}{e}_1\cdot\underset{\sim}{e}_3)(\underset{\sim}{e}_2\cdot\underset{\sim}{e}_3) + 2(\underset{\sim}{e}_1\cdot\underset{\sim}{e}_1)(\underset{\sim}{e}_2\cdot\underset{\sim}{e}_3)^2\Big]\Big\}$$

$$\times (1-\cos\pi a_0 \underset{\sim}{k}_1\cdot\underset{\sim}{n})(1-\cos\pi a_0 \underset{\sim}{k}_2\cdot\underset{\sim}{n})(1-\cos\pi a_0 \underset{\sim}{k}_3\cdot\underset{\sim}{n})$$

The above summation is over the nearest neighbour vectors for same atom and r_o is the nearest neighbour separation. The dimensionless vector $\underset{\sim}{n}$ is defined by

$$r_0^{\ell} = \frac{a_0}{2}\underset{\sim}{n} \qquad (a_o \text{ is the lattice constant}) \qquad (34)$$

We have also made use of the following definitions:

$$C(r_0) = \left\{ \phi'''(r) - \frac{3}{r}\phi''(r) + \frac{3}{r^2}\phi'(r) \right\}\Big|_{r=r_0} \tag{35}$$

$$D(r_0) = \left\{ \phi^{iv}(r) - \frac{6}{r}\phi'''(r) + \frac{15}{r^2}\phi''(r) - \frac{15}{r^3}\phi'(r) \right\}\Big|_{r=r_0}$$

$$E(r_0) = \left\{ \phi^{v}(r) - \frac{10}{r}\phi^{iv}(r) + \frac{45}{r^2}\phi'''(r) - \frac{105}{r^3}\phi''(r) + \frac{105}{r^4}\phi'(r) \right\}\Big|_{r=r_0}$$

$$F(r_0) = \left\{ \phi^{vi}(r) - \frac{15}{r}\phi^{v}(r) + \frac{105}{r^2}\phi^{iv}(r) - \frac{420}{r^3}\phi'''(r) + \frac{945}{r^4}\phi''(r) - \frac{945}{r^5}\phi'(r) \right\}\Big|_{r=r_0}$$

For future use define also

$$B(r_0) = \left\{ \phi''(r) - \frac{1}{r}\phi'(r) \right\}\Big|_{r=r_0} \tag{36}$$

Z_1 can be evaluated in exactly the same way as Z_3. This time we need to evaluate a matrix element of the form

$$\langle n | A_{\lambda_1} A_{\lambda_2} A_{\lambda_3} A_{\lambda_4} | n \rangle$$

The number of different ways in which we can pair the λ_i to get a non-zero result is 3. The contribution from Z_1 to the free energy is easily calculated to be

$$F_1 = -\frac{1}{\beta}\frac{Z_1}{Z_0} \tag{37}$$
$$= \frac{\hbar^2}{96N} \times 3 \times \sum_{\lambda_1\lambda_2} \Phi(\lambda_1 -\lambda_1 \lambda_2 -\lambda_2)\frac{1}{\omega_1\omega_2}(2\bar{n}_1+1)(2\bar{n}_2+1)$$

From the previous definitions of $\Phi(\lambda_1\lambda_2\lambda_3\lambda_4)$ and $\phi_{xyzu}(l)$ we get

$$\Phi(\lambda_1 -\lambda_1 \lambda_2 -\lambda_2) \tag{38}$$
$$= \sum_{\underset{\sim}{n}} \Big\{ \frac{1}{8M^2}\left(\frac{a_0}{r_0}\right)^4 D(r_0) \times (\underset{\sim}{n}\cdot\underset{\sim}{e}_1)^2(\underset{\sim}{n}\cdot\underset{\sim}{e}_2)^2 + \frac{1}{2M^2}\frac{a_0^2}{r_0^3}C(r_0)$$
$$\times\left[4(\underset{\sim}{n}\cdot\underset{\sim}{e}_1)(\underset{\sim}{n}\cdot\underset{\sim}{e}_2)(\underset{\sim}{e}_1\cdot\underset{\sim}{e}_2) + (\underset{\sim}{n}\cdot\underset{\sim}{e}_1)^2(\underset{\sim}{e}_2\cdot\underset{\sim}{e}_2) + (\underset{\sim}{n}\cdot\underset{\sim}{e}_2)^2(\underset{\sim}{e}_1\cdot\underset{\sim}{e}_1)\right]$$
$$+\frac{2}{M^2}\frac{1}{r_0^2}B(r_0)\left[2(\underset{\sim}{e}_1\cdot\underset{\sim}{e}_2)^2 + (\underset{\sim}{e}_1\cdot\underset{\sim}{e}_1)(\underset{\sim}{e}_2\cdot\underset{\sim}{e}_2)\right]\Big\}(1-\cos\pi a_0\underset{\sim}{k}_1\cdot\underset{\sim}{n})(1-\cos\pi a_0\underset{\sim}{k}_2\cdot\underset{\sim}{n})$$

1 One can show analytically that the terms Z', Z'', and Z''' do not contribute to the Z_i (APPENDIX H). Consider first Z_4 and Z_6. In APPENDIX D it is shown that they are identical. The exact expression for Z_4 is

$$Z_4 = \beta\sum_{m,n} e^{-\beta E_n}\frac{\langle n|H_3|m\rangle\langle m|H_5|n\rangle}{E_m - E_n} \tag{39}$$

We shall also ignore Z" and Z"' in the other Z_i's. The only non-zero contribution to Z_4 occurs when the three A_{λ_i}'s in H_3 are paired with three A_{λ_i}'s in H_5 and the remaining two being paired. This can be done in 60 different ways. Following the same logic as was used in evaluating F_3 we get

$$F_4 = -\frac{1}{\beta}\frac{Z_4}{Z_0} \tag{40}$$

$$= -\frac{2^{-4}\hbar^3}{3!\,5!\,N^2} \times 60 \times \sum_{\lambda_1\lambda_2\lambda_3\lambda_4} \Delta(k_1+k_2+k_3)$$

$$\times\, \Phi(\lambda_1\lambda_2\lambda_3)\,\Phi(-\lambda_1,-\lambda_2,-\lambda_3,-\lambda_4\,\lambda_4) \times \frac{1}{\omega_1\omega_2\omega_3\omega_4}$$

$$\times\,(2\bar{n}_4+1)\left[\frac{(\bar{n}_1+1)(\bar{n}_2+1)(\bar{n}_3+1)-\bar{n}_1\bar{n}_2\bar{n}_3}{\omega_1+\omega_2+\omega_3} + 3\,\frac{(\bar{n}_1+1)(\bar{n}_2+1)\bar{n}_3-\bar{n}_1\bar{n}_2(\bar{n}_3+1)}{\omega_1+\omega_2-\omega_3}\right]$$

Although each of H_3 and H_5 contains a delta function, one of them becomes redundant as a result of the pairing of operators so that only one remains in F_4. The term in the square brackets has been reduced to its present form by using the fact that the rest of the summand is invariant under permutations of λ_1, λ_2 and λ_3.

We have

$$\Phi(-\lambda_1-\lambda_2-\lambda_3-\lambda_4\,\lambda_4) \tag{41}$$

$$= \sum_{\mathbf{n}} \Big\{ \frac{E(r_0)}{32M^{5/2}}\left(\frac{a_0}{r_0}\right)^5 (\mathbf{n}\cdot\mathbf{e}_1)(\mathbf{n}\cdot\mathbf{e}_2)(\mathbf{n}\cdot\mathbf{e}_3)(\mathbf{n}\cdot\mathbf{e}_4)^2 + \frac{D(r_0)}{8M^{5/2}}\frac{a_0^3}{r_0^4}$$

$$\times\Big[2(\mathbf{e}_1\cdot\mathbf{e}_4)(\mathbf{n}\cdot\mathbf{e}_2)(\mathbf{n}\cdot\mathbf{e}_3)(\mathbf{n}\cdot\mathbf{e}_4) + 2(\mathbf{e}_2\cdot\mathbf{e}_4)(\mathbf{n}\cdot\mathbf{e}_1)(\mathbf{n}\cdot\mathbf{e}_3)(\mathbf{n}\cdot\mathbf{e}_4)$$

$$+ 2(\mathbf{e}_3\cdot\mathbf{e}_4)(\mathbf{n}\cdot\mathbf{e}_1)(\mathbf{n}\cdot\mathbf{e}_2)(\mathbf{n}\cdot\mathbf{e}_4) + (\mathbf{e}_4\cdot\mathbf{e}_4)(\mathbf{n}\cdot\mathbf{e}_1)(\mathbf{n}\cdot\mathbf{e}_2)(\mathbf{n}\cdot\mathbf{e}_3)$$

$$+ (\mathbf{e}_2\cdot\mathbf{e}_3)(\mathbf{n}\cdot\mathbf{e}_1)(\mathbf{n}\cdot\mathbf{e}_4)^2 + (\mathbf{e}_1\cdot\mathbf{e}_3)(\mathbf{n}\cdot\mathbf{e}_2)(\mathbf{n}\cdot\mathbf{e}_4)^2 + (\mathbf{e}_1\cdot\mathbf{e}_2)(\mathbf{n}\cdot\mathbf{e}_3)(\mathbf{n}\cdot\mathbf{e}_4)^2\Big]$$

$$+ \frac{C(r_0)}{2M^{5/2}}\frac{a_0}{r_0^3}\Big[2(\mathbf{n}\cdot\mathbf{e}_2)(\mathbf{e}_3\cdot\mathbf{e}_4)(\mathbf{e}_1\cdot\mathbf{e}_4) + 2(\mathbf{n}\cdot\mathbf{e}_1)(\mathbf{e}_3\cdot\mathbf{e}_4)(\mathbf{e}_2\cdot\mathbf{e}_4)$$

$$+ 2(\mathbf{n}\cdot\mathbf{e}_3)(\mathbf{e}_1\cdot\mathbf{e}_4)(\mathbf{e}_2\cdot\mathbf{e}_4) + 2(\mathbf{n}\cdot\mathbf{e}_4)(\mathbf{e}_2\cdot\mathbf{e}_3)(\mathbf{e}_1\cdot\mathbf{e}_4)$$

$$+ (\mathbf{n}\cdot\mathbf{e}_1)(\mathbf{e}_2\cdot\mathbf{e}_3)(\mathbf{e}_4\cdot\mathbf{e}_4) + 2(\mathbf{n}\cdot\mathbf{e}_4)(\mathbf{e}_1\cdot\mathbf{e}_3)(\mathbf{e}_2\cdot\mathbf{e}_4)$$

$$+ (\mathbf{n}\cdot\mathbf{e}_2)(\mathbf{e}_1\cdot\mathbf{e}_3)(\mathbf{e}_4\cdot\mathbf{e}_4) + 2(\mathbf{n}\cdot\mathbf{e}_4)(\mathbf{e}_1\cdot\mathbf{e}_2)(\mathbf{e}_3\cdot\mathbf{e}_4)$$

$$+ (\mathbf{n}\cdot\mathbf{e}_3)(\mathbf{e}_1\cdot\mathbf{e}_2)(\mathbf{e}_4\cdot\mathbf{e}_4)\Big]\Big\}(1-\cos\pi a_0\mathbf{k}_4\cdot\mathbf{n})\prod_{j=1}^{3}(1-e^{\pi a_0 i\mathbf{k}_j\cdot\mathbf{n}})$$

$$\Phi(\lambda_1\lambda_2\lambda_3) = \sum_{\mathbf{n}}\Big\{\frac{C(r_0)}{16M^{3/2}}\left(\frac{a_0}{r_0}\right)^3(\mathbf{n}\cdot\mathbf{e}_1)(\mathbf{n}\cdot\mathbf{e}_2)(\mathbf{n}\cdot\mathbf{e}_3) + \frac{B(r_0)}{4M^{3/2}}\frac{a_0}{r_0^2}$$

$$\times\Big[(\mathbf{e}_1\cdot\mathbf{e}_2)(\mathbf{n}\cdot\mathbf{e}_3) + (\mathbf{e}_2\cdot\mathbf{e}_3)(\mathbf{n}\cdot\mathbf{e}_1) + (\mathbf{e}_1\cdot\mathbf{e}_3)(\mathbf{n}\cdot\mathbf{e}_2)\Big]\Big\}$$

$$\times\prod_{j=1}^{3}(1-e^{-\pi a_0 i\mathbf{k}_j\cdot\mathbf{n}})$$

Next consider the term Z_2. The exact expression is

$$Z_2 = \beta\sum_{m,n} e^{-\beta E_n}\frac{\langle n|H_3|m\rangle\langle m|H_3|n\rangle}{E_m-E_n} \tag{42}$$

The only contribution occurs when each of the $A^{+s}_{\lambda_i}$ in one of the H_3's has its index λ_i paired with that of an A_{λ_i} in the other H_3. The number of distinct pairings is 6. Thus

$$F_2 = -\frac{1}{\beta}\frac{Z_2}{Z_0} \tag{43}$$

$$= -\frac{\hbar^2}{48N}\sum_{\lambda_1\lambda_2\lambda_3} \Delta(k_1+k_2+k_3)\,|\Phi(\lambda_1\lambda_2\lambda_3)|^2 \frac{1}{\omega_1\omega_2\omega_3}$$

$$\times\left[\frac{(\bar{n}_1+1)(\bar{n}_2+\bar{n}_3+1)+\bar{n}_2\bar{n}_3}{\omega_1+\omega_2+\omega_3} + 3\,\frac{\bar{n}_1\bar{n}_2+\bar{n}_1\bar{n}_3-\bar{n}_2\bar{n}_3+\bar{n}_1}{\omega_2+\omega_3-\omega_1}\right]$$

Use has been made of the property

$$\Phi(-\lambda_1,-\lambda_2,-\lambda_3) = -\Phi^*(\lambda_1\lambda_2\lambda_3) \tag{44}$$

which follows from the definition of $\Phi(\lambda_1\lambda_2\lambda_3)$ in Eq. (28) The * denotes complex conjugation. The summation indices λ_1, λ_2, λ_3 were permuted to reduce the term in the square brackets to the form shown. Again, only one delta function is needed.

The other possible scheme of pairing indices is to pair only one of the A_{λ_i} in one H_3 with an A_{λ_i} in the other H_3. However, this gives no contribution to Z_2 because one gets a factor $\Phi(\lambda_1, -\lambda_1\,\lambda_2)$ which can be shown to be zero for all Bravais lattices as well as for any lattice in which each atom is at a center of inversion symmetry (21). Consider now the term Z_5 where we take

$$Z_5 = \beta \sum_{m,n} e^{-\beta E_n} \frac{\langle n|H_4|m\rangle\langle m|H_4|n\rangle}{E_m - E_n} \tag{45}$$

One contribution to Z_5 arises from the pairing scheme in which each of the four operators A_{λ_i} in one of the H_4's has its index paired with that of an A_{λ_i} in the other H_4. The number of different ways in which this pairing can be performed is 24. The free energy contribution from this scheme "a" is

$$F_5^a = -\frac{1}{\beta}\frac{Z_5^a}{Z_0} \tag{46}$$

$$= -\frac{2^{-4}\hbar^3}{(4!)^2 N^2} \times 24 \times \sum_{\lambda_1\lambda_2\lambda_3\lambda_4} \Delta(\underset{\sim}{k}_1 + \underset{\sim}{k}_2 + \underset{\sim}{k}_3 + \underset{\sim}{k}_4)$$

$$\times |\Phi(\lambda_1\lambda_2\lambda_3\lambda_4)|^2 \frac{1}{\omega_1\omega_2\omega_3\omega_4}\Big[\frac{(\bar n_1+1)(\bar n_2+1)(\bar n_3+1)(\bar n_4+1) - \bar n_1\bar n_2\bar n_3\bar n_4}{\omega_1+\omega_2+\omega_3+\omega_4}$$

$$+4\frac{(\bar n_1+1)(\bar n_2+1)(\bar n_3+1)\bar n_4 - \bar n_1\bar n_2\bar n_3(\bar n_4+1)}{\omega_1+\omega_2+\omega_3-\omega_4} + 3\frac{(\bar n_1+1)(\bar n_2+1)\bar n_3\bar n_4 - \bar n_1\bar n_2(\bar n_3+1)(\bar n_4+1)}{\omega_1+\omega_2-\omega_3-\omega_4}\Big]$$

where

$$\Phi(\lambda_1\lambda_2\lambda_3\lambda_4) = \sum_{\underset{\sim}{n}}\Big\{\frac{D(r_0)}{32M^2}\left(\frac{a_0}{r_0}\right)^4 (\underset{\sim}{n}\cdot\underset{\sim}{e}_1)(\underset{\sim}{n}\cdot\underset{\sim}{e}_2)(\underset{\sim}{n}\cdot\underset{\sim}{e}_3)(\underset{\sim}{n}\cdot\underset{\sim}{e}_4) + \frac{C(r_0)}{8M^2}\frac{a_0^2}{r_0^3}\Big[(\underset{\sim}{n}\cdot\underset{\sim}{e}_1)(\underset{\sim}{n}\cdot\underset{\sim}{e}_2)(\underset{\sim}{e}_3\cdot\underset{\sim}{e}_4) \tag{47}$$

$$+ (\underset{\sim}{n}\cdot\underset{\sim}{e}_1)(\underset{\sim}{n}\cdot\underset{\sim}{e}_4)(\underset{\sim}{e}_2\cdot\underset{\sim}{e}_3) + (\underset{\sim}{n}\cdot\underset{\sim}{e}_3)(\underset{\sim}{n}\cdot\underset{\sim}{e}_4)(\underset{\sim}{e}_1\cdot\underset{\sim}{e}_2) + (\underset{\sim}{n}\cdot\underset{\sim}{e}_2)(\underset{\sim}{n}\cdot\underset{\sim}{e}_3)(\underset{\sim}{e}_1\cdot\underset{\sim}{e}_4) + (\underset{\sim}{n}\cdot\underset{\sim}{e}_1)(\underset{\sim}{n}\cdot\underset{\sim}{e}_3)(\underset{\sim}{e}_2\cdot\underset{\sim}{e}_4)$$

$$+ (\underset{\sim}{n}\cdot\underset{\sim}{e}_2)(\underset{\sim}{n}\cdot\underset{\sim}{e}_4)(\underset{\sim}{e}_1\cdot\underset{\sim}{e}_3)\Big] + \frac{B(r_0)}{2M^2 r_0^2}\Big[(\underset{\sim}{e}_1\cdot\underset{\sim}{e}_2)(\underset{\sim}{e}_3\cdot\underset{\sim}{e}_4) + (\underset{\sim}{e}_1\cdot\underset{\sim}{e}_3)(\underset{\sim}{e}_2\cdot\underset{\sim}{e}_4) + (\underset{\sim}{e}_1\cdot\underset{\sim}{e}_4)(\underset{\sim}{e}_2\cdot\underset{\sim}{e}_3)\Big]\Big\}$$

$$\times \prod_{j=1}^{4}(1 - e^{-\pi a_0 i \underset{\sim}{k}_j\cdot\underset{\sim}{n}})(1 - e^{\pi a_0 i \underset{\sim}{k}_j\cdot\underset{\sim}{n}})$$

Another contribution to Z_5 arises by pairing only two A_{λ_i} from one H_4 with two A_{λ_i} in the other H_4 and pairing the remaining two in each H_4. The number of distinct pairings is 72. The free energy from this scheme "b" is

$$F_5^b = -\frac{1}{\beta}\frac{Z_5^b}{Z_0} \tag{48}$$

$$= -\frac{2^{-4}\hbar^3}{(576)N^2} \times 72 \times \sum_{\lambda_1\lambda_2\lambda_3\lambda_4} \Phi(\lambda_1 -\lambda_1 \lambda_2 \lambda_3)\,\Phi(\lambda_4 -\lambda_4 -\lambda_2 -\lambda_3)$$

$$\times \frac{1}{\omega_1\omega_2\omega_3\omega_4}(2\bar{n}_1+1)(2\bar{n}_4+1)\left[\frac{\bar{n}_2+\bar{n}_3+1}{\omega_2+\omega_3} + \frac{\bar{n}_3-\bar{n}_2}{\omega_2-\omega_3}\right]$$

In this result λ_3 denotes the index pair $-\underset{\sim}{k}_2\, j_3$. This is due to the fact that our pairing scheme yields a delta function of the form $\Delta(\underset{\sim}{k}_2+\underset{\sim}{k}_3)$ and from the relations

$$\underset{\sim}{e}\left(\begin{matrix}\underset{\sim}{k}+2\pi\underset{\sim}{\tau}\\ j\end{matrix}\right) = \underset{\sim}{e}\left(\begin{matrix}\underset{\sim}{k}\\ j\end{matrix}\right) \tag{49}$$

$$\omega_{\underset{\sim}{k}+2\pi\underset{\sim}{\tau},j} = \omega_{\underset{\sim}{k}j}$$

which follow from the form of u_α^l assumed. (see (13)).
In the above $\underset{\sim}{k}$ is restricted by the periodic boundary conditions (Eq. (6)) and $\underset{\sim}{\tau}$ is a reciprocal lattice vector defined in Eq. (7). The Φ factors in F_5^b can be obtained from the previously defined $\Phi(\lambda_1\lambda_2\lambda_3\lambda_4)$ by suitable sign and label changes.

Turning now to the evaluation of Z_7, Z_8, and Z_9 we note that Z_7 and Z_9 are in fact identical (see APPENDIX D) but that Z_8 is in general different. We take

$$Z_7 = -\beta \sum_{n,m,p} e^{-\beta E_n} \frac{\langle n|H_3|m\rangle\langle m|H_3|p\rangle\langle p|H_4|n\rangle}{(E_p - E_n)\,(E_m - E_n)} \tag{50}$$

$$Z_8 = -\beta \sum_{n,m,p} e^{-\beta E_n} \frac{\langle n|H_3|m\rangle\langle m|H_4|p\rangle\langle p|H_3|n\rangle}{(E_p - E_n)(E_m - E_n)} \tag{51}$$

There are only two contributing pairing schemes. In the first one we take two A_{λ_i} from H_4 and pair them with two A_{λ_i} in one of the H_3's. Then we pair the remaining two A_{λ_i} in H_4 with two A_{λ_i} in the other H_3. This leaves one A_{λ_i} in each H_3 which are then paired. The number of possible pairings in this scheme "a" is 216. The free energy contributions are

$$
\begin{aligned}
F_7^a &= -\frac{1}{\beta}\frac{Z_7^a}{Z_0} \qquad (52)\\
&= -\frac{2^{-5}\hbar^3}{864 N^2} \times 216 \times \sum_{\substack{\lambda_1\lambda_2\lambda_3\\ \lambda_4\lambda_5}} \Delta(\underset{\sim}{k}_1+\underset{\sim}{k}_2+\underset{\sim}{k}_3)\,\Delta(-\underset{\sim}{k}_3+\underset{\sim}{k}_4+\underset{\sim}{k}_5)\,\Phi(\lambda_1\lambda_2\lambda_3)\,\Phi(-\lambda_3\lambda_4\lambda_5)\\
&\times \Phi(-\lambda_1-\lambda_2-\lambda_4-\lambda_5)\,\frac{1}{\omega_1\omega_2\omega_3\omega_4\omega_5} \times \Big[\Big\{\frac{\bar n_3\bar n_4\bar n_5}{-\omega_3-\omega_4-\omega_5} + \frac{\bar n_3(\bar n_4+1)(\bar n_5+1)}{-\omega_3+\omega_4+\omega_5}\\
&+ \frac{\bar n_3(\bar n_4+1)\bar n_5}{-\omega_3+\omega_4-\omega_5} + \frac{\bar n_3\bar n_4(\bar n_5+1)}{-\omega_3-\omega_4+\omega_5}\Big\}\Big\{\frac{\bar n_1\bar n_2}{-\omega_1-\omega_2-\omega_3} + \frac{\bar n_1(\bar n_2+1)}{-\omega_1+\omega_2-\omega_3} + \frac{(\bar n_1+1)\bar n_2}{\omega_1-\omega_2-\omega_3}\\
&+ \frac{(\bar n_1+1)(\bar n_2+1)}{\omega_1+\omega_2-\omega_3}\Big\} + \Big\{\frac{(\bar n_3+1)\bar n_4\bar n_5}{\omega_3-\omega_4-\omega_5} + \frac{(\bar n_3+1)(\bar n_4+1)\bar n_5}{\omega_3+\omega_4-\omega_5} + \frac{(\bar n_3+1)\bar n_4(\bar n_5+1)}{\omega_3-\omega_4+\omega_5}\\
&+ \frac{(\bar n_3+1)(\bar n_4+1)(\bar n_5+1)}{\omega_3+\omega_4+\omega_5}\Big\}\Big\{\frac{\bar n_1\bar n_2}{-\omega_1-\omega_2+\omega_3} + \frac{\bar n_1(\bar n_2+1)}{-\omega_1+\omega_2+\omega_3} + \frac{(\bar n_1+1)\bar n_2}{\omega_1-\omega_2+\omega_3}\\
&+ \frac{(\bar n_1+1)(\bar n_2+1)}{\omega_1+\omega_2+\omega_3}\Big\}\Big]
\end{aligned}
$$

$$F_8^a = -\frac{1}{\beta}\frac{Z_8^a}{Z_0} \tag{53}$$

$$= \frac{2^{-5}\hbar^3}{864\,N^2} \times 216 \times \sum_{\lambda_1 \ldots \lambda_5} \Delta(\underset{\sim}{k}_1 + \underset{\sim}{k}_2 + \underset{\sim}{k}_3)\Delta(-\underset{\sim}{k}_3 + \underset{\sim}{k}_4 + \underset{\sim}{k}_5)$$

$$\times\, \Phi(\lambda_1\lambda_2\lambda_3)\,\Phi(-\lambda_3\lambda_4\lambda_5)\,\Phi(-\lambda_1 -\lambda_2 -\lambda_4 -\lambda_5)\,\frac{1}{\omega_1\omega_2\omega_3\omega_4\omega_5}$$

$$\times\Big[\Big\{\frac{\bar n_3}{-\omega_1-\omega_2-\omega_3} + \frac{\bar n_3+1}{-\omega_1-\omega_2+\omega_3}\Big\}\Big\{\frac{\bar n_1\bar n_2\bar n_4\bar n_5}{-\omega_1-\omega_2-\omega_4-\omega_5} + \frac{\bar n_1\bar n_2(\bar n_4+1)\bar n_5}{-\omega_1-\omega_2+\omega_4-\omega_5}$$

$$+ \frac{\bar n_1\bar n_2\bar n_4(\bar n_5+1)}{-\omega_1-\omega_2-\omega_4+\omega_5} + \frac{\bar n_1\bar n_2(\bar n_4+1)(\bar n_5+1)}{-\omega_1-\omega_2+\omega_4+\omega_5}\Big\} + \Big\{\frac{\bar n_3}{\omega_1-\omega_2-\omega_3} + \frac{\bar n_3+1}{\omega_1-\omega_2+\omega_3}\Big\}$$

$$\times\Big\{\frac{(\bar n_1+1)\bar n_2\bar n_4\bar n_5}{\omega_1-\omega_2-\omega_4-\omega_5} + \frac{(\bar n_1+1)\bar n_2(\bar n_4+1)\bar n_5}{\omega_1-\omega_2+\omega_4-\omega_5} + \frac{(\bar n_1+1)\bar n_2\bar n_4(\bar n_5+1)}{\omega_1-\omega_2-\omega_4+\omega_5} + \frac{(\bar n_1+1)\bar n_2(\bar n_4+1)(\bar n_5+1)}{\omega_1-\omega_2+\omega_4+\omega_5}\Big\}$$

$$+\Big\{\frac{\bar n_3}{\omega_1+\omega_2-\omega_3} + \frac{\bar n_3+1}{\omega_1+\omega_2+\omega_3}\Big\}\Big\{\frac{(\bar n_1+1)(\bar n_2+1)\bar n_4\bar n_5}{\omega_1+\omega_2-\omega_4-\omega_5} + \frac{(\bar n_1+1)(\bar n_2+1)(\bar n_4+1)\bar n_5}{\omega_1+\omega_2+\omega_4-\omega_5}$$

$$+ \frac{(\bar n_1+1)(\bar n_2+1)\bar n_4(\bar n_5+1)}{\omega_1+\omega_2-\omega_4+\omega_5} + \frac{(\bar n_1+1)(\bar n_2+1)(\bar n_4+1)(\bar n_5+1)}{\omega_1+\omega_2+\omega_4+\omega_5}\Big\} + \Big\{\frac{\bar n_3}{-\omega_1+\omega_2-\omega_3}$$

$$+ \frac{\bar n_3+1}{-\omega_1+\omega_2+\omega_3}\Big\}\Big\{\frac{\bar n_1(\bar n_2+1)\bar n_4\bar n_5}{-\omega_1+\omega_2-\omega_4-\omega_5} + \frac{\bar n_1(\bar n_2+1)(\bar n_4+1)\bar n_5}{-\omega_1+\omega_2+\omega_4-\omega_5} + \frac{\bar n_1(\bar n_2+1)\bar n_4(\bar n_5+1)}{-\omega_1+\omega_2-\omega_4+\omega_5}$$

$$+ \frac{\bar n_1(\bar n_2+1)(\bar n_4+1)(\bar n_5+1)}{-\omega_1+\omega_2+\omega_4+\omega_5}\Big\}\Big]$$

The total contribution to the free energy from Z_7, Z_8, Z_9 for this pairing scheme is

$$F_{789}^{a} = 2F_7^{a} + F_8^{a} \tag{54}$$

$$= \frac{2^{-5}\hbar^3}{864 N^2} \times 432 \times \sum_{\lambda_1 \cdots \lambda_5} \Delta(k_1 + k_2 + k_3)\Delta(-k_3 + k_4 + k_5)$$

$$\times \Phi(\lambda_1 \lambda_2 \lambda_3)\Phi(-\lambda_3 \lambda_4 \lambda_5)\Phi(-\lambda_1 -\lambda_2 -\lambda_4 -\lambda_5)\frac{1}{\omega_1\omega_2\omega_3\omega_4\omega_5}$$

$$\times\Big[\Big\{\frac{(\bar n_1+1)(\bar n_2+1)(\bar n_3+1)-\bar n_1\bar n_2\bar n_3}{\omega_1+\omega_2+\omega_3} + \frac{(\bar n_1+1)(\bar n_2+1)\bar n_3 - \bar n_1\bar n_2(\bar n_3+1)}{\omega_1+\omega_2-\omega_3}\Big\}$$

$$\times\Big\{\frac{\bar n_4+\bar n_5+1}{\omega_1+\omega_2+\omega_4+\omega_5} + 2\,\frac{\bar n_5-\bar n_4}{\omega_1+\omega_2+\omega_4-\omega_5} - \frac{\bar n_4+\bar n_5+1}{\omega_1+\omega_2-\omega_4-\omega_5}\Big\}$$

$$+\Big\{\frac{(\bar n_1+1)\bar n_2(\bar n_3+1)-\bar n_1(\bar n_2+1)\bar n_3}{\omega_1-\omega_2+\omega_3} + \frac{(\bar n_1+1)\bar n_2\bar n_3 - \bar n_1(\bar n_2+1)(\bar n_3+1)}{\omega_1-\omega_2-\omega_3}\Big\}$$

$$\times\Big\{\frac{\bar n_4+\bar n_5+1}{-\omega_1+\omega_2+\omega_4+\omega_5} + 2\,\frac{\bar n_4-\bar n_5}{-\omega_1+\omega_2-\omega_4+\omega_5} - \frac{\bar n_4+\bar n_5+1}{-\omega_1+\omega_2-\omega_4-\omega_5}\Big\}\Big]$$

The pairing scheme yields three delta functions, the two above and also one of the form $\Delta(-k_1-k_2-k_4-k_5)$. This last one, however, is implied by the other two so it is omitted from the summand.

In the other contributing pairing scheme we pair one of the A_{λ_i} in each of the H_3's with different A_{λ_i} in the H_4. The remaining two A_{λ_i} in each of the H_3's and H_4 are then paired. This pairing scheme "b" also can be realized in 216 distinct ways.

The contribution from Z_7 is

$$F_7^b = -\frac{1}{\beta}\frac{Z_7^b}{Z_0} \tag{55}$$

$$= \frac{2^{-5}\hbar^3}{864\,N^2} \times 216 \times \sum_{\lambda_1 \cdots \lambda_5} \Delta(\underset{\sim}{k}_1 + \underset{\sim}{k}_3 + \underset{\sim}{k}_4)\, \Phi(\lambda_1\lambda_3\lambda_4)\, \Phi(-\lambda_2 -\lambda_3 -\lambda_4)$$

$$\times\, \Phi(-\lambda_5\lambda_5 -\lambda_1\lambda_2)\, \frac{1}{\omega_1\omega_2\omega_3\omega_4\omega_5} \times (2\bar{n}_5+1)\Big[\Big\{ \frac{\bar{n}_1\bar{n}_3\bar{n}_4}{-\omega_1-\omega_3-\omega_4}$$

$$+ \frac{\bar{n}_1\bar{n}_3(\bar{n}_4+1)}{-\omega_1-\omega_3+\omega_4} + \frac{\bar{n}_1(\bar{n}_3+1)\bar{n}_4}{-\omega_1+\omega_3-\omega_4} + \frac{\bar{n}_1(\bar{n}_3+1)(\bar{n}_4+1)}{-\omega_1+\omega_3+\omega_4}\Big\}\Big\{\frac{\bar{n}_2}{\omega_1+\omega_2}$$

$$+ \frac{\bar{n}_2+1}{\omega_1-\omega_2}\Big\} - \Big\{\frac{(\bar{n}_1+1)\bar{n}_3\bar{n}_4}{\omega_1-\omega_3-\omega_4} + \frac{(\bar{n}_1+1)\bar{n}_3(\bar{n}_4+1)}{\omega_1-\omega_3+\omega_4} + \frac{(\bar{n}_1+1)(\bar{n}_3+1)\bar{n}_4}{\omega_1+\omega_3-\omega_4}$$

$$+ \frac{(\bar{n}_1+1)(\bar{n}_3+1)(\bar{n}_4+1)}{\omega_1+\omega_3+\omega_4}\Big\}\Big\{\frac{\bar{n}_2}{\omega_1-\omega_2} + \frac{\bar{n}_2+1}{\omega_1+\omega_2}\Big\}\Big]$$

where λ_2 denotes the index pair $\underset{\sim}{k}_1 j_2$. This is because the pairing scheme results in a delta function of the form $\Delta(\underset{\sim}{k}_1 - \underset{\sim}{k}_2)$. Only one delta is required in this case.

From Z_9 get

$$F_9^b = -\frac{1}{\beta}\frac{Z_9^b}{Z_0}$$

$$= \frac{2^{-5}\hbar^3}{864\,N^2} \times 216 \times \sum_{\lambda_1\cdots\lambda_5} \Delta(\underset{\sim}{k}_1+\underset{\sim}{k}_3+\underset{\sim}{k}_4)\,\Phi(\lambda_1\lambda_3\lambda_4)\,\Phi(-\lambda_2-\lambda_3-\lambda_4)$$

$$\times\,\Phi(-\lambda_5\lambda_5-\lambda_1\lambda_2)\,\frac{1}{\omega_1\omega_2\omega_3\omega_4\omega_5}\,(2\bar{n}_5+1)\Big[\Big\{\frac{\bar{n}_2\bar{n}_3\bar{n}_4}{\omega_2+\omega_3+\omega_4}$$

$$-\frac{(\bar{n}_2+1)\bar{n}_3\bar{n}_4}{\omega_2-\omega_3-\omega_4}\Big\}\Big\{\frac{\bar{n}_1}{-\omega_1-\omega_3-\omega_4}+\frac{\bar{n}_1+1}{\omega_1-\omega_3-\omega_4}\Big\}$$

$$+\Big\{\frac{\bar{n}_2\bar{n}_3(\bar{n}_4+1)}{\omega_2+\omega_3-\omega_4}-\frac{(\bar{n}_2+1)\bar{n}_3(\bar{n}_4+1)}{\omega_2-\omega_3+\omega_4}\Big\}\Big\{\frac{\bar{n}_1}{-\omega_1-\omega_3+\omega_4}+\frac{\bar{n}_1+1}{\omega_1-\omega_3+\omega_4}\Big\}$$

$$+\Big\{\frac{\bar{n}_2(\bar{n}_3+1)\bar{n}_4}{\omega_2-\omega_3+\omega_4}-\frac{(\bar{n}_2+1)(\bar{n}_3+1)\bar{n}_4}{\omega_2+\omega_3-\omega_4}\Big\}\Big\{\frac{\bar{n}_1}{-\omega_1+\omega_3-\omega_4}+\frac{\bar{n}_1+1}{\omega_1+\omega_3-\omega_4}\Big\}$$

$$+\Big\{\frac{\bar{n}_2(\bar{n}_3+1)(\bar{n}_4+1)}{\omega_2-\omega_3-\omega_4}-\frac{(\bar{n}_2+1)(\bar{n}_3+1)(\bar{n}_4+1)}{\omega_2+\omega_3+\omega_4}\Big\}\Big\{\frac{\bar{n}_1}{-\omega_1+\omega_3+\omega_4}+\frac{\bar{n}_1+1}{\omega_1+\omega_3+\omega_4}\Big\}\Big]$$

Again λ_2 denotes the pair $\underset{\sim}{k}_1 j_2$.

The total contribution to the free energy from Z_7, Z_8, Z_9 for this pairing scheme is

$$F_{789}^b = \frac{2^{-5}\hbar^3}{864\,N^2} \times 432 \times \sum_{\lambda_1\cdots\lambda_5} \Delta(\underset{\sim}{k}_1+\underset{\sim}{k}_3+\underset{\sim}{k}_4) \tag{56}$$

$$\times\ \Phi(\lambda_1\lambda_3\lambda_4)\,\Phi(-\lambda_2-\lambda_3-\lambda_4)\,\Phi(-\lambda_5\lambda_5-\lambda_1\lambda_2)\ (2\bar{n}_5+1)$$

$$\times\left(\frac{1}{\omega_1+\omega_2}+\frac{1}{\omega_2-\omega_1}\right)\left\{\frac{(\bar{n}_1+1)(\bar{n}_3+1)(\bar{n}_4+1)-\bar{n}_1\bar{n}_3\bar{n}_4}{\omega_1+\omega_3+\omega_4}\right.$$

$$+\frac{(\bar{n}_1+1)(\bar{n}_3+1)\bar{n}_4-\bar{n}_1\bar{n}_3(\bar{n}_4+1)}{\omega_1+\omega_3-\omega_4}+\frac{(\bar{n}_1+1)\bar{n}_3(\bar{n}_4+1)-\bar{n}_1(\bar{n}_3+1)\bar{n}_4}{\omega_1-\omega_3+\omega_4}$$

$$\left.+\frac{(\bar{n}_1+1)\bar{n}_3\bar{n}_4-\bar{n}_1(\bar{n}_3+1)(\bar{n}_4+1)}{\omega_1-\omega_3-\omega_4}\right\}$$

Consider now the last term Z_{10}. We take

$$Z_{10}=\beta\sum_{n,m,p,q} e^{-\beta E_n}\frac{\langle n|H_3|m\rangle\langle m|H_3|p\rangle\langle p|H_3|q\rangle\langle q|H_3|n\rangle}{(E_q-E_n)\,(E_p-E_n)\,(E_m-E_n)}$$

One contributing pairing scheme is that for which no two A_{λ_i} in the same H_3 are paired and where each of the three A_{λ_i} in same H_3 is paired with an A_{λ_i} in a different H_3. Hence no two H_3's have more than one pair of A_{λ_i} in common. The number of distinct pairings in this scheme is 1296, and we get

$$Z_{10}^{a}=\beta\,\frac{2^{-6}\,\hbar^{6}}{(3!)^4N^2}\times 1296\times\sum_{\lambda_1\ldots\lambda_6}\Delta(k_1+k_2+k_3)\Delta(-k_1+k_4+k_5)$$

$$\times\,\Delta(-\underset{\sim}{k}_2-\underset{\sim}{k}_5+\underset{\sim}{k}_6)\,\Delta(-\underset{\sim}{k}_3-\underset{\sim}{k}_4-\underset{\sim}{k}_6)\;\Phi(\lambda_1\lambda_2\lambda_3)\,\Phi(-\lambda_1\lambda_4\lambda_5)$$

$$\times\,\Phi(-\lambda_2-\lambda_5\lambda_6)\,\Phi(-\lambda_3-\lambda_4-\lambda_6)\;\frac{1}{\omega_1\omega_2\omega_3\omega_4\omega_5\omega_6}$$

$$\times\sum_{n,m,p,q} e^{-\beta E_n}\,\frac{\langle n|A_{\lambda_1}A_{\lambda_2}A_{\lambda_3}|m\rangle\langle m|A_{-\lambda_1}A_{\lambda_4}A_{\lambda_5}|p\rangle\langle p|A_{-\lambda_2}A_{-\lambda_5}A_{\lambda_6}|q\rangle\langle q|A_{-\lambda_3}A_{-\lambda_4}A_{-\lambda_6}|n\rangle}{(E_m-E_n)(E_p-E_n)(E_q-E_n)}$$

The only other pairing scheme is the one in which again no two A_{λ_i} in the same H_3 are paired but now we consider two sets of two H_3's. In each set we pair two A_{λ_i} from one H_3 with two in the other H_3. This leaves two unpaired A_{λ_i} in each set of H_3's, which are then paired. The number of distinct pairings is 324 and we get a typical contribution:

$$Z_{10}^{6} = \beta\,\frac{2^{-6}\hbar^{6}}{(3!)^4N^2}\times 324\times\sum_{\lambda_1\ldots\lambda_6}\Delta(\underset{\sim}{k}_1+\underset{\sim}{k}_2+\underset{\sim}{k}_3)\,\Delta(-\underset{\sim}{k}_2-\underset{\sim}{k}_3+\underset{\sim}{k}_4)\,\Delta(-\underset{\sim}{k}_4+\underset{\sim}{k}_5+\underset{\sim}{k}_6)\,\Delta(\underset{\sim}{k}_1+\underset{\sim}{k}_5+\underset{\sim}{k}_6)$$

$$\times\;\Phi(\lambda_1\lambda_2\lambda_3)\,\Phi(-\lambda_2-\lambda_3\lambda_4)\,\Phi(-\lambda_4\lambda_5\lambda_6)\,\Phi(-\lambda_1-\lambda_5-\lambda_6)\;\frac{1}{\omega_1\omega_2\omega_3\omega_4\omega_5\omega_6}$$

$$\times\sum_{n,m,p,q} e^{-\beta E_n}\,\frac{\langle n|A_{\lambda_1}A_{\lambda_2}A_{\lambda_3}|m\rangle\langle m|A_{-\lambda_2}A_{-\lambda_3}A_{\lambda_4}|p\rangle\langle p|A_{-\lambda_4}A_{\lambda_5}A_{\lambda_6}|q\rangle\langle q|A_{-\lambda_1}A_{-\lambda_5}A_{-\lambda_6}|n\rangle}{(E_m-E_n)(E_p-E_n)(E_q-E_n)}$$

There are actually six contributions like the one above because two sets of two H_3's can be formed in only 3 possible ways and for each way there are only two possible ways of pairing the final two unpaired A_{λ_i} of each set of H_3's. We are thus left with the evaluation of the following sums:

$$\sum_{n,m,p,q} e^{-\beta E_n} \frac{\langle n|A_{\lambda_1}A_{\lambda_2}A_{\lambda_3}|m\rangle\langle m|A_{-\lambda_2}A_{-\lambda_3}A_{\lambda_4}|p\rangle\langle p|A_{\lambda_4}A_{\lambda_5}A_{\lambda_6}|q\rangle\langle q|A_{-\lambda_1}A_{-\lambda_5}A_{-\lambda_6}|n\rangle}{(E_m-E_n)(E_p-E_n)(E_q-E_n)}$$

$$\sum_{n,m,p,q} e^{-\beta E_n} \frac{\langle n|A_{\lambda_1}A_{\lambda_2}A_{\lambda_3}|m\rangle\langle m|A_{-\lambda_2}A_{-\lambda_3}A_{\lambda_4}|p\rangle\langle p|A_{-\lambda_1}A_{\lambda_5}A_{\lambda_6}|q\rangle\langle q|A_{-\lambda_4}A_{-\lambda_5}A_{-\lambda_6}|n\rangle}{(E_m-E_n)(E_p-E_n)(E_q-E_n)}$$

$$\sum_{n,m,p,q} e^{-\beta E_n} \frac{\langle n|A_{\lambda_1}A_{\lambda_2}A_{\lambda_3}|m\rangle\langle m|A_{\lambda_4}A_{\lambda_5}A_{\lambda_6}|p\rangle\langle p|A_{-\lambda_2}A_{-\lambda_3}A_{-\lambda_4}|q\rangle\langle q|A_{-\lambda_1}A_{-\lambda_5}A_{-\lambda_6}|n\rangle}{(E_m-E_n)(E_p-E_n)(E_q-E_n)}$$

$$\sum_{n,m,p,q} e^{-\beta E_n} \frac{\langle n|A_{\lambda_1}A_{\lambda_2}A_{\lambda_3}|m\rangle\langle m|A_{-\lambda_1}A_{\lambda_5}A_{\lambda_6}|p\rangle\langle p|A_{-\lambda_2}A_{-\lambda_3}A_{\lambda_4}|q\rangle\langle q|A_{-\lambda_4}A_{-\lambda_5}A_{-\lambda_6}|n\rangle}{(E_m-E_n)(E_p-E_n)(E_q-E_n)}$$

$$\sum_{n,m,p,q} e^{-\beta E_n} \frac{\langle n|A_{\lambda_1}A_{\lambda_2}A_{\lambda_3}|m\rangle\langle m|A_{\lambda_4}A_{\lambda_5}A_{\lambda_6}|p\rangle\langle p|A_{-\lambda_1}A_{-\lambda_5}A_{-\lambda_6}|q\rangle\langle q|A_{-\lambda_2}A_{-\lambda_3}A_{-\lambda_4}|n\rangle}{(E_m-E_n)(E_p-E_n)(E_q-E_n)}$$

$$\sum_{n,m,p,q} e^{-\beta E_n} \frac{\langle n|A_{\lambda_1}A_{\lambda_2}A_{\lambda_3}|m\rangle\langle m|A_{-\lambda_1}A_{\lambda_5}A_{\lambda_6}|p\rangle\langle p|A_{\lambda_4}A_{-\lambda_5}A_{-\lambda_6}|q\rangle\langle q|A_{-\lambda_2}A_{-\lambda_3}A_{-\lambda_4}|n\rangle}{(E_m-E_n)(E_p-E_n)(E_q-E_n)}$$

Due to the complexity of the algebra involved in evaluating these contributions and also the fact that in order to obtain meaningful results an exceedingly large amount of computer time would have been necessary(see next section),the contributions from Z_{10}^{a} and Z_{10}^{b} were not obtained.

The harmonic free energy is(15):

$$F_0 = -\frac{1}{\beta}\ln Z_0$$
$$= -\frac{1}{\beta}\ln \prod_{\underset{\sim}{k}j}\sum_{n_{\underset{\sim}{k}j}} e^{-\beta\hbar\omega_{\underset{\sim}{k}j}(n_{\underset{\sim}{k}j}+\frac{1}{2})}$$
$$= -\frac{1}{\beta}\sum_{\underset{\sim}{k}j}\ln\frac{e^{-\frac{1}{2}\beta\hbar\omega_{\underset{\sim}{k}j}}}{1-e^{-\beta\hbar\omega_{\underset{\sim}{k}j}}}$$
$$= \frac{1}{2}\hbar\sum_{\underset{\sim}{k}j}\omega_{\underset{\sim}{k}j} + \frac{1}{\beta}\sum_{\underset{\sim}{k}j}\ln(1-e^{-\beta\hbar\omega_{\underset{\sim}{k}j}})$$

In the high temperature limit the free energy contributions are as follows:

$$F_0 = k_BT\sum_{\underset{\sim}{k}j}\ln\beta\hbar\omega_{\underset{\sim}{k}j} + k_BT\sum_{\underset{\sim}{k}j}\left[\frac{1}{24}\left(\frac{\hbar\omega_{\underset{\sim}{k}j}}{k_BT}\right)^2 - \frac{1}{2880}\left(\frac{\hbar\omega_{\underset{\sim}{k}j}}{k_BT}\right)^4 + \cdots\right] \tag{58}$$

$$F_1 = \frac{\hbar^2}{8N}\sum_{\lambda_1\lambda_2}\Phi(-\lambda_1\lambda_1-\lambda_2\lambda_2)\frac{1}{\omega_1^2\omega_2^2}\times\left[\left(\frac{k_BT}{\hbar}\right)^2 + \frac{\omega_1^2}{6}\right.$$
$$\left. + \frac{1}{720}\left(-2\omega_1^4+5\omega_1^2\omega_2^2\right)\left(\frac{\hbar}{k_BT}\right)^2 + \cdots\right]$$

$$F_2 = -\frac{\hbar^2}{12N}\sum_{\lambda_1\lambda_2\lambda_3}\Delta(\underset{\sim}{k}_1+\underset{\sim}{k}_2+\underset{\sim}{k}_3)\,|\Phi(\lambda_1\lambda_2\lambda_3)|^2\frac{1}{\omega_1^2\omega_2^2\omega_3^2}\left[\left(\frac{k_BT}{\hbar}\right)^2\right.$$
$$\left. + \frac{\omega_1^2\omega_2^2}{240}\left(\frac{\hbar}{k_BT}\right)^2 + \cdots\right]$$

$$F_3 = \frac{\hbar^3}{48N^2} \sum_{\lambda_1\lambda_2\lambda_3} \Phi(\lambda_1 -\lambda_1\, \lambda_2 -\lambda_2\, \lambda_3 -\lambda_3)\, \frac{1}{\omega_1^2\omega_2^2\omega_3^2} \times \Big[\Big(\frac{k_B T}{\hbar}\Big)^3 + \frac{\omega_1^2}{4}\Big(\frac{k_B T}{\hbar}\Big)$$

$$+ \Big(-\frac{\omega_1^4}{240} + \frac{\omega_1^2\omega_2^2}{48} \Big)\Big(\frac{\hbar}{k_B T}\Big) + \cdots \Big]$$

$$F_{46} = -\frac{\hbar^3}{12N^2} \sum_{\lambda_1\lambda_2\lambda_3\lambda_4} \Delta(\underset{\sim}{k}_1 + \underset{\sim}{k}_2 + \underset{\sim}{k}_3)\, \Phi(\lambda_1\lambda_2\lambda_3)\, \Phi(-\lambda_1 -\lambda_2 -\lambda_3 \lambda_4 \lambda_4)$$

$$\times \frac{1}{\omega_1\omega_2\omega_3\omega_4} \Big[\Big(\frac{k_B T}{\hbar}\Big)^3 + \frac{\omega_4^2}{12}\Big(\frac{k_B T}{\hbar}\Big) + \frac{1}{240}\Big(\omega_1^2\omega_2^2 - \frac{\omega_4^4}{3} - 30\,\omega_1\omega_2^3\Big)\frac{\hbar}{k_B T} + \cdots \Big]$$

$$F_5^a = -\frac{\hbar^3}{48N^2} \sum_{\lambda_1\lambda_2\lambda_3\lambda_4} \Delta(\underset{\sim}{k}_1 + \underset{\sim}{k}_2 + \underset{\sim}{k}_3 + \underset{\sim}{k}_4)\, \big|\Phi(\lambda_1\lambda_2\lambda_3\lambda_4)\big|^2\, \frac{1}{\omega_1^2\omega_2^2\omega_3^2\omega_4^2}$$

$$\times \Big[\Big(\frac{k_B T}{\hbar}\Big)^3 + \Big(\frac{\omega_1^4}{180} + \frac{\omega_1\omega_2^3}{16} + \frac{97}{240}\,\omega_1^2\omega_2^2 + \omega_1\omega_2\omega_3^2 + \frac{3}{16}\,\omega_1\omega_2\omega_3\omega_4 \Big)\frac{\hbar}{k_B T} + \cdots \Big]$$

$$F_5^b = -\frac{\hbar^3}{16N^2} \sum_{\lambda_1\lambda_2\lambda_3\lambda_4} \Delta(\underset{\sim}{k}_2 + \underset{\sim}{k}_3)\, \Phi(-\lambda_1\lambda_1\lambda_2\lambda_3)\, \Phi(-\lambda_4\lambda_4 -\lambda_2 -\lambda_3)\, \frac{1}{\omega_1^2\omega_2^2\omega_3^2\omega_4^2}$$

$$\times \Big[\Big(\frac{k_B T}{\hbar}\Big)^3 + \frac{\omega_1^2}{6}\Big(\frac{k_B T}{\hbar}\Big) + \frac{1}{8}\Big(-\frac{\omega_1^4}{45} + \frac{\omega_2^2\omega_3^2}{90} + \frac{\omega_1^2\omega_4^2}{18} \Big)\frac{\hbar}{k_B T} + \cdots \Big]$$

$$F_{789}^a = \frac{\hbar^3}{8N^2} \sum_{\lambda_1\cdots\lambda_5} \Delta(\underset{\sim}{k}_1 + \underset{\sim}{k}_2 + \underset{\sim}{k}_3)\, \Delta(-\underset{\sim}{k}_1 - \underset{\sim}{k}_2 + \underset{\sim}{k}_4 + \underset{\sim}{k}_5)\, \Phi(\lambda_1\lambda_2\lambda_3)\, \Phi(-\lambda_1 -\lambda_2 \lambda_4\lambda_5)\, \Phi(-\lambda_3 -\lambda_4 -\lambda_5)$$

$$\times \frac{1}{\omega_1^2\omega_2^2\omega_3^2\omega_4^2\omega_5^2} \times \Big[\Big(\frac{k_B T}{\hbar}\Big)^3 + O\Big(\frac{1}{T}\Big) \Big]$$

$$F_{789}^b = \frac{\hbar^3}{8N^2} \sum_{\lambda_1\cdots\lambda_5} \Delta(-\underset{\sim}{k}_1 + \underset{\sim}{k}_2)\, \Phi(\lambda_1\lambda_3\lambda_4)\, \Phi(-\lambda_5\lambda_5 -\lambda_1\lambda_2)\, \Phi(-\lambda_2 -\lambda_3 -\lambda_4)$$

$$\times \frac{1}{\omega_1^2\omega_2^2\omega_3^2\omega_4^2\omega_5^2} \Big[\Big(\frac{k_B T}{\hbar}\Big)^3 + \frac{\omega_5^2}{12}\Big(\frac{k_B T}{\hbar}\Big) + \cdots \Big]$$

In performing these high temperature expansions it was of primary interest to determine whether or not there were any free energy contributions of order λ^4 which were proportional to T^2, since they would contribute a term linear in T to the high temperature specific heat. There were none. For $T \to 0$ each of the $\bar{n}_i$ tends to zero. Thus we can easily find the low temperature limits of the free energy expressions.

It should be pointed out here that in each of Z_5, Z_7, Z_9, and Z_{10} it is possible to find pairing schemes such that not every operator H_i will be linked to every other operator H_i contained in the matrix element by means of paired operators A_{λ_i}. Terms arising from such pairing schemes and also the last term in Eq.(25) do not contribute to the free energy since they do not correspond to "linked clusters" (see ref.(22) and APPENDIX G).

4. NUMERICAL CALCULATIONS

The anharmonic free energy contributions in the high-temperature limit were evaluated for a face-centered cubic monatomic crystal with nearest neighbour central force interactions.

For our model the harmonic dynamical matrix is a 3 x 3 matrix with elements given by (15)

$$D_{xy}(\mathbf{k}) = \frac{1}{M}\sum_{\boldsymbol{l}} \phi_{xy}(\boldsymbol{l})\,(1 - e^{-2\pi i\,\mathbf{k}\cdot\mathbf{r}_0^{l}}) \tag{60}$$

where the $\boldsymbol{l}$-summation is over the 12 nearest neighbours for the f.c.c. structure. Using the definition of $\phi_{xy}(\boldsymbol{l})$ in Eq. (27) and the already mentioned assumption that $\phi'(r_0) = 0$ where r_0 is the nearest neighbour distance we get

$$D_{xx}(\mathbf{k}) = \left[\frac{2\phi''(r_0)}{M}\right]\left\{2 - \cos\pi a_0 k_x\,(\cos\pi a_0 k_y + \cos\pi a_0 k_z)\right\} \tag{61}$$

$$D_{xy}(\mathbf{k}) = \left[\frac{2\phi''(r_0)}{M}\right]\sin\pi a_0 k_x \,\sin\pi a_0 k_y$$

The other elements of the dynamical matrix are obtained from the above by change of labels.

The eigenvalue equation (Eq. (8)) for the normal mode frequencies $\omega_{\mathbf{k}j}$ becomes

$$\sum_y D_{xy}(\mathbf{k})\, e_y\binom{\mathbf{k}}{j} = \omega_{\mathbf{k}j}^2\, e_x\binom{\mathbf{k}}{j}$$

For convenience we introduce the dimensionless frequencies $\gamma_{\underset{\sim}{k}j}$ defined by

$$\gamma^2_{\underset{\sim}{k}j} = \frac{M}{2\phi''(r_0)}\,\omega^2_{\underset{\sim}{k}j} \tag{62}$$

These are the eigenvalues of a dimensionless dynamical matrix which is derivable from the previously defined elements upon division by $\frac{2\phi''(r_0)}{M}$.

The dynamical matrix is now real (and symmetric) so that we have from Eq. (12)

$$e_\alpha\left(\begin{smallmatrix}\underset{\sim}{k}\\ j\end{smallmatrix}\right) = -\,e_\alpha\left(\begin{smallmatrix}-\underset{\sim}{k}\\ j\end{smallmatrix}\right) \tag{63}$$

This shows that $\underset{\sim}{e}$ is odd in k. Without loss of generality we can also assume that $\underset{\sim}{e}$ transforms in exactly the same way as $\underset{\sim}{k}$ does. Since the eigenvectors of a real symmetric matrix can always be made orthonormal we get the important relations

$$\sum_\alpha e_\alpha\left(\begin{smallmatrix}\underset{\sim}{k}\\ j\end{smallmatrix}\right) e_\alpha\left(\begin{smallmatrix}\underset{\sim}{k}\\ j'\end{smallmatrix}\right) = \delta_{jj'} \tag{64}$$

and

$$\sum_j e_\alpha\left(\begin{smallmatrix}\underset{\sim}{k}\\ j\end{smallmatrix}\right) e_\beta\left(\begin{smallmatrix}\underset{\sim}{k}\\ j\end{smallmatrix}\right) = \delta_{\alpha\beta} \tag{65}$$

Here j takes on only three labels since there are only three normal modes. Using these orthomormality relations and the fact that $\underset{\sim}{e}$ transforms as $\underset{\sim}{k}$ we easily derive the relation (15)

$$\sum_{xy}\sum_{kj}\frac{e_x\binom{k}{j}e_y\binom{k}{j}x_0^l y_0^l}{\omega_{kj}^2\, r_0^2}(1-\cos\pi a_0\, k\cdot r_0^l)=\frac{NM}{4\phi''(r_0)} \tag{66}$$

where $\underset{\sim}{r_0^l}=\langle x_0^l, y_0^l, z_0^l\rangle$ is a nearest neighbour vector, x and y run over the Cartesian indices x, y and z and the sum over $\underset{\sim}{k}$ extends over the permitted wave vectors in the first Brillouin zone. Another useful relation which can be derived is

$$\sum_{xy}\sum_{l}\frac{x_0^l y_0^l e_x\binom{k}{j_1}e_y\binom{k}{j_2}}{\omega_{kj_1}\omega_{kj_2}\, r_0^2}(1-\cos 2\pi\, k\cdot r_0^l)=\frac{M}{\phi''(r_0)}\delta_{j_1 j_2} \tag{67}$$

the l -summation being over nearest neighbours. A theorem of great importance in what is to follow is Born's theorem (APPENDIX E)

$$\sum_{j}\frac{e_\alpha\binom{k}{j}e_\beta\binom{k}{j}}{\omega_{kj}^2}=\left[D^{-1}(k)\right]_{\alpha\beta} \tag{68}$$

where $D^{-1}(k)$ is the inverse of the harmonic dynamical matrix D(k) discussed above.

In order to evaluate the contributions to the free energy it was necessary to evaluate sums of the form

$$\sum_{qj}\frac{e_\alpha\binom{q}{j}e_\beta\binom{q}{j}}{\gamma_{qj}^2}\cos q\cdot n \tag{69}$$

where $\underset{\sim}{q}=\pi a_0\underset{\sim}{k}$ and $\underset{\sim}{k}$ lies in the first Brillouin zone. Such sums were evaluated in the following way. Each of the forty-eight symmetry operations of a cube was applied to the vector $\underset{\sim}{q}$ of the summand. Use was then made of the fact that $\underset{\sim}{e}\binom{k}{j}$ transforms like $\underset{\sim}{k}$ itself. Thus forty-eight new summands (many identical) were produced, each of which when summed over $\underset{\sim}{q}$ and j yielded the original sum. This is because the components q_x, q_y, q_z of q are merely permuted or have their sign changed so that when the summation over $\underset{\sim}{q}$ is performed the same combinations of q_x, q_y, q_z occur as for the original summand. If we add all these new summands together we obtain a term which is invariant under the 48 symmetry operations of a cube. Assuming that the wave vectors $\underset{\sim}{k}$ are symmetrically distributed about the origin we need only sum this invariant "total" summand over $\frac{1}{48}$ of the Brillouin zone, introducing for each vector $\underset{\sim}{q}$ in this portion a multiplying weighting factor to account for the number of $\underset{\sim}{q}$'s equivalent to it by symmetry, special care being taken in assigning weighting factors for vectors on the zone boundaries. The result is 48 times the original sum. For example we get the following:

$$S_{xx} = \sum_{\underset{\sim}{q}j} \frac{e_x\binom{\underset{\sim}{q}}{j} e_x\binom{\underset{\sim}{q}}{j}}{\gamma^2_{\underset{\sim}{q}j}} \cos \underset{\sim}{q}\cdot\underset{\sim}{n} \tag{70}$$

$$= \sum_{\underset{\sim}{q}}^{1/48} \frac{W(\underset{\sim}{q})}{6} \Big[(D^{-1})_{xx} \cos q_x n_x (\cos q_y n_y \cos q_z n_z + \cos q_z n_y \cos q_y n_z) + (D^{-1})_{yy} \cos q_y n_x (\cos q_z n_y \cos q_x n_z + \cos q_x n_y \cos q_z n_z) + (D^{-1})_{zz} \cos q_z n_x (\cos q_x n_y \cos q_y n_z + \cos q_y n_y \cos q_x n_z)\Big]$$

$$S_{xy} = \sum_{\underset{\sim}{q}j} \frac{e_x\binom{\underset{\sim}{q}}{j} e_y\binom{\underset{\sim}{q}}{j}}{\gamma^2_{\underset{\sim}{q}j}} \cos \underset{\sim}{q}\cdot\underset{\sim}{n}$$

$$= -\sum_{\underset{\sim}{q}}^{1/48} \frac{W(\underset{\sim}{q})}{6} \Big[(D^{-1})_{xy} \cos q_z n_z (\sin q_x n_x \sin q_y n_y$$

$$+ \sin q_x n_y \sin q_y n_x) + (D^{-1})_{yz} \cos q_x n_z (\sin q_y n_x \sin q_z n_y$$

$$+ \sin q_z n_x \sin q_y n_y + (D^{-1})_{xz} \cos q_y n_z (\sin q_x n_x \sin q_z n_y$$

$$+ \sin q_x n_y \sin q_z n_x)]$$

The summations $\sum_{q}^{1/48}$ are over a $\frac{1}{48}$ portion of the entire Brillouin zone and $W(q)$ is the weighting factor for the vector q. The factors

$$(D^{-1})_{xy} \;,\; (D^{-1})_{yz} \;,\; (D^{-1})_{xz}$$

are elements of the inverse of the dimensionless dynamical matrix and arise here by the use of Born's theorem. Other sums, S_{yy}, S_{xz}, etc. can be derived from the above by proper interchanges of the components n_x, n_y, n_z of the vector n (recall that $r_0^{\ell} = \frac{a_0}{2} n$)

Another type of sum which was required was of the form

$$S_{\alpha\beta\gamma\delta} = \sum_{q} \sum_{j'} \sum_{j^2} \frac{e_\alpha\binom{q}{j_1} e_\beta\binom{q}{j_1} e_\gamma\binom{q}{j_2} e_\delta\binom{q}{j_2}}{\gamma^2_{qj_1}\,\gamma^2_{qj_2}} \cos q \cdot n \tag{71}$$

As before we generate a summand which is invariant under the point group of a cube and then employ Born's theorem to eliminate the sums over j_1 and j_2, getting, for example

$$S_{xxxx} = \sum_{q} \sum_{j'} \sum_{j^2} \frac{e_x^2\binom{q}{j_1} \cdot e_x^2\binom{q}{j_2}}{\gamma^2_{qj_1}\,\gamma^2_{qj_2}} \cos q \cdot n \tag{72}$$

$$= \sum_{\underset{\sim}{q}}^{1/48} \frac{W(\underset{\sim}{q})}{6} \Big[(D^{-1})^2_{xx} \cos q_x n_x (\cos q_y n_y \cos q_z n_z$$

$$+ \cos q_z n_y \cos q_y n_z) + (D^{-1})^2_{yy} \cos q_y n_x (\cos q_z n_y$$

$$\times \cos q_x n_z + \cos q_x n_y \cos q_z n_z) + (D^{-1})^2_{zz} \cos q_z n_x$$

$$\times (\cos q_x n_y \cos q_y n_z + \cos q_y n_y \cos q_x n_z) \Big]$$

$$S_{xxyy} = \sum_{\underset{\sim}{q}} \sum_{j'} \sum_{j^2} \frac{e_x^2\binom{\underset{\sim}{q}}{j_1} e_y^2\binom{\underset{\sim}{q}}{j_2}}{\gamma^2_{\underset{\sim}{q}j_1} \gamma^2_{\underset{\sim}{q}j_2}} \cos \underset{\sim}{q} \cdot \underset{\sim}{n}$$

$$= \sum_{\underset{\sim}{q}}^{1/48} \frac{W(\underset{\sim}{q})}{6} \Big[(D^{-1})_{xx} (D^{-1})_{yy} \cos q_z n_z (\cos q_x n_x \cos q_y n_y$$

$$+ \cos q_y n_x \cos q_x n_y) + (D^{-1})_{xx} (D^{-1})_{zz} \cos q_y n_z (\cos q_z n_x$$

$$\times \cos q_x n_y + \cos q_x n_x \cos q_z n_y) + (D^{-1})_{yy} (D^{-1})_{zz} \cos q_x n_z$$

$$\times (\cos q_y n_x \cos q_z n_y + \cos q_z n_x \cos q_y n_y) \Big]$$

$$S_{xxxy} = \sum_{\underset{\sim}{q}} \sum_{j'} \sum_{j^2} \frac{e_x^2\binom{\underset{\sim}{q}}{j_1} e_x\binom{\underset{\sim}{q}}{j_2} e_y\binom{\underset{\sim}{q}}{j_2}}{\gamma^2_{\underset{\sim}{q}j_1} \gamma^3_{\underset{\sim}{q}j_2}} \cos \underset{\sim}{q} \cdot \underset{\sim}{n}$$

$$= - \sum_{\underset{\sim}{q}}^{1/48} \frac{W(\underset{\sim}{q})}{6} \Big[(D^{-1})_{xx} (D^{-1})_{xy} \sin q_x n_x \sin q_y n_y \cos q_z n_z$$

$$+ (D^{-1})_{xx}(D^{-1})_{xz} \sin q_x n_x \sin q_z n_y \cos q_y n_z + (D^{-1})_{zz}$$

$$\times (D^{-1})_{xz} \sin q_z n_x \sin q_x n_y \cos q_y n_z + (D^{-1})_{yy}(D^{-1})_{yz}$$

$$\times \sin q_y n_x \sin q_z n_y \cos q_x n_z + (D^{-1})_{yy}(D^{-1})_{xy} \sin q_y n_x$$

$$\sin q_x n_y \cos q_z n_z + (D^{-1})_{zz}(D^{-1})_{yz} \sin q_z n_x \sin q_y n_y$$

$$\times \cos q_x n_z]$$

$$S_{xxyz} = \sum_{q} \sum_{j'} \sum_{j^2} \frac{e_x^2\binom{q}{j_1} e_y\binom{q}{j_2} e_z\binom{q}{j_2}}{\gamma^2_{qj'}\,\gamma^2_{qj^2}} \cos q \cdot n$$

$$= -\sum_{q}^{1/48} \frac{W(q)}{6} [(D^{-1})_{xx}(D^{-1})_{yz} \cos q_x n_x (\sin q_y n_y \sin q_z n_z$$

$$+ \sin q_z n_y \sin q_y n_z) + (D^{-1})_{zz}(D^{-1})_{xy} \cos q_z n_x (\sin q_x n_y$$

$$\times \sin q_y n_z + \sin q_y n_y \sin q_x n_z) + (D^{-1})_{yy}(D^{-1})_{xz} \cos q_y n_x$$

$$\times (\sin q_z n_y \sin q_x n_z + \sin q_x n_y \sin q_z n_z)]$$

$$S_{xyxy} = \sum_{\mathbf{q}} \sum_{j'} \sum_{j^2} \frac{e_x\binom{\mathbf{q}}{j_1} e_y\binom{\mathbf{q}}{j_1} e_x\binom{\mathbf{q}}{j_2} e_y\binom{\mathbf{q}}{j_2}}{\gamma^2_{\mathbf{q}j_1}\,\gamma^2_{\mathbf{q}j_2}} \cos \mathbf{q}\cdot\mathbf{n}$$

$$= \sum_{\mathbf{q}}^{1/48} \frac{W(\mathbf{q})}{6} \Big[(D^{-1})^2_{xy} \cos q_z n_z (\cos q_x n_x \cos q_y n_y + \cos q_y n_x \cos q_x n_y)$$

$$+ (D^{-1})^2_{xz} \cos q_y n_z (\cos q_z n_x \cos q_x n_y + \cos q_x n_x \cos q_z n_y)$$

$$+ (D^{-1})^2_{yz} \cos q_x n_z (\cos q_y n_x \cos q_z n_y + \cos q_z n_x \cos q_y n_y) \Big]$$

$$S_{xyxz} = \sum_{\mathbf{q}} \sum_{j'} \sum_{j^2} \frac{e_x\binom{\mathbf{q}}{j_1} e_y\binom{\mathbf{q}}{j_1} e_x\binom{\mathbf{q}}{j_2} e_z\binom{\mathbf{q}}{j_2}}{\gamma^2_{\mathbf{q}j_1}\,\gamma^2_{\mathbf{q}j_2}} \cos \mathbf{q}\cdot\mathbf{n}$$

$$= -\sum_{\mathbf{q}}^{1/48} \frac{W(\mathbf{q})}{6} \Big[(D^{-1})_{xy} (D^{-1})_{xz} \cos q_x n_x \sin q_y n_y \sin q_z n_z$$

$$+ (D^{-1})_{xz} (D^{-1})_{yz} \cos q_z n_x \sin q_x n_y \sin q_y n_z + (D^{-1})_{yz} (D^{-1})_{xy}$$

$$\times \cos q_y n_x \sin q_z n_y \sin q_x n_z + (D^{-1})_{xz} (D^{-1})_{xy} \cos q_x n_x$$

$$\times \sin q_z n_y \sin q_y n_z + (D^{-1})_{xy} (D^{-1})_{yz} \cos q_y n_x \sin q_x n_y$$

$$\times \sin q_z n_z + (D^{-1})_{yz} (D^{-1})_{xz} \cos q_z n_x \sin q_y n_y \sin q_x n_z \Big]$$

Using these six sums we can, by suitably interchanging n_x, n_y, and n_z generate all twenty-one of the possible distinct sums of this type.

For computational purpose a simple cubic lattice of points in k-space was used with the components of k being given by

$$k_\alpha = \pm \frac{p_\alpha}{L\, a_0} \quad ; \qquad p_\alpha = 1, 2, \ldots, L \; ; \; \alpha = x, y, z \tag{73}$$

For L = 7 this yields a mesh of 1372 points in the entire zone, including the origin (0,0,0). The previously discussed types of sums $S_{\alpha\beta}$, $S_{\alpha\beta\gamma\delta}$ were computed for the $\frac{1}{48}$ portion of the zone defined by

$$L \geq p_x \geq p_y \geq p_z > 0 \; ; \; p_x + p_y + p_z \leq \frac{3}{2} L$$

and were tabulated for a large number of vectors $\underset{\sim}{n}$. The origin was omitted from the sum over $\underset{\sim}{k}$ since both $e_\alpha(\underset{j}{\overset{k}{}})$ and $\omega_{\underset{\sim}{k}j}$ approach zero as $\underset{\sim}{k} \rightarrow (0,0,0)$.

The sums were therefore normalized by dividing them by a factor 1371. In the expressions for the anharmonic free energy contributions (Eqs.(58)) only the leading terms in T were calculated. In F_1 and F_3, if we substitute in full for the $\Phi(\lambda_1 \ldots \lambda_n)$ functions and factor out sums over different λ_i we get respectively a single and double summation over nearest neighbours. In each case the summand is some function of the sums $S_{\alpha\beta}$. For F_1 the computed result is

$$F_1 = \frac{N\,(k_B T)^2}{64\,[\phi(r_0)]^2} \left\{ D(r_0)\,(S1A) + \frac{2\,C(r_0)}{r_0}\,(S1B) + \frac{4\,B(r_0)}{r_0^2}\,(S1C) \right\} \tag{74}$$

where we have used $r_0 = \frac{a_0}{\sqrt{2}}$

The coefficients S1A, S1B, S1C are given in APPENDIX F analytically.

The numerical result is: S1A = 12.00000

S1B = 67.05850

S1C = 64.73280

(The sums which follow (i.e. S2A,...,S8I) are all given in analytical form in APPENDIX F)

S1A is also an exact result as shown by Maradudin et al. (15). We note that if in sums like $S_{\alpha\beta}$ and $S_{\alpha\beta\gamma\delta}$ we put $X_{\underset{\sim}{q}j}=1$ we can use the orthonormality relations for the eigenvectors $\underset{\sim}{e}$ and get sums of the form

$$\sum_{\underset{\sim}{q}j} e_\alpha\left(\begin{smallmatrix}\underset{\sim}{q}\\ j\end{smallmatrix}\right) e_\beta\left(\begin{smallmatrix}\underset{\sim}{q}\\ j\end{smallmatrix}\right) \cos \underset{\sim}{q}\cdot\underset{\sim}{n} = \sum_{\underset{\sim}{q}} \delta_{\alpha\beta} \cos \underset{\sim}{q}\cdot\underset{\sim}{n} \tag{75}$$

$$= \delta_{\alpha\beta}\, N\Delta(\underset{\sim}{n})$$

$$\sum_{\underset{\sim}{q}} \sum_{j_1 j_2} e_\alpha\left(\begin{smallmatrix}\underset{\sim}{q}\\ j_1\end{smallmatrix}\right) e_\beta\left(\begin{smallmatrix}\underset{\sim}{q}\\ j_1\end{smallmatrix}\right) e_\gamma\left(\begin{smallmatrix}\underset{\sim}{q}\\ j_2\end{smallmatrix}\right) e_\delta\left(\begin{smallmatrix}\underset{\sim}{q}\\ j_2\end{smallmatrix}\right) \cos \underset{\sim}{q}\cdot\underset{\sim}{n} = \delta_{\alpha\beta}\delta_{\gamma\delta} N\Delta(\underset{\sim}{n})$$

where use has been made of the fact that

$$\sum_{\underset{\sim}{q}} e^{\underset{\sim}{q}\cdot\underset{\sim}{n}} = N\Delta(\underset{\sim}{n}) \tag{76}$$

and $\Delta(\underset{\sim}{n})$ = 1 if $\underset{\sim}{n} = \langle 0,0,0\rangle$

= 0 otherwise

($\underset{\sim}{n}$ has the usual meaning)

Hence if we put $\chi_{\ell j}' = 1$ (which is equivalent to putting $(D^{-1})_{\alpha\beta} = \delta_{\alpha\beta}$) in our computer program for calculating, say, S1B, and compute the result we can check this number against the analytical result which we can now easily obtain. Thus we have a way of testing the accuracy of the terms being computed, such as S1A, S1B and S1C, as well as our summation procedure. All of the terms computed above and those which follow have been tested in this way. In the case above the test sums corresponding to S1A, S1B and S1C are TS1A, TS1B and TS1C respectively, where

TS1A = 48

TS1B = 240

TS1C = 180

For F_3 the result is

$$F_3 = \frac{N\,(k_B T)^3}{768\,[\phi''(r_0)]^3}\left\{ F(r_0)\,(S3A) + \frac{2\,E(r_0)}{r_0}\,(S3B) + \frac{4\,D(r_0)}{r_0^2}\,(S3C) + \frac{8\,C(r_0)}{r_0^3}\,(S3D) \right\} \tag{77}$$

The sums S3A, etc. along with their corresponding test sums TS3A, etc. are given below

S3A = 12.00000	TS3A = 96
S3B = 136.5878	TS3B = 1008
S3C = 395.3739	TS3C = 2520
S3D = 273.9112	TS3D = 1260

The analytically evaluated and the computed test sums were identical to at least seven significant figures in the above cases and in all that follow. As a second test of the computations the term S3A was calculated analytically using Eq. (66) the result being exactly 12.

The expressions for F_2, F_{46} and $F_5^{\,a}$ each contains a delta function of the type $\Delta(\underset{\sim}{k}_1+\dots+\underset{\sim}{k}_n)$. We can express the delta function by

$$\Delta(\underset{\sim}{k}) = \frac{1}{N}\sum_{\underset{\sim}{n}} e^{\pi a_0 i \underset{\sim}{k}\cdot\underset{\sim}{n}}$$

the summation being over the N direct lattice vectors $\frac{a_0}{2}\underset{\sim}{n}$ of the "macrocrystal". For each of the above, we thus have a double summation over nearest neighbour vectors from the two Φ functions as well as a summation over the N lattice vectors. The summands are again functions of the $S_{\alpha\beta}$.

The expressions are of the form

$$\sum_{\underset{\sim}{n}}\sum_{\underset{\sim}{n}_1}\sum_{\underset{\sim}{n}_2} f(\underset{\sim}{n},\underset{\sim}{n}_1,\underset{\sim}{n}_2)$$

where $\underset{\sim}{n}_1$, $\underset{\sim}{n}_2$ range over the twelve nearest neighbours and $f(\underset{\sim}{n},\underset{\sim}{n}_1,\underset{\sim}{n}_2)$ can be expressed in terms of the $S_{\alpha\beta}$ for fixed $\underset{\sim}{n}$, $\underset{\sim}{n}_1$ and $\underset{\sim}{n}_2$. The actual calculation was carried out as follows. For a fixed vector $\underset{\sim}{n}$ the sums over $\underset{\sim}{n}_1$ and $\underset{\sim}{n}_2$ were carried out. Then, noting that for each of the above three cases the result of summing over $\underset{\sim}{n}_1$ and $\underset{\sim}{n}_2$ was an expression having cubic symmetry in the components of $\underset{\sim}{n}$, the result was multiplied by the number of lattice vectors $\underset{\sim}{n}$ equal in magnitude to the fixed one. Then the next larger $\underset{\sim}{n}$ was selected, and so on until a suitable number of $\underset{\sim}{n}$ vectors had been used. Thus, by exploiting the symmetry of the integrand, it was necessary to use only one $\underset{\sim}{n}$ vector of each magnitude (or "shell").

The result for F_2 is

$$F_2 = -\frac{N(k_BT)^2}{(96)(32)[\phi''(r_0)]^3}\Big\{ C^2(r_0)\ (S2A) \tag{78}$$

$$+\frac{12}{r_0} B(r_0)C(r_0)\ (S2B) + \frac{4}{r_0^2} B^2(r_0)\ (S2C)\Big\}$$

The terms S2A, S2B, S2C have been computed for $\underset{\sim}{n}$ vectors in the first seven shells (i.e. up to the vector $\underset{\sim}{n} = \langle 2,2,2\rangle$ and the results are given in TABLE I. Also given are the corresponding computed test sums TS2A, TS2B, and TS2C.

For F_{46} we have

$$F_{46} = -\frac{N(k_BT)^3}{(192)(32)[\phi''(r_0)]^4}\Big\{ C(r_0)E(r_0)\ (S4A) + \frac{2}{r_0} C(r_0)D(r_0)(S4B) \tag{79}$$

$$+\frac{4}{r_0^2} C^2(r_0)\ (S4C) + \frac{2}{r_0} B(r_0)E(r_0)\ (S4D)$$

$$+\frac{4}{r_0^2} B(r_0)D(r_0)\ (S4E) + \frac{8}{r_0^3} B(r_0)C(r_0)\ (S4F)\Big\}$$

In TABLE II are given S4A, etc. for seven shells, as well as the computed test sums TS4A, etc. Analytically we get S4A = S2A, which is also the numerical result.

For $F_5^{\,a}$ we get

$$F_5^a = -\frac{N(k_BT)^3}{(64)(16)(48)[\phi''(r_0)]^4}\Big\{ D^2(r_0)\ (S5A) + \frac{24}{r_0} D(r_0)C(r_0)\ (S5B) + \frac{24\,B(r_0)D(r_0)}{r_0^2}(S5C)$$

$$+24\frac{C^2(r_0)}{r_0^2}\ (S5D) + \frac{96}{r_0^3} B(r_0)C(r_0)\ (S5E) + \frac{48}{r_0^4} B^2(r_0)\ (S5F)\Big\}$$

The results for S5A, etc. and the test sums TS5A etc. are given in TABLE III.

Next consider F_5^b and F_{789}^b. In these expressions sums of the type $S_{\alpha\beta\gamma\delta}$ arise as well as $S_{\alpha\beta}$. In the case of F_5^b in which there is no delta function, there is only a double summation over nearest neighbours. We have

$$F_5^b = - \frac{N(k_BT)^3}{(1024)[\phi''(r_0)]^4} \Big\{ D^2(r_0)(S6A) + \frac{4}{r_0} D(r_0)C(r_0)(S6B) \tag{80}$$

$$+ \frac{8}{r_0^2} B(r_0)D(r_0)(S6C) + \frac{4}{r_0^3} C^2(r_0)(S6D) + \frac{16}{r_0^3} B(r_0)C(r_0)(S6E)$$

$$+ \frac{16}{r_0^4} B^2(r_0)(S6F) \Big\}$$

Below are given S6A, etc. along with their corresponding test sums TS6A, etc.

S6A = 48.00000	TS6A = 960
S6B = 268.2340	TS6B = 4608
S6C = 258.7215	TS6C = 3120
S6D = 1524.376	TS6D = 22368
S6E = 1246.314	TS6E = 12792
S6F = 1632.251	TS6F = 11700

The expressions for F_{789}^b contains only one delta function and three Φ functions, so that we get a sum of the form

$$\sum_{\underset{\sim}{m}} \sum_{\underset{\sim}{n_1}} \sum_{\underset{\sim}{n_2}} \sum_{\underset{\sim}{n_3}} g(\underset{\sim}{m}, \underset{\sim}{n_1}, \underset{\sim}{n_2}, \underset{\sim}{n_3})$$

where $\underset{\sim}{n}_1$, $\underset{\sim}{n}_2$ and $\underset{\sim}{n}_3$ extend over nearest neighbours and $\underset{\sim}{m}$ over general lattice vectors. Again the symmetry of the summand required only one $\underset{\sim}{m}$ from each shell.

We have

$$F^{b}_{789} = -\frac{N(k_BT)^3}{(16)(1024)\,[\phi''(r_0)]^5}\Big\{D(r_0)C^2(r_0)(S7A) + \frac{4}{r_0}B(r_0)C(r_0)D(r_0)(S7B)$$
$$+\frac{4}{r_0^2}B^2(r_0)D(r_0)(S7C) + \frac{2}{r_0}C^3(r_0)(S7D) + \frac{8}{r_0^2}B(r_0)C^2(r_0)(S7E)$$
$$+\frac{8}{r_0^3}B^2(r_0)C(r_0)(S7F) + \frac{4}{r_0^2}B(r_0)C^2(r_0)(S7G) + \frac{16}{r_0^3}B^2(r_0)C(r_0)(S7H)$$
$$+\frac{16}{r_0^4}B^3(r_0)(S7I)\Big\} \tag{81}$$

Because of limitations imposed by the available computing facilities it was feasible to get contributions only from the $\underset{\sim}{m}$ vectors $\langle 0,0,0\rangle$, $\langle 1,1,0\rangle$ and $\langle 2,0,0\rangle$. The results for S7A etc., along with the test sums TS7A, etc. are given in TABLE IV .

We note that S7A can be obtained analytically from S2A if we use Eq. (67). The result is S7A = (4)×S2A = 688.949.

The result in TABLE IV for only three shells thus looks reasonable.

In F^a_{789} there are two delta functions and three Φ functions so that we get a sum of the form

$$\sum_{\underset{\sim}{m}_1}\sum_{\underset{\sim}{m}_2}\sum_{\underset{\sim}{n}_1}\sum_{\underset{\sim}{n}_2}\sum_{\underset{\sim}{n}_3} g(\underset{\sim}{m}_1, \underset{\sim}{m}_2, \underset{\sim}{n}_1, \underset{\sim}{n}_2, \underset{\sim}{n}_3)$$

where $\underset{\sim}{n}_1, \underset{\sim}{n}_2, \underset{\sim}{n}_3$ extend over nearest neighbour vectors and $\underset{\sim}{m}_1, \underset{\sim}{m}_2$ are over general lattice vectors. The numerical evaluation of this sum was seen to be very time consuming so that only the contribution from $\underset{\sim}{m}_1 = \underset{\sim}{m}_2 = \langle 0,0,0\rangle$ was obtained. We have

$$\begin{aligned} F^a_{789} = \frac{N(k_BT)^3}{(256)^2[\phi''(r_0)]^5}\Big\{ & D(r_0)C^2(r_0)(S8A) + \frac{4}{r_0}B(r_0)C(r_0)D(r_0)(S8B) \\ & + \frac{4}{r_0^2}B^2(r_0)D(r_0)(S8C) + \frac{2}{r_0}C^3(r_0)(S8D) + \frac{8}{r_0^2}B(r_0)C^2(r_0)(S8E) \\ & + \frac{8}{r_0^3}B^2(r_0)C(r_0)(S8F) + \frac{4}{r_0^2}B(r_0)C^2(r_0)(S8G) + \frac{16}{r_0^3}B^2(r_0)C(r_0)(S8H) \\ & + \frac{16}{r_0^4}B^3(r_0)(S8I)\Big\} \end{aligned} \tag{82}$$

where S8A, etc. and the test sums TS8A are

S8A = 349.9122	TS8A = 10176
S8B = 522.2178	TS8B = 15552
S8C = 866.9633	TS8C = 24960
S8D = 1085.052	TS8D = 32256
S8E = 1953.876	TS8E = 54528
S8F = 4169.629	TS8F = 106368
S8G = 353.4028	TS8G = 10368
S8H = 727.9011	TS8H = 19008
S8I = 2245.212	TS8I = 47520

about 350 while the total result obtained by Shukla and Cowley(18) is about 1285. Hence we can multiply S8B,etc. by $\frac{1285}{350}$ to obtain a rough estimate of the full contribution. The results for both the roughly estimated full calculation as well as for the leading term approximation are given in TABLE V. In the case of F^a_{789} , where there were summations over $\underset{\sim}{m}_1$ and $\underset{\sim}{m}_2$, and three sums over nearest neighbours the number obtained required about 25 minutes of computer time. This was for only one combination of $\underset{\sim}{m}_1$ and $\underset{\sim}{m}_2$. As was mentioned previously the omitted calculations for F^a_{10} and F^a_{10} would have required a great deal of computer time because we would have had a triple summation over general lattice vectors $\underset{\sim}{m}_1,\underset{\sim}{m}_2,\underset{\sim}{m}_3$ and a quadruple summation over nearest neighbour vectors.

5. DISCUSSION

In TABLES I,II,and III the sums have been evaluated for $\underset{\sim}{n}$-vectors up to $\underset{\sim}{n}$=(2,2,2). As was pointed out by Maradudin et al (15) the contributions from successive shells to the sums closely parallel the contributions to their corresponding test sums, being large where the test sums are large and small where the test sums are small. Since there is no contribution to the test sums from $\underset{\sim}{n}$-vectors larger than (2,2,0) (this follows as a result of using Eqs.(75 and 76) we expect rather small contributions to the (non-test) sums from such $\underset{\sim}{n}$-vectors. This is indeed true for $\underset{\sim}{n}$=(3,1,0) and $\underset{\sim}{n}$= (2,2,2) so that cutting off the $\underset{\sim}{n}$-summation at $\underset{\sim}{n}$=(2,2,2) should not significantly affect the values of the sums. It was found that using a mesh larger than 1372 points in the full zone did not appreciably change the values of the computed sums. All of the tabulated sums are believed to be accurate to at least three significant figures. For illustrative purposes TABLE VI gives some numbers which were evaluated for a mesh of 256 k-vectors in the whole first Brillouin zone.Increasing the mesh size tends to increase the values of the sums.

Looking at TABLE V it is apparent that the leading term approximation in the high temperature limit is not in general very good. The corrections to the values from the leading term approximation range from 0.3% for F_2 to 47% for F_5^b. The largest contribution of order λ^4 comes from F_{789}^b but the number given is only a crude estimate. Also, as was previously mentioned, we have neglected contributions from the terms Z_{10}^a and Z_{10}^b . Had they been included the incomplete total for λ^4 given under TABLE V, $F(\lambda^4)=0.25\ N(k_BT)^3/\epsilon^2$, would probably have been reduced somewhat. This follows from the results of Shukla and Cowley, since their leading term numbers (2(f) and 2(h) in their TABLE II) are both negative. The trend in TABLE V seems to be a decrease in magnitude from the leading term numbers to the full term numbers and where there is an increase it is small. It seems likely therefore that the decrease in the total for λ^4 from these neglected contributions should be somewhere between $0.5\ N(k_BT)^3/\epsilon^2$ and $0.2\ N(k_BT)^3/\epsilon^2$ (assuming a 50% maximum decrease in magnitudes) so that the maximum value of the ratio of the total contribution of order λ^4 to that of order λ^2 would be about

$$\frac{F(\lambda^4)}{F(\lambda^2)} = -0.7\ k_BT/\epsilon$$

In the leading term approximation Shukla and Cowley obtained

$$\frac{F(\lambda^4)}{F(\lambda^2)} = -0.554\ k_BT/\epsilon$$

For the inert gas crystals the potential well depth ϵ is approximately twice the melting temperature so that in the high temperature limit both the full and leading term calculations indicate satisfactory convergence of the perturbation series to this order if the temperature is less than approximately 1/3 of the crystal's melting temperature. It should be emphasized that the magnitude of the ratio for the non-leading term approximation given above is an estimated <u>maximum</u> value. A more realistic estimate would make the ratio close to zero so that convergence should be good even for temperatures close to melting. The model chosen for these calculations was the same as that of Shukla and Cowley since it was desired to assess the reliability to the leading term approximation which they employed in their calculations. The restriction to nearest neighbour interactions considerably simplified the calculations and for the inert gas solids this approximation is expected to be good. As was mentioned previously, there is no contribution linear in T to the high temperature specific heat from terms of order λ^4 in the free energy. Experimentally the specific heat at high tempeatures rises steadily above the Dulong-Petit value. Calculations using second order perturbation theory (22) result in a theoretical curve which falls below the Dulong-Petit value for high T(40-60°K). Attempts to account theoretically for the experimental specific heat evidently involve at least sixth-order perturbation theory.

An important objective of this report was the determination of the feasibility of calculations of the free energy using higher order perturbation theory. It was found that the computations were made practical by the generation of the invariant summands (as described on page 44) so that only summations over 1/48 of the Brillouin zone were required.

The theory given in this thesis can be used to perform similar calculations for other types of lattices. In the case of b.c.c. lattice it would be necessary to include the effects of more neighbours (at least next-nearest).

TABLE I

$\underset{\sim}{n}$

	(0,0,0)	(1,1,0)	(2,0,0)	(2,1,1)	(2,2,0)	(3,1,0)	(2,2,2)
S2A	90.85683	178.1563	178.2009	176.0530	172.4018	172.4057	172.4021
S2B	46.65683	100.3290	100.2629	94.00965	92.15313	92.14101	92.13481
S2C	408.4331	816.1218	817.2104	767.3066	743.0359	742.7789	742.5510
TS2A	672	1296	1296	1248	1152	1152	1152
TS2B	336	720	720	624	576	576	576
TS2C	2520	5400	5400	4680	4320	4320	4320

The entries in each column are the contributions to the sums S2A, etc. from the shell of vectors $\underset{\sim}{n}$ labelling that column plus the contributions to the sums from all inner shells. The same is true for TABLES II, III, and IV. The numbers above were obtained for a mesh of 1372 $\underset{\sim}{k}$-vectors in the whole zone.

TABLE II

	$\underset{\sim}{n}$						
	(0,0,0)	(1,1,0)	(2,0,0)	(2,1,1)	(2,2,0)	(3,1,0)	(2,2,2)
S4A	90.85683	178.1563	178.2009	176.0530	172.4018	172.4057	172.4021
S4B	575.5476	1155.087	1155.103	1126.046	1102.972	1102.954	1102.918
S4C	532.1605	1151.717	1150.875	1075.269	1054.112	1053.961	1053.887
S4D	139.9705	300.9871	300.7888	282.0290	276.4594	276.4230	276.4044
S4E	1079.466	2259.086	2259.223	2119.383	2068.411	2067.980	2067.663
S4F	1608.345	3204.642	3209.163	3013.232	2916.407	2915.372	2914.453
TS4A	1344	2592	2592	2496	2304	2304	2304
TS4B	8064	15984	15984	14976	13824	13824	13824
TS4C	7056	15120	15120	13104	12096	12096	12096
TS4D	2016	4320	4320	3744	3456	3456	3456
TS4E	14112	30240	30240	26208	24192	24192	24192
TS4F	17640	37800	37800	32760	30240	30240	30240

(MESH=1372 $\underset{\sim}{k}$-vectors in whole zone)

TABLE III

	n						
	(0,0,0)	(1,1,0)	(2,0,0)	(2,1,1)	(2,2,0)	(3,1,0)	(2,2,2)
S5A	195.8047	396.0105	396.0197	397.0576	399.6691	399.6693	399.6699
S5B	101.9095	212.1757	212.1930	214.8647	216.1978	216.1985	216.1995
S5C	147.1828	374.4824	383.9826	398.2438	399.7622	399.8319	399.8369
S5D	496.5243	1046.802	1051.578	1067.409	1074.899	1074.912	1074.924
S5E	468.0906	1198.260	1224.560	1267.929	1273.812	1273.979	1274.009
S5F	572.0707	1443.625	1470.364	1518.485	1530.147	1530.405	1530.476
TS5A	3360	7056	7056	7104	7296	7296	7296
TS5B	1824	4032	4032	4128	4224	4224	4224
TS5C	2592	6624	6816	7200	7296	7296	7296
TS5D	7680	17424	17520	18048	18432	18432	18432
TS5E	6480	16560	17040	18000	18240	18240	18240
TS5F	4860	12420	12780	13500	13680	13680	13680

(MESH=1372 k-vectors in whole zone)

TABLE IV

$\underset{\sim}{n}$

	(0,0,0)	(1,1,0)	(2,0,0)
S7A	294.6544	707.0442	707.7844
S7B	457.2632	1199.701	1200.117
S7C	1356.750	3187.813	3200.699
S7D	1679.922	3985.039	3989.177
S7E	2563.639	6609.646	6611.821
S7F	7796.019	17975.55	18064.63
S7G	1692.226	3917.471	3921.459
S7H	2545.925	6387.565	6392.879
S7I	6598.644	14424.49	14538.78
TS7A	13152	25344	25344
TS7B	19584	42048	42048
TS7C	47136	103104	103104
TS7D	63216	121536	121536
TS7E	93888	200736	200736
TS7F	228336	494784	494784
TS7G	42960	82080	82080
TS7H	63360	133920	133920
TS7I	139392	294624	294624

(MESH=1372 $\underset{\sim}{k}$-vectors in whole zone)

TABLE V

TERM	FULL	LEADING
F_1	$0.691\ N(k_BT)^2/\epsilon$	$0.966\ N(k_BT)^2/\epsilon$
F_2	$-0.342\ N(k_BT)^2/\epsilon$	$-0.344\ N(k_BT)^2/\epsilon$
F_3	$0.205\ N(k_BT)^3/\epsilon^2$	$0.345\ N(k_BT)^3/\epsilon^2$
F_{46}	-0.601 "	-0.732 "
F_5^a	-0.227 "	-0.216 "
F_5^b	-0.663 "	-1.244 "
F_{789}^a	0.63 "	0.619 "
F_{789}^b	0.91 "	1.328 "

The full contribution from terms of order λ^2 is $0.349\ N(k_BT)^2/\epsilon$. The total from terms of order λ^4 is $0.25\ N(k_BT)^3/\epsilon^2$.

TABLE VI

$\underset{\sim}{n}$

	(0,0,0)	(1,1,0)	(2,0,0)	(2,1,1)	(2,2,0)	(3,1,0)	(2,2,2)
S5A	195.9540	396.4614	396.4695	397.5151	400.2692	400.2694	400.2699
S5B	102.0387	212.5659	212.5826	215.2991	216.7039	216.7046	216.7056
S5C	147.7120	376.0192	385.6339	400.2712	401.8641	401.9347	401.9395
S5D	496.8803	1048.263	1053.087	1069.178	1077.075	1077.088	1077.099
S5E	469.2563	1201.669	1228.269	1272.824	1279.010	1279.181	1279.211
S5F	572.5414	1445.830	1472.773	1522.468	1534.803	1535.084	1535.160
S4A	90.70057	177.6317	177.6995	175.4794	171.6517	171.6540	171.6493
S4B	574.1428	1150.649	1150.632	1120.965	1096.775	1096.748	1096.701
S4C	529.9306	1144.753	1143.916	1066.704	1044.502	1044.346	1044.252
S4D	139.4676	299.3632	299.1649	279.9941	274.1474	274.1097	274.0861
S4E	1074.678	2244.369	2244.359	2101.396	2047.998	2047.502	2047.141
S4F	1598.738	3176.937	3180.846	2980.373	2879.205	2877.934	2876.938
S2A	90.70057	177.6317	177.6695	175.4794	171.6517	171.6540	171.6493
S2B	46.48921	99.78774	99.72164	93.33135	91.38247	91.36989	91.36203
S2C	406.2910	809.6947	810.6355	759.5473	734.1684	733.8533	733.6060

(MESH=256 $\underset{\sim}{k}$-vectors in whole zone(origin omitted)

APPENDIX A

In this appendix it will be shown how the exponential $e^{-\beta H}$ was expanded to yield the partition function of Eq. (19), H being the anharmonic hamiltonian defined in Eq.(13). For convenience put

$$H = H_o + H_I$$

where

$$H_I = \sum_{n=3}^{6} \lambda^{n-2} H_n$$

Since H_o and H_I in general do not commute we cannot simply factor out $e^{-\beta H_o}$ from $e^{-\beta H}$ as would be possible if we were not dealing with operators. Instead let us define a function $S(\beta)$ such that

$$e^{-\beta H} = e^{-\beta H_o} S(\beta) \tag{A.1}$$

We now must determine $S(\beta)$. If we differentiate both sides of Eq. (A.1) with respect to β we get

$$-H_I e^{-\beta H} = e^{-\beta H_o} \frac{\partial S}{\partial \beta}$$

or

$$-\widetilde{H}_I(\beta)\, S(\beta) = \frac{\partial S}{\partial \beta} \quad ; \quad (\widetilde{H}_I(\beta) = e^{\beta H_o} H_I e^{-\beta H_o})$$

Thus

$$S(\beta) = 1 - \int_0^{\beta} \widetilde{H}_I(\beta') S(\beta') d\beta' \tag{A.2}$$

Eq. (A.2) satisfies the condition $S(0) = 1$ which follows from Eq. (A.1).

Iterating Eq. (A.2) we get

$$S(\beta) = 1 - \int_0^\beta \tilde{H}_I(\beta')\,d\beta' + \int_0^\beta d\beta' \int_0^{\beta'} \tilde{H}_I(\beta')\tilde{H}_I(\beta'')\,d\beta''$$

$$- \int_0^\beta d\beta' \int_0^{\beta'} d\beta'' \int_0^{\beta''} \tilde{H}_I(\beta')\tilde{H}_I(\beta'')\tilde{H}_I(\beta''')\,d\beta'''$$

$$+ \int_0^\beta d\beta' \int_0^{\beta'} d\beta'' \int_0^{\beta''} d\beta''' \int_0^{\beta'''} \tilde{H}_I(\beta')\tilde{H}_I(\beta'')\tilde{H}_I(\beta''')\tilde{H}_I(\beta^{IV})\,d\beta^{IV}$$

$$+ \cdots$$

Using the definition of $\tilde{H}_I$ we have

$$Z = \mathrm{Tr}\, e^{-\beta H}$$

$$= \mathrm{Tr}\, e^{-\beta H_0} - \beta\, \mathrm{Tr}\, e^{-\beta H_0} \int_0^1 ds\, e^{s_1\beta H_0} H_I\, e^{-s_1\beta H_0}$$

$$+ \beta^2\, \mathrm{Tr}\, e^{-\beta H_0} \int_0^1 ds_1 \int_0^{s_1} ds_2\, e^{s_1\beta H_0} H_I\, e^{(s_2-s_1)\beta H_0} H_I\, e^{-s_2\beta H_0}$$

$$- \beta^3\, \mathrm{Tr}\, e^{-\beta H_0} \int_0^1 ds_1 \int_0^{s_1} ds_2 \int_0^{s_2} ds_3\, e^{s_1\beta H_0} H_I\, e^{(s_2-s_1)\beta H_0} H_I\, e^{(s_3-s_2)\beta H_0} H_I\, e^{-s_3\beta H_0}$$

$$+ \beta^4\, \mathrm{Tr}\, e^{-\beta H_0} \int_0^1 ds_1 \int_0^{s_1} ds_2 \int_0^{s_2} ds_3 \int_0^{s_3} ds_4\, e^{s_1\beta H_0} H_I\, e^{(s_2-s_1)\beta H_0} H_I\, e^{(s_3-s_2)\beta H_0}$$

$$\times H_I\, e^{(s_4-s_3)\beta H_0} H_I\, e^{-s_4\beta H_0}$$

APPENDIX B

We here show how the terms Z_0, $Z_1, \ldots, Z_{10}$ of the partition function were reduced from their forms in Eqs. (20) to those in Eqs. (24). There is only one term of the form Z_0, and using the definition of a trace and Eq. (22) it is

$$Z_0 = \mathrm{Tr}\, e^{-\beta H_0} = \sum_n \langle n| e^{-\beta H_0} |n\rangle = \sum_n e^{-\beta E_n}$$

where the eigenstates $|n\rangle$ of H_o were assumed to be normalized. The terms Z_1 and Z_3 are of similar form and are easily reduced if one uses the cyclic property of a trace, i.e.

$$\mathrm{TrABC} = \mathrm{TrCAB} = \mathrm{TrBCA} \tag{B.1}$$

where A,B,C are some operators.

Hence

$$Z_1 = -\beta\, \mathrm{Tr}\, e^{-\beta H_0} \int_0^1 ds_1\, e^{s_1 \beta H_0} H_4 e^{-s_1 \beta H_0}$$

$$= -\beta\, \mathrm{Tr}\, e^{-\beta H_0} \int_0^1 ds_1\, H_4$$

$$= -\beta \sum_n \langle n| e^{-\beta H_0} H_4 |n\rangle$$

$$= -\beta \sum_n e^{-\beta E_n} \langle n| H_4 |n\rangle$$

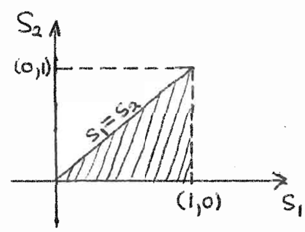
The terms Z_2, Z_4, Z_5, and Z_6 can be evaluated by using the cyclic property of the trace and a change of integration variables. First suppose that we wish to evaluate a double integral I of the form

$$I = \int_0^1 ds_1 \int_0^{s_1} ds_2 \; f(s_1 - s_2) \tag{B.2}$$

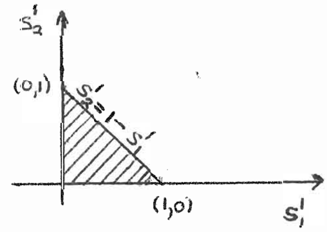
Introduce new coordinates s_1', s_2'

$$\begin{aligned} s_1' &= s_2 \\ s_2' &= s_1 - s_2 \; . \end{aligned} \tag{B.3}$$

In Eq. (B2) the region of integration in the s_1, s_2 plane is the shaded region below



The transformation defined by Eq. (B3) maps the above region into the shaded region below



Since the magnitude of the Jacobian of the transformation is unity we thus get

$$I = \int_0^1 ds_2' \int_0^{1-s_2'} ds_1' \; f(s_1')$$

$$= \int_0^1 ds_2' \int_{s_2'}^1 ds_2$$

Using this result we have

$$Z_2 = \beta^2 \, \mathrm{Tr}\, e^{-\beta H_0} \int_0^1 ds_1 \int_0^{s_1} ds_2 \, e^{(s_1-s_2)\beta H_0} H_3 e^{(s_2-s_1)\beta H_0} H_3$$

$$= \beta^2 \, \mathrm{Tr}\, e^{-\beta H_0} \int_0^1 ds_2' \int_{s_2'}^1 ds_2 \, e^{s_2'\beta H_0} H_3 e^{-s_2'\beta H_0} H_3$$

$$= \beta^2 \, \mathrm{Tr}\, e^{-\beta H_0} \int_0^1 ds\,(1-s) e^{s\beta H_0} H_3 e^{-s\beta H_0} H_3$$

$$= \beta^2 \sum_n e^{-\beta E_n} \int_0^1 ds(1-s) e^{s\beta E_n} \langle n| H_3 e^{-s\beta H_0} H_3 |n\rangle$$

We now make use of the resolution of identity for the complete set of states $|n\rangle$:

$$1 = \sum_n |n\rangle\langle n|$$

where 1 is the identity operator.

Thus
$$Z_2 = \beta^2 \sum_{n,m} e^{-\beta E_n} \int_0^1 ds\,(1-s) e^{s\beta E_n} \langle n|H_3|m\rangle\langle m|e^{-s\beta H_0} H_3|n\rangle$$

$$= \beta^2 \sum_{n,m} e^{-\beta E_n} \langle n|H_3|m\rangle\langle m|H_3|n\rangle \int_0^1 ds(1-s) e^{s\beta(E_n-E_m)}$$

If the integration is performed the result is that of Eqs. (24). The remaining terms $Z_7,\ldots,Z_{10}$ are reduced by using the resolution of identity as for Z_7 below

$$Z_7 = -\beta^3 \int_0^1 ds_1 \int_0^{s_1} ds_2 \int_0^{s_2} ds_3 \sum_{n,m,p} \langle n| e^{-\beta H_0(1-s_1)} H_3 e^{(s_2-s_1)\beta H_0} |m\rangle\langle m| e^{(s_3-s_2)\beta H_0} |p\rangle$$
$$\times \langle p| H_4 e^{-s_3\beta H_0} |n\rangle$$

$$= -\beta^3 \sum_{n,m,p} e^{-\beta E_n} \langle n| H_3 |m\rangle\langle m| H_3 |p\rangle\langle p| H_4 |n\rangle \int_0^1 ds_1 \int_0^{s_1} ds_2 \int_0^{s_2} ds_3\, e^{\beta s_1 E_n}$$
$$\times e^{\beta(s_2-s_1)E_m} e^{\beta(s_3-s_2)E_p} e^{-\beta s_3 E_n}$$

The final result is stated in Eqs. (24).

APPENDIX C

Here we evaluate the quotient

$$\frac{\sum_{n} e^{-\beta E_n}(2n_1+1)(2n_2+1)(2n_3+1)}{\sum_{n} e^{-\beta E_n}} \tag{C.1}$$

where the summations are over all sets $\{n_1, n_2, \ldots\}$ of 3N positive integers(including zero)which are used to label the eigenstates $|n_1 n_2, \ldots\rangle \equiv |n\rangle$ of the system of phonons.In Eq.(21) we have defined the harmonic energy of the lattice to be

$$E_n = \sum_{\underset{\sim}{k}_j} \hbar\omega_{\underset{\sim}{k}_j}(n_{\underset{\sim}{k}_j}+\tfrac{1}{2})$$

Thus we can make the following factorization:

$$\sum_{n} e^{-\beta E_n} = \Big(\sum_{n_1} e^{-\beta\hbar\omega_1 n_1}\Big)\Big(\sum_{n_2} e^{-\beta\hbar\omega_2 n_2}\Big)\ldots\Big(\sum_{n_{3N}} e^{-\beta\hbar\omega_{3N} n_{3N}}\Big) \times e^{-(\beta\hbar/2)(\omega_1+\ldots+\omega_{3N})} \tag{C.2}$$

Similarly

$$\sum_{n} e^{-\beta E_n}(2n_1+1)(2n_2+1)(2n_3+1)$$

$$= \Big\{\sum_{n_1} e^{-\beta\hbar\omega_1 n_1}(2n_1+1)\Big\}\Big\{\sum_{n_2} e^{-\beta\hbar\omega_2 n_2}(2n_2+1)\Big\}\Big\{\sum_{n_3} e^{-\beta\hbar\omega_3 n_3}(n_3+1)\Big\} \tag{C.3}$$

$$\times \Big\{\sum_{n_4} e^{-\beta\hbar\omega_4 n_4}\Big\}\times\ldots\times\Big\{\sum_{n_{3N}} e^{-\beta\hbar\omega_{3N} n_{3N}}\Big\} e^{-(\beta\hbar/2)(\omega_1+\ldots+\omega_{3N})}$$

The quotient in Eq.(C.1) thus becomes

$$\prod_{i=1}^{3}\left\{\frac{\sum_{n_i} e^{-\beta\hbar\omega_i n_i}(2n_i+1)}{\sum_{n_i} e^{-\beta\hbar\omega_i n_i}}\right\}$$

All we need to do now is evaluate the quotient

$$\frac{\sum_{n_i} n_i e^{-\beta\hbar\omega_i n_i}}{\sum_{n_i} e^{-\beta\hbar\omega_i n_i}}$$

The denominator is an infinite geometric series which has the sum

$$\sum_{n_i} e^{-\beta\hbar\omega_i n_i} = \frac{1}{1-e^{-\beta\hbar\omega_i}} \tag{C.4}$$

Consider $\sum_{n_i} n_i e^{-\beta\hbar\omega_i n_i}$ .Since this series is uniformly convergent for all $\beta > 0$ and $e^{-\beta\hbar\omega_i n_i}$ is a continuously differentiable function of β , we can differentiate under the summation in Eq.(C.4) so that differentiating both sides with respect to β we get

$$\sum_{n_i} n_i e^{-\beta\hbar\omega_i n_i} = \frac{e^{-\beta\hbar\omega_i}}{(1 - e^{-\beta\hbar\omega_i})^2}$$

Hence

$$\frac{\sum_{n_i} n_i e^{-\beta\hbar\omega_i n_i}}{\sum_{n_i} e^{-\beta\hbar\omega_i n_i}} = \frac{e^{-\beta\hbar\omega_i}}{1 - e^{-\beta\hbar\omega_i}} = \frac{1}{e^{\beta\hbar\omega_i} - 1}$$

so that using the new notation $n_i = \frac{1}{e^{\beta\hbar\omega_i} - 1}$ the quotient in Eq.(C.1) becomes

$$(2n_1+1)(2n_2+1)(2n_3+1)$$

APPENDIX D

Consider a term of the form

$$T_{\alpha\beta} = \sum_n \sum_m e^{-\beta E_n} \frac{\langle n|H_\alpha|m\rangle\langle m|H_\beta|n\rangle}{E_m - E_n} \tag{D.1}$$

where α, β are integers 3, 4, ...Then

$$\begin{aligned} T_{\beta\alpha} &= \sum_n \sum_m e^{-\beta E_n} \frac{\langle n|H_\beta|m\rangle\langle m|H_\alpha|n\rangle}{E_m - E_n} \\ &= \sum_n \sum_m e^{-\beta E_n} \frac{\langle m|H_\alpha|n\rangle\langle n|H_\beta|m\rangle}{E_m - E_n} \end{aligned} \tag{D.2}$$

Now H_α contains the operator product

$$A_{\lambda_1} A_{\lambda_2} \cdots A_{\lambda_\alpha}$$

Using the resolution of identity

$$1 = \sum_n |n\rangle\langle n|$$

get

$$\langle m|A_{\lambda_1} \cdots A_{\lambda_\alpha}|n\rangle = \sum_{p_1} \sum_{p_2} \cdots \sum_{p_{\alpha-1}} \langle m|A_{\lambda_1}|p_1\rangle\langle p_1|A_{\lambda_2}|p_2\rangle \cdots \langle p_{\alpha-1}|A_{\lambda_\alpha}|n\rangle \tag{D.3}$$

By the definition of A_{λ_i} and using Eqs. (11) we get

$$\langle n|A_{\lambda_i}|m\rangle = - \langle m|A_{\lambda_i}|n\rangle \tag{D.4}$$

From D.3, D.4 and the fact that the A_{λ_i} commute we have

$$\langle m|A_{\lambda_1}A_{\lambda_2}\cdots A_{\lambda_\alpha}|n\rangle = (-1)^{\alpha}\langle n|A_{\lambda_1}A_{\lambda_2}\cdots A_{\alpha}|m\rangle$$

Thus $$\langle m|H_\alpha|n\rangle = (-1)^{\alpha}\langle n|H_\alpha|m\rangle$$

Returning now to D.2 we see that

$$T_{\beta\alpha} = (-1)^{\alpha+\beta}\,T_{\alpha\beta}$$

Hence in Eqs. (24), $Z_6 = Z_4$ because $\alpha+\beta$ is even.

If we have another term of the form

$$T_{\alpha\beta\gamma} = \sum_n\sum_m\sum_p e^{-\beta E_n}\,\frac{\langle n|H_\alpha|m\rangle\langle m|H_\beta|p\rangle\langle p|H_\gamma|n\rangle}{(E_p-E_n)(E_m-E_n)}$$

the previous results show that

$$T_{\gamma\beta\alpha} = (-1)^{\alpha+\beta+\gamma}\,T_{\alpha\beta\gamma}$$

so that in Eqs. (24), $Z_9 = Z_7$.

APPENDIX E

It is shown that

$$\sum_j \frac{e_\alpha\binom{\mathbf{k}}{j} e_\beta\binom{\mathbf{k}}{j}}{\omega^2_{\mathbf{k}j}} = [D^{-1}]_{\alpha\beta}$$

where D^{-1} is the inverse of dynamical matrix D. We start with the eigenvalue equation

$$\sum_y D_{xy}\, e_y\binom{\mathbf{k}}{j} = \omega^2_{\mathbf{k}j}\, e_x\binom{\mathbf{k}}{j} \tag{E.1}$$

Since $\sum_x [D^{-1}]_{\alpha x} D_{xy} = \delta_{\alpha y}$ by definition, then multiplying both sides of E.1 by $[D^{-1}]_{\alpha x}$ and summing over x we get

$$e_\alpha\binom{\mathbf{k}}{j} = \sum_x \omega^2_{\mathbf{k}j}\, e_x\binom{\mathbf{k}}{j} [D^{-1}]_{\alpha x}$$

Divide both sides by $\omega^2_{\mathbf{k}j}$, multiply by $e_\beta\binom{\mathbf{k}}{j}$ and sum over j, getting

$$\sum_j \frac{e_\alpha\binom{\mathbf{k}}{j} e_\beta\binom{\mathbf{k}}{j}}{\omega^2_{\mathbf{k}j}} = \sum_x \left(\sum_j e_x\binom{\mathbf{k}}{j} e_\beta\binom{\mathbf{k}}{j}\right) [D^{-1}]_{\alpha x}$$

But we also have

$$\sum_j e_\alpha\binom{\mathbf{k}}{j} e_\beta\binom{\mathbf{k}}{j} = \delta_{\alpha\beta}$$

from the orthornormality of the eigenvectors $\underset{\sim}{e}\binom{\mathbf{k}}{j}$

Thus

$$\sum_j \frac{e_\alpha\binom{\mathbf{k}}{j} e_\beta\binom{\mathbf{k}}{j}}{\omega^2_{\mathbf{k}j}} = \sum_x \delta_{\beta x} [D^{-1}]_{\alpha x} = [D^{-1}]_{\alpha\beta}$$

APPENDIX F

In this appendix are given the analytical expressions for the sums S1A,etc. which are tabulated in the section "NUMERICAL CALCULATIONS". The notation used is the same as that used previously except where otherwise indicated. As before $\gamma^2_{\underset{\sim}{k}j} = \frac{M}{2\varphi''(r_0)}\omega^2_{\underset{\sim}{k}j}$; $\underset{\sim}{q} = \pi a_0 \underset{\sim}{k}$ and λ denotes the index pair $\underset{\sim}{k}j$. Whenever we write $\underset{\sim}{e}$ or γ we mean $\underset{\sim}{e}\binom{\underset{\sim}{k}}{j}$ and $\gamma^2_{\underset{\sim}{k}j}$ respectively.

In the case of S1A,S1B,and S1C, and S3A,...,S3D,the $\underset{\sim}{n}$-summation is over nearest neighbour lattice vectors.

Put

$$T1 = \frac{1}{N}\sum_{\lambda} \frac{1}{\gamma^2} (\underset{\sim}{n}\cdot\underset{\sim}{e})^2(1-\cos \underset{\sim}{q}\cdot\underset{\sim}{n})$$

$$T2 = \frac{1}{N}\sum_{\lambda} \frac{1}{\gamma^2} (\underset{\sim}{e}\cdot\underset{\sim}{e})(1-\cos \underset{\sim}{q}\cdot\underset{\sim}{n})$$

$$T_\alpha = \frac{1}{N}\sum_{\lambda} \frac{1}{\gamma^2} e_\alpha(\underset{\sim}{n}\cdot\underset{\sim}{e})(1-\cos \underset{\sim}{q}\cdot\underset{\sim}{n})$$

$$T_{\alpha\beta} = \frac{1}{N}\sum_{\lambda} \frac{1}{\gamma^2} e_\alpha e_\beta(1-\cos \underset{\sim}{q}\cdot\underset{\sim}{n})$$

where $\alpha,\beta = x,y,z$ and N is the number of allowed $\underset{\sim}{k}$-vectors

Then

$$S1A = \sum_{\underset{\sim}{n}} (T1)^2$$

$$S1B = \sum_{\underset{\sim}{n}} \left[4\sum_{\alpha} (T_\alpha)^2 + 2(T1)(T2)\right]$$

$$S1C = \sum_{\underset{\sim}{n}} \left[2\sum_{\alpha}\sum_{\beta} (T_{\alpha\beta})^2 + (T2)^2\right]$$

$$S3A = \sum_{\underset{\sim}{n}} (T1)^3$$

$$S3B = \sum_{\underset{\sim}{n}} \left[3(T2)(T1)^2 + 12\sum_{\alpha} (T1)(T_\alpha)^2 \right]$$

$$S3C = \sum_{\underset{\sim}{n}} \Big[3(T1)(T2)^2 + 6(T1)\sum_{\alpha}\sum_{\beta} (T_{\alpha\beta})^2$$

$$+ 24\sum_{\alpha}\sum_{\beta} (T_\alpha)(T_\beta)(T_{\alpha\beta}) + 12\sum_{\alpha} (T_\alpha)^2(T2) \Big]$$

$$S3D = \sum_{\underset{\sim}{n}} \Big[6(T2)\sum_{\alpha}\sum_{\beta} (T_{\alpha\beta})^2 + (T2)^3$$

$$+ 8\sum_{\alpha,\beta,\gamma} (T_{\alpha\beta})(T_{\alpha\gamma})(T_{\beta\gamma}) \Big]$$

In the following for S2A,etc.,S4A,etc.,S5A,etc. the sums over n_1 and n_2 extend over nearest neighbours but the sum over n extends over general lattice vectors.

First define the following:

$$H = \cos \underset{\sim}{q}\cdot\underset{\sim}{n} - \cos \underset{\sim}{q}\cdot(\underset{\sim}{n}+\underset{\sim}{n}_2) - \cos \underset{\sim}{q}\cdot(\underset{\sim}{n}-\underset{\sim}{n}_1) + \cos \underset{\sim}{q}\cdot(\underset{\sim}{n}-\underset{\sim}{n}_1+\underset{\sim}{n}_2)$$

$$H1 = \frac{1}{N}\sum_{\lambda} \frac{1}{\gamma^2} (\underset{\sim}{n}_1\cdot\underset{\sim}{e})(\underset{\sim}{n}_2\cdot\underset{\sim}{e})\, H$$

$$N1_\alpha = \frac{1}{N}\sum_{\lambda} \frac{1}{\gamma^2} (\underset{\sim}{n}_1\cdot\underset{\sim}{e})\, e_\alpha\, H$$

$$N2_\alpha = \frac{1}{N}\sum_{\lambda} \frac{1}{\gamma^2} (\underset{\sim}{n}_2\cdot\underset{\sim}{e})\, e_\alpha\, H$$

$$N_{\alpha\beta} = \frac{1}{N}\sum_{\lambda} \frac{1}{\gamma^2}\, e_\alpha e_\beta\, H$$

$$H2=\frac{1}{N}\sum_{\lambda}\frac{1}{\gamma^2}(\underset{\sim}{n_2}\cdot\underset{\sim}{e})^2(1-\cos\underset{\sim}{q}\cdot\underset{\sim}{n_2})$$

$$H3=\frac{1}{N}\sum_{\lambda}\frac{1}{\gamma^2}(\underset{\sim}{e}\cdot\underset{\sim}{e})(1-\cos\underset{\sim}{q}\cdot\underset{\sim}{n_2})$$

$$Q_\alpha=\frac{1}{N}\sum_{\lambda}\frac{1}{\gamma^2}(\underset{\sim}{n_2}\cdot\underset{\sim}{e})\,e_\alpha(1-\cos\underset{\sim}{q}\cdot\underset{\sim}{n_2})$$

$$Q_{\alpha\beta}=\frac{1}{N}\sum_{\lambda}\frac{1}{\gamma^2}\,e_\alpha e_\beta(1-\cos\underset{\sim}{q}\cdot\underset{\sim}{n_2})$$

Using the above definitions get

$$S2A=\sum_{\underset{\sim}{n}}\sum_{\underset{\sim}{n_1}}\sum_{\underset{\sim}{n_2}}(H1)^3$$

$$S2B=\sum_{\underset{\sim}{n}}\sum_{\underset{\sim}{n_1}}\sum_{\underset{\sim}{n_2}}\left\{(H1)\sum_{\alpha}(N1_\alpha)^2\right\}$$

$$S2C=\sum_{\underset{\sim}{n}}\sum_{\underset{\sim}{n_1}}\sum_{\underset{\sim}{n_2}}\left[3(H1)\sum_{\alpha}\sum_{\beta}(N_{\alpha\beta})^2+6\sum_{\alpha}\sum_{\beta}(N2_\alpha)(N_{\alpha\beta})(N1_\beta)\right]$$

$$S4A=\sum_{\underset{\sim}{n}}\sum_{\underset{\sim}{n_1}}\sum_{\underset{\sim}{n_2}}(H1)^3(H2)$$

$$S4B=\sum_{\underset{\sim}{n}}\sum_{\underset{\sim}{n_1}}\sum_{\underset{\sim}{n_2}}\Big[6(H1)^2\sum_{\alpha}(N1_\alpha)(Q_\alpha)+3(H1)(H2)\sum_{\alpha}(N1_\alpha)^2$$

$$+(H1)^3(H3)\Big]$$

$$S4C=\sum_{\underset{\sim}{n}}\sum_{\underset{\sim}{n_1}}\sum_{\underset{\sim}{n_2}}\left\{3\sum_{\alpha}(N2_\alpha)^2\times H1\times H2\right\}$$

$$S4D = \sum_{\underset{\sim}{n}} \sum_{\underset{\sim}{n_1}} \sum_{\underset{\sim}{n_2}} \Big[12 \sum_{\alpha} \sum_{\beta} (N_{\alpha\beta})(N2_{\alpha})(H1)\, Q_{\beta}$$

$$+ 6 \sum_{\alpha} \sum_{\beta} (N1_{\alpha})(N2_{\beta})^2\, Q_{\alpha} + 6\,(H2) \sum_{\alpha} \sum_{\beta} (N2_{\alpha})(N1)_{\beta}\, N_{\alpha\beta}$$

$$+ 3\,(H1)(H2) \sum_{\alpha} \sum_{\beta} (N_{\alpha\beta})^2 + 3(H1)(H3) \sum_{\alpha} (N2_{\alpha})^2 \Big]$$

$$S4E = \sum_{\underset{\sim}{n}} \sum_{\underset{\sim}{n_1}} \sum_{\underset{\sim}{n_2}} \Big[12 \sum_{\alpha,\beta,\gamma} (N2_{\alpha})(N1)_{\beta}\, N_{\alpha\gamma}\, Q_{\beta\gamma}$$

$$+ 6 \sum_{\alpha,\beta,\gamma} (H1)\, N_{\alpha\beta} N_{\alpha\gamma} Q_{\beta\gamma} + 12 \sum_{\alpha,\beta,\gamma} N_{\alpha\beta} N_{\alpha\gamma} (N1_{\beta}) Q_{\gamma}$$

$$+ 6 \sum_{\alpha,\beta,\gamma} (N1_{\gamma})\, Q_{\alpha} (N_{\alpha\beta})^2 + 6 \sum_{\alpha,\beta} (N2_{\alpha})(N1_{\beta}) N_{\alpha\beta} (H3)$$

$$+ 3\,(H1)(H3) \sum_{\alpha,\beta} (N_{\alpha\beta})^2 \Big]$$

$$S4F = \sum_{\underset{\sim}{n}} \sum_{\underset{\sim}{n_1}} \sum_{\underset{\sim}{n_2}} \Big[6\,(H1) \sum_{\alpha,\beta} (N1_{\beta})(N1_{\alpha})\, Q_{\alpha\beta}$$

$$+ 6 \sum_{\alpha,\beta} (N1_{\beta})(N1_{\alpha})^2\, Q_{\beta} + 3\,(H1)(H3) \sum_{\alpha} (N1_{\alpha})^2 \Big]$$

$$S5A = \sum_{\underset{\sim}{n}} \sum_{\underset{\sim}{n_1}} \sum_{\underset{\sim}{n_2}} (H1)^4$$

$$S5B = \sum_{\underset{\sim}{n}} \sum_{\underset{\sim}{n}_1} \sum_{\underset{\sim}{n}_2} \left\{ (H1)^2 \times \sum_{\alpha} (N1_\alpha)^2 \right\}$$

$$S5C = \sum_{\underset{\sim}{n}} \sum_{\underset{\sim}{n}_1} \sum_{\underset{\sim}{n}_2} \sum_{\alpha} \sum_{\beta} (N1_\alpha)^2 (N1_\beta)^2$$

$$S5D = \sum_{\underset{\sim}{n}} \sum_{\underset{\sim}{n}_1} \sum_{\underset{\sim}{n}_2} \Big[\sum_{\alpha} \sum_{\beta} (H1)^2 (N_{\alpha\beta})^2 + \sum_{\alpha} \sum_{\beta} (N2_\alpha)^2 (N1_\beta)^2$$

$$+ 4 \sum_{\alpha} \sum_{\beta} (H1)(N2_\alpha)(N1_\beta)(N_{\alpha\beta}) \Big]$$

$$S5E = \sum_{\underset{\sim}{n}} \sum_{\underset{\sim}{n}_1} \sum_{\underset{\sim}{n}_2} \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \left[(N1_\alpha)^2 (N_{\beta\gamma})^2 + 2 (N1_\alpha)(N1_\beta) N_{\alpha\gamma} N_{\beta\gamma} \right]$$

$$S5F = \sum_{\underset{\sim}{n}} \sum_{\underset{\sim}{n}_1} \sum_{\underset{\sim}{n}_2} \left[\sum_{\alpha,\beta,\gamma} \sum_{\delta} (N_{\alpha\gamma})^2 (N_{\beta\delta})^2 + 2 \sum_{\alpha} \sum_{\beta} \left\{ \sum_{\gamma} N_{\alpha\gamma} N_{\beta\gamma} \right\}^2 \right]$$

In S6A,...,S6F there is a double summation over nearest neighbour vectors. We now define the following sums:

$$R3 = \frac{1}{N} \sum_{\lambda} \frac{1}{\gamma^2} (\underset{\sim}{e} \cdot \underset{\sim}{e}) (1 - \cos \underset{\sim}{q} \cdot \underset{\sim}{n}_1)$$

$$P1 = \frac{1}{N} \sum_{\lambda} \frac{1}{\gamma^2} (\underset{\sim}{n}_1 \cdot \underset{\sim}{e})^2 (1 - \cos \underset{\sim}{q} \cdot \underset{\sim}{n}_1)$$

$$P2 = \frac{1}{N} \sum_{\lambda} \frac{1}{\gamma^2} (\underset{\sim}{n}_2 \cdot \underset{\sim}{e})^2 (1 - \cos \underset{\sim}{q} \cdot \underset{\sim}{n}_2)$$

$$P_\alpha = \frac{1}{N} \sum_{\lambda} \frac{1}{\gamma^2} (\underset{\sim}{n}_1 \cdot \underset{\sim}{e}) e_\alpha (1 - \cos \underset{\sim}{q} \cdot \underset{\sim}{n}_1)$$

$$Q_\alpha = \frac{1}{N} \sum_{\lambda} \frac{1}{\gamma^2} (\underset{\sim}{n}_2 \cdot \underset{\sim}{e}) e_\alpha (1 - \cos \underset{\sim}{q} \cdot \underset{\sim}{n}_2)$$

$$R_{\alpha\beta} = \frac{1}{N} \sum_{\lambda} \frac{1}{\gamma^2} e_\alpha e_\beta (1 - \cos \underset{\sim}{q} \cdot \underset{\sim}{n}_1)$$

Below we adopt the notation

$$\underset{\sim}{e}_1 = \underset{\sim}{e}\binom{\underset{\sim}{q}}{j_1}; \quad \underset{\sim}{e}_2 = \underset{\sim}{e}\binom{\underset{\sim}{q}}{j_2}; \quad e_{1\alpha} = e_\alpha\binom{\underset{\sim}{q}}{j_1}; \quad e_{2\alpha} = e_\alpha\binom{\underset{\sim}{q}}{j_2}$$

$$\gamma_1^2 = \gamma^2_{\underset{\sim}{q} j_1}; \quad \gamma_2^2 = \gamma^2_{\underset{\sim}{q} j_2}$$

Define

$$P3=\sum_{\mathbf{q}}\sum_{j^1 j^2}\frac{1}{\gamma_1^2\gamma_2^2}(\mathbf{n}_1\cdot\mathbf{e}_1)(\mathbf{n}_2\cdot\mathbf{e}_1)(\mathbf{n}_1\cdot\mathbf{e}_2)(\mathbf{n}_2\cdot\mathbf{e}_2)(1-\cos\mathbf{q}\cdot\mathbf{n}_1)(1-\cos\mathbf{q}\cdot\mathbf{n}_2)$$

$$P4_{\alpha\beta}=\sum_{\mathbf{q}}\sum_{j^1 j^2}\frac{1}{\gamma_1^2\gamma_2^2}(\mathbf{n}_1\cdot\mathbf{e}_1)(\mathbf{n}_1\cdot\mathbf{e}_2)\,e_{1\alpha}e_{2\beta}(1-\cos\mathbf{q}\cdot\mathbf{n}_1)(1-\cos\mathbf{q}\cdot\mathbf{n}_2)$$

$$P5_{\alpha}=\sum_{\mathbf{q}}\sum_{j^1 j^2}\frac{1}{\gamma_1^2\gamma_2^2}(\mathbf{n}_1\cdot\mathbf{e}_1)(\mathbf{n}_2\cdot\mathbf{e}_1)(\mathbf{n}_1\cdot\mathbf{e}_2)\,e_{2\alpha}(1-\cos\mathbf{q}\cdot\mathbf{n}_1)(1-\cos\mathbf{q}\cdot\mathbf{n}_2)$$

$$P6_{\alpha\beta}=\sum_{\mathbf{q}}\sum_{j^1 j^2}\frac{1}{\gamma_1^2\gamma_2^2}(\mathbf{n}_1\cdot\mathbf{e}_1)(\mathbf{n}_2\cdot\mathbf{e}_1)\,e_{2\alpha}e_{2\beta}(1-\cos\mathbf{q}\cdot\mathbf{n}_1)(1-\cos\mathbf{q}\cdot\mathbf{n}_2)$$

$$R_{\alpha\beta\gamma\delta}=\sum_{\mathbf{q}}\sum_{j^1 j^2}\frac{1}{\gamma_1^2\gamma_2^2}\,e_{1\alpha}e_{1\beta}e_{2\gamma}e_{2\delta}(1-\cos\mathbf{q}\cdot\mathbf{n}_1)(1-\cos\mathbf{q}\cdot\mathbf{n}_2)$$

$$P7_{\alpha\beta\gamma}=\sum_{\mathbf{q}}\sum_{j^1 j^2}\frac{1}{\gamma_1^2\gamma_2^2}(\mathbf{n}_2\cdot\mathbf{e}_1)\,e_{1\alpha}e_{2\beta}e_{2\gamma}(1-\cos\mathbf{q}\cdot\mathbf{n}_1)(1-\cos\mathbf{q}\cdot\mathbf{n}_2)$$

$$P8_{\alpha}=\sum_{\mathbf{q}}\sum_{j^1 j^2}\frac{1}{\gamma_1^2\gamma_2^2}(\mathbf{n}_2\cdot\mathbf{e}_1)(\mathbf{n}_2\cdot\mathbf{e}_2)\,e_{1\alpha}e_{2\alpha}(1-\cos\mathbf{q}\cdot\mathbf{n}_1)(1-\cos\mathbf{q}\cdot\mathbf{n}_2)$$

$$P9_{\alpha}=\sum_{\mathbf{q}}\sum_{j^1 j^2}\frac{1}{\gamma_1^2\gamma_2^2}(\mathbf{n}_1\cdot\mathbf{e}_1)(\mathbf{n}_2\cdot\mathbf{e}_1)(\mathbf{n}_2\cdot\mathbf{e}_2)\,e_{2\alpha}(1-\cos\mathbf{q}\cdot\mathbf{n}_1)(1-\cos\mathbf{q}\cdot\mathbf{n}_2)$$

$$R1_{\alpha\beta\gamma}=\sum_{\mathbf{q}}\sum_{j^1 j^2}\frac{1}{\gamma_1^2\gamma_2^2}(\mathbf{n}_1\cdot\mathbf{e}_1)\,e_{1\alpha}e_{2\beta}e_{2\gamma}(1-\cos\mathbf{q}\cdot\mathbf{n}_1)(1-\cos\mathbf{q}\cdot\mathbf{n}_2)$$

$$R2_{\alpha\beta}=\sum_{\mathbf{q}}\sum_{j^1 j^2}\frac{1}{\gamma_1^2\gamma_2^2}(\mathbf{n}_1\cdot\mathbf{e}_1)(\mathbf{n}_2\cdot\mathbf{e}_2)\,e_{1\alpha}e_{2\beta}(1-\cos\mathbf{q}\cdot\mathbf{n}_1)(1-\cos\mathbf{q}\cdot\mathbf{n}_2)$$

Thus we get

$$S6A = \sum_{\underset{\sim}{n_1}} \sum_{\underset{\sim}{n_2}} (P1)(P2)(P3)$$

$$S6B = \sum_{\underset{\sim}{n_1}} \sum_{\underset{\sim}{n_2}} \Big[(P1)(P2) \sum_{\alpha} (P4_{\alpha\alpha}) + 4(P1) \sum_{\alpha} (Q_{\alpha})(P5_{\alpha})$$
$$+ (P1)(H3)(P3) \Big]$$

$$S6C = \sum_{\underset{\sim}{n_1}} \sum_{\underset{\sim}{n_2}} \Big[\sum_{\alpha} (P1)(H3)(P4_{\alpha\alpha}) + 2(P1) \sum_{\alpha,\beta} (Q_{\alpha\beta})(P4_{\alpha\beta}) \Big]$$

$$S6D = \sum_{\underset{\sim}{n_1}} \sum_{\underset{\sim}{n_2}} \Big[\sum_{\alpha,\beta} (P1)(P2)(R_{\alpha\beta\alpha\beta}) + 8(P1) \sum_{\alpha,\beta} (Q_{\beta})(P7_{\alpha\alpha\beta})$$
$$+ 2\sum_{\alpha} (P1)(H3)(P8_{\alpha}) + 8 \sum_{\alpha,\beta} (P_{\alpha})(Q_{\beta})(P6_{\alpha\beta})$$
$$+ 8 \sum_{\alpha,\beta} (P_{\alpha})(Q_{\beta})(R2_{\beta\alpha}) + 8 \sum_{\alpha} (P_{\alpha})(H3)(P9_{\alpha})$$
$$+ (H3)(R3)(P3) \Big]$$

$$S6E = \sum_{\underset{\sim}{n_1}} \sum_{\underset{\sim}{n_2}} \Big[\sum_{\alpha,\beta} (P1)(H3)(R_{\alpha\beta\alpha\beta}) + 2 \sum_{\alpha,\beta,\gamma} (P1)(Q_{\beta\gamma})(R_{\alpha\beta\alpha\gamma})$$
$$+ 4 \sum_{\alpha,\beta} (P_{\alpha})(H3)(R1_{\beta\alpha\beta}) + 8 \sum_{\alpha,\beta,\gamma} (P_{\alpha})(Q_{\beta\gamma})(R1_{\beta\alpha\gamma})$$
$$+ \sum_{\alpha} (R3)(H3)(R2_{\alpha\alpha}) + 2 \sum_{\alpha,\beta} (R3)(Q_{\alpha\beta})(P4_{\alpha\beta}) \Big]$$

$$S6F = \sum_{\underset{\sim}{n_1}} \sum_{\underset{\sim}{n_2}} \Big[\sum_{\alpha,\beta} (R3)(H3)(R_{\alpha\beta\alpha\beta}) + 4 \sum_{\alpha,\beta,\gamma} (R3)(Q_{\beta\gamma})(R_{\alpha\beta\alpha\gamma})$$
$$+ 4 \sum_{\alpha,\beta,\gamma,\delta} (R_{\alpha\beta})(Q_{\gamma\delta})(R_{\alpha\gamma\beta\delta} \Big]$$

In S7A,...,S7I, there is a triple summation over nearest neighbour vectors $\underset{\sim}{n}_1, \underset{\sim}{n}_2, \underset{\sim}{n}_3$, and a single summation over general lattice vectors $\underset{\sim}{n}$. We must first define the following:

$$L = (1-\cos \underset{\sim}{q}\cdot\underset{\sim}{n}_3)\{\cos \underset{\sim}{q}\cdot\underset{\sim}{n} - \cos \underset{\sim}{q}\cdot(\underset{\sim}{n}+\underset{\sim}{n}_2) - \cos\underset{\sim}{q}\cdot(\underset{\sim}{n}-\underset{\sim}{n}_1) + \cos\underset{\sim}{q}\cdot(\underset{\sim}{n}-\underset{\sim}{n}_1+\underset{\sim}{n}_2)\}$$

$$L1 = \frac{1}{N}\sum_{\underset{\sim}{q}}\sum_{j_1 j_2}\frac{1}{\gamma_1^2\gamma_2^2}(\underset{\sim}{n}_1\cdot\underset{\sim}{e}_1)(\underset{\sim}{n}_3\cdot\underset{\sim}{e}_1)(\underset{\sim}{n}_2\cdot\underset{\sim}{e}_2)(\underset{\sim}{n}_3\cdot\underset{\sim}{e}_2)L$$

$$L2 = \frac{1}{N}\sum_{\lambda}\frac{1}{\gamma^2}(\underset{\sim}{n}_3\cdot\underset{\sim}{e})^2(1-\cos\underset{\sim}{q}\cdot\underset{\sim}{n}_3)$$

$$L3_\alpha = \frac{1}{N}\sum_{\underset{\sim}{q}}\sum_{j_1 j_2}\frac{1}{\gamma_1^2\gamma_2^2}(\underset{\sim}{n}_1\cdot\underset{\sim}{e}_1)(\underset{\sim}{n}_3\cdot\underset{\sim}{e}_1)e_{2\alpha}(\underset{\sim}{n}_3\cdot\underset{\sim}{e}_2)L$$

$$L4 = \frac{1}{N}\sum_{\lambda}\frac{1}{\gamma^2}(\underset{\sim}{n}_1\cdot\underset{\sim}{e})^2(1-\cos\underset{\sim}{q}\cdot\underset{\sim}{n}_3)$$

$$L5_\alpha = \frac{1}{N}\sum_{\underset{\sim}{q}}\sum_{j_1 j_2}\frac{1}{\gamma_1^2\gamma_2^2}(\underset{\sim}{n}_2\cdot\underset{\sim}{e}_1)(\underset{\sim}{n}_3\cdot\underset{\sim}{e}_1)(\underset{\sim}{n}_3\cdot\underset{\sim}{e}_2)e_{2\alpha}L$$

$$L6_{\alpha\beta} = \frac{1}{N}\sum_{\underset{\sim}{q}}\sum_{j_1 j_2}\frac{1}{\gamma_1^2\gamma_2^2}e_{1\alpha}(\underset{\sim}{n}_3\cdot\underset{\sim}{e}_1)e_{2\beta}(\underset{\sim}{n}_3\cdot\underset{\sim}{e}_2)L$$

$$L7_{\alpha\beta} = \frac{1}{N}\sum_{\underset{\sim}{q}}\sum_{j_1 j_2}\frac{1}{\gamma_1^2\gamma_2^2}e_{1\alpha}(\underset{\sim}{n}_3\cdot\underset{\sim}{e}_1)e_{2\beta}(\underset{\sim}{n}_3\cdot\underset{\sim}{e}_2)L$$

$$L8 = \frac{1}{N}\sum_{\lambda}\frac{1}{\gamma^2}(\underset{\sim}{e}\cdot\underset{\sim}{e})(1-\cos\underset{\sim}{q}\cdot\underset{\sim}{n}_3)$$

$$L9_\alpha = \frac{1}{N}\sum_{\underset{\sim}{q}}\sum_{j_1 j_2}\frac{1}{\gamma_1^2\gamma_2^2}(\underset{\sim}{n}_1\cdot\underset{\sim}{e}_1)(\underset{\sim}{n}_3\cdot\underset{\sim}{e}_1)(\underset{\sim}{n}_2\cdot\underset{\sim}{e}_2)e_{2\alpha}L$$

$$L10_\alpha = \frac{1}{N}\sum_{\lambda}\frac{1}{\gamma^2}(\underset{\sim}{n}_3\cdot\underset{\sim}{e})e_\alpha(1-\cos\underset{\sim}{q}\cdot\underset{\sim}{n}_3)$$

$$L11_{\alpha} = \frac{1}{N}\sum_{\mathbf{q}}\sum_{j_1 j_2} \frac{1}{\gamma_1^2\gamma_2^2} (\mathbf{n}_1\cdot\mathbf{e}_1)\, e_{1\alpha} (\mathbf{n}_2\cdot\mathbf{e}_2)(\mathbf{n}_3\cdot\mathbf{e}_2)\, L$$

$$L12_{\alpha\beta} = \frac{1}{N}\sum_{\mathbf{q}}\sum_{j_1 j_2} \frac{1}{\gamma_1^2\gamma_2^2} (\mathbf{n}_1\cdot\mathbf{e}_1)\, e_{1\alpha} (\mathbf{n}_2\cdot\mathbf{e}_2)\, e_{2\beta}\, L$$

$$L13_{\alpha\beta} = \frac{1}{N}\sum_{\mathbf{q}}\sum_{j_1 j_2} \frac{1}{\gamma_1^2\gamma_2^2} (\mathbf{n}_1\cdot\mathbf{e}_1)(\mathbf{n}_3\cdot\mathbf{e}_1)\, e_{2\alpha}\, e_{2\beta}\, L$$

$$L14_{\alpha\beta} = \frac{1}{N}\sum_{\mathbf{q}}\sum_{j_1 j_2} \frac{1}{\gamma_1^2\gamma_2^2} (\mathbf{n}_1\cdot\mathbf{e}_1)\, e_{1\alpha} (\mathbf{n}_3\cdot\mathbf{e}_2)\, e_{2\beta}\, L$$

$$L15_{\alpha\beta\gamma} = \frac{1}{N}\sum_{\mathbf{q}}\sum_{j_1 j_2} \frac{1}{\gamma_1^2\gamma_2^2} (\mathbf{n}_1\cdot\mathbf{e}_1)\, e_{1\alpha}\, e_{2\beta}\, e_{2\gamma}\, L$$

$$L16_{\alpha\beta\gamma} = \frac{1}{N}\sum_{\mathbf{q}}\sum_{j_1 j_2} \frac{1}{\gamma_1^2\gamma_2^2} (\mathbf{n}_3\cdot\mathbf{e}_1)\, e_{1\alpha}\, e_{2\beta}\, e_{2\gamma}\, L$$

$$L_{\alpha\beta\gamma\delta} = \frac{1}{N}\sum_{\mathbf{q}}\sum_{j_1 j_2} \frac{1}{\gamma_1^2\gamma_2^2}\, e_{1\alpha}\, e_{1\beta}\, e_{2\gamma}\, e_{2\delta}\, L$$

$$L17_{\alpha\beta} = \frac{1}{N}\sum_{\mathbf{q}}\sum_{j_1 j_2} \frac{1}{\gamma_1^2\gamma_2^2} (\mathbf{n}_3\cdot\mathbf{e}_1)\, e_{1\alpha} (\mathbf{n}_2\cdot\mathbf{e}_2)\, e_{2\beta}\, L$$

$$L18_{\alpha\beta\gamma} = \frac{1}{N}\sum_{\mathbf{q}}\sum_{j_1 j_2} \frac{1}{\gamma_1^2\gamma_2^2} (\mathbf{n}_2\cdot\mathbf{e}_1)\, e_{1\alpha}\, e_{2\beta}\, e_{2\gamma}\, L$$

$$L19_{\alpha\beta} = \frac{1}{N}\sum_{\lambda} \frac{1}{\gamma^2}\, e_\alpha e_\beta (1-\cos \mathbf{q}\cdot\mathbf{n}_3)$$

Thus

$$S7A = \sum_{\underset{\sim}{n}} \sum_{\substack{\underset{\sim}{n_1}\,\underset{\sim}{n_2} \\ \underset{\sim}{n_3}}} (L1)(H1)^2(L2)$$

$$S7B = \sum_{\underset{\sim}{n}} \sum_{\substack{\underset{\sim}{n_1}\,\underset{\sim}{n_2} \\ \underset{\sim}{n_3}}} \left[2\sum_{\alpha} (L3_{\alpha})(N1_{\alpha})(H1)(L2) + (L1)(L4)\sum_{\alpha} (N1_{\alpha})^2 \right]$$

$$S7C = \sum_{\underset{\sim}{n}} \sum_{\substack{\underset{\sim}{n_1}\,\underset{\sim}{n_2} \\ \underset{\sim}{n_3}}} \Big[2\sum_{\alpha,\beta} (L6_{\alpha\beta})(N_{\alpha\beta})(H1)(L2) + 2\sum_{\alpha,\beta} (L5_{\alpha})(N_{\alpha\beta})(N1_{\beta})(L2)$$

$$+ 2\sum_{\alpha,\beta} (L6_{\alpha\beta})(N2_{\alpha})(N1_{\beta})(L2) + 2\sum_{\alpha,\beta} (L3_{\beta})(N_{\alpha\beta})(N2_{\alpha})(L2)$$

$$+ \sum_{\alpha,\beta} (L1)(N_{\alpha\beta})^2(L2) \Big]$$

$$S7D = \sum_{\underset{\sim}{n}} \sum_{\substack{\underset{\sim}{n_1}\,\underset{\sim}{n_2} \\ \underset{\sim}{n_3}}} \Big[(L1)(H1)^2(L8) + 2\sum_{\alpha} (L9_{\alpha})(H1)^2(L10_{\alpha})$$

$$+ 2\sum_{\alpha} (L11_{\alpha})(H1)^2(L10_{\alpha}) + \sum_{\alpha} (L12_{\alpha\alpha})(H1)^2(L2) \Big]$$

$$S7E = \sum_{\underset{\sim}{n}} \sum_{\substack{\underset{\sim}{n_1}\,\underset{\sim}{n_2} \\ \underset{\sim}{n_3}}} \Big[2\sum_{\alpha} (L3_{\alpha})(N1_{\alpha})(H1)(L8) + \sum_{\alpha} (L1)(N1_{\alpha})^2(L8)$$

$$+ 4\sum_{\alpha,\beta} (L13_{\alpha\beta})(N1_{\alpha})(H1)(L10_{\beta}) + 2\sum_{\alpha\beta} (L9_{\beta})(N1_{\alpha})^2(L10_{\beta})$$

$$+ 4\sum_{\alpha\beta} (L14_{\beta\alpha})(N1_{\alpha})(H1)(L10_{\beta}) + 2\sum_{\alpha,\beta} (L11_{\beta})(N1_{\alpha})^2(L10_{\beta})$$

$$+ 2\sum_{\alpha,\beta} (L15_{\beta\beta\alpha})(N1_{\alpha})(H1)(L2) + \sum_{\alpha,\beta} (L12_{\beta\beta})(N1_{\alpha})^2(L2) \Big]$$

$$
\begin{aligned}
S7F = \sum_{\underset{\sim}{n}} \sum_{\substack{\underset{\sim}{n_1}\,\underset{\sim}{n_2} \\ \underset{\sim}{n_3}}} \Big[& 2\sum_{\alpha,\beta} (L7_{\alpha\beta})(N_{\alpha\beta})(H1)(L8) + 8\sum_{\alpha,\beta,\gamma} (L16_{\alpha\beta\gamma})(N_{\alpha\beta})(H1)(L10_{\gamma}) \\
& + 2\sum_{\alpha\beta\gamma} (L_{\alpha\gamma\beta\gamma})(N_{\alpha\beta})(H1)(L2) + 2\sum_{\alpha\beta} (L5_{\alpha})(N_{\alpha\beta})(N1_{\beta})(L8) \\
& + 8\sum_{\alpha\beta\gamma} (L17_{\alpha\gamma})(N_{\alpha\beta})(N1_{\beta})(L10_{\gamma}) + 2\sum_{\alpha\beta\gamma} (L18_{\gamma\gamma\alpha})(N_{\alpha\beta})(N1_{\beta})(L2) \\
& + 2\sum_{\alpha\beta} (L3_{\beta})(N_{\alpha\beta})(N2_{\alpha})(L8) + 8\sum_{\alpha\beta\gamma} (L13_{\beta\gamma})(N_{\alpha\beta})(N2_{\alpha})(L10_{\gamma}) \\
& + 2\sum_{\alpha\beta\gamma} (L15_{\gamma\gamma\beta})(N_{\alpha\beta})(N2_{\alpha})(L2) + \sum_{\alpha\beta} (L1)(N_{\alpha\beta})^2(L8) \\
& + 4\sum_{\alpha\beta\gamma} (L9_{\gamma})(N_{\alpha\beta})^2(L10_{\gamma}) + \sum_{\alpha\beta\gamma} (L12_{\gamma\gamma})(N_{\alpha\beta})^2(L2) \\
& + 2\sum_{\alpha\beta} (L6_{\alpha\beta})(N1_{\beta})(N2_{\alpha})(L8) + 8\sum_{\alpha\beta\gamma} (L16_{\alpha\beta\gamma})(N1_{\gamma})(N2_{\alpha})(L10_{\beta}) \\
& + 2\sum_{\alpha\beta\gamma} (L_{\alpha\gamma\beta\gamma})(N1_{\beta})(N2_{\alpha})(L2) \Big]
\end{aligned}
$$

$$
S7G = \sum_{\underset{\sim}{n}} \sum_{\substack{\underset{\sim}{n_1}\,\underset{\sim}{n_2} \\ \underset{\sim}{n_3}}} \Big[\sum_{\alpha} (L12_{\alpha\alpha})(H1)^2(L8) + 2\sum_{\alpha\beta} (L12_{\alpha\beta})(H1)^2(L19_{\alpha\beta}) \Big]
$$

$$
\begin{aligned}
S7H = \sum_{\underset{\sim}{n}} \sum_{\substack{\underset{\sim}{n_1}\,\underset{\sim}{n_2} \\ \underset{\sim}{n_3}}} \Big[& 2\sum_{\alpha\beta} (L15_{\beta\beta\alpha})(N1_{\alpha})(H1)(L8) + 4\sum_{\alpha\beta\gamma} (L15_{\beta\alpha\gamma})(N1_{\alpha})(H1)(L19_{\beta\gamma}) \\
& + \sum_{\alpha,\beta} (L12_{\beta\beta})(N1_{\alpha})^2(L8) + 2\sum_{\alpha\beta\gamma} (L12_{\beta\gamma})(N1_{\alpha})^2(L19_{\beta\gamma}) \Big]
\end{aligned}
$$

$$S7I=\sum_{\underset{\sim}{n}}\sum_{\substack{\underset{\sim}{n_1}\underset{\sim}{n_2}\\ \underset{\sim}{n_3}}}\Big[\sum_{\alpha\beta\gamma}(L_{\alpha\gamma\beta\gamma})(N_{\alpha\beta})(H1)(L8)+4\sum_{\alpha\beta\gamma}(L18_{\gamma\gamma\alpha})$$

$$\times(N_{\alpha\beta})(N1_{\beta})(L8)+2\sum_{\alpha\beta\gamma}(L_{\alpha\gamma\beta\gamma})(N2_{\alpha})(N1_{\beta})(L8)$$

$$+4\sum_{\alpha\beta\gamma\delta}(L_{\alpha\gamma\beta\delta})(N_{\alpha\beta})(H1)(L19_{\gamma\delta})$$

$$+8\sum_{\substack{\alpha\beta\\ \gamma\delta}}(L18_{\delta\alpha\gamma})(N_{\alpha\beta})(N1_{\beta})(L19_{\gamma\delta})+4\sum_{\substack{\alpha\beta\\ \gamma\delta}}(L_{\alpha\gamma\beta\delta})(N2_{\alpha})(N1_{\beta})(L19_{\gamma\delta})$$

$$+\sum_{\alpha\beta\gamma}(L12_{\gamma\gamma})(N_{\alpha\beta})^2(L8)+2\sum_{\substack{\alpha\beta\\ \gamma\delta}}(L12_{\gamma\delta})(N_{\alpha\beta})^2(L19_{\gamma\delta})\Big]$$

In S8A,...,S8I there is a triple summation over nearest neighbours $\underset{\sim}{n}_1, \underset{\sim}{n}_2, \underset{\sim}{n}_3$, and a double summation over general lattice vectors $\underset{\sim}{m}_1$ and $\underset{\sim}{m}_2$. We introduce the following definitions:

$$W=\cos\underset{\sim}{q}\cdot(\underset{\sim}{m}_1-\underset{\sim}{m}_2)-\cos\underset{\sim}{q}\cdot(\underset{\sim}{m}_1-\underset{\sim}{m}_2+\underset{\sim}{n}_2)-\cos\underset{\sim}{q}\cdot(\underset{\sim}{m}_1-\underset{\sim}{m}_2-\underset{\sim}{n}_1)$$
$$+\cos\underset{\sim}{q}\cdot(\underset{\sim}{m}_1-\underset{\sim}{m}_2-\underset{\sim}{n}_1+\underset{\sim}{n}_2)$$

$$X=\cos\underset{\sim}{q}\cdot\underset{\sim}{m}_2-\cos\underset{\sim}{q}\cdot(\underset{\sim}{m}_2+\underset{\sim}{n}_3)-\cos\underset{\sim}{q}\cdot(\underset{\sim}{m}_2-\underset{\sim}{n}_2)+\cos\underset{\sim}{q}\cdot(\underset{\sim}{m}_2-\underset{\sim}{n}_2+\underset{\sim}{n}_3)$$

$$Y=\cos\underset{\sim}{q}\cdot\underset{\sim}{m}_1-\cos\underset{\sim}{q}\cdot(\underset{\sim}{m}_1+\underset{\sim}{n}_3)-\cos\underset{\sim}{q}\cdot(\underset{\sim}{m}_1-\underset{\sim}{n}_1)+\cos\underset{\sim}{q}\cdot(\underset{\sim}{m}_1-\underset{\sim}{n}_1+\underset{\sim}{n}_3)$$

$$W1=\frac{1}{N}\sum_{\lambda}\frac{W}{\gamma^2}(\underset{\sim}{n}_1\cdot\underset{\sim}{e})(\underset{\sim}{n}_2\cdot\underset{\sim}{e})\ ;\ X1=\frac{1}{N}\sum_{\lambda}\frac{X}{\gamma^2}(\underset{\sim}{n}_1\cdot\underset{\sim}{e})(\underset{\sim}{n}_2\cdot\underset{\sim}{e})$$

$$W2=\frac{1}{N}\sum_{\lambda}\frac{W}{\gamma^2}(\underset{\sim}{n}_1\cdot\underset{\sim}{e})(\underset{\sim}{n}_3\cdot\underset{\sim}{e})\ ;\ X2=\frac{1}{N}\sum_{\lambda}\frac{X}{\gamma^2}(\underset{\sim}{n}_1\cdot\underset{\sim}{e})(\underset{\sim}{n}_3\cdot\underset{\sim}{e})$$

$$W3=\frac{1}{N}\sum_{\lambda}\frac{W}{\gamma^2}(\underset{\sim}{n}_2\cdot\underset{\sim}{e})(\underset{\sim}{n}_3\cdot\underset{\sim}{e})\ ;\ X3=\frac{1}{N}\sum_{\lambda}\frac{X}{\gamma^2}(\underset{\sim}{n}_2\cdot\underset{\sim}{e})(\underset{\sim}{n}_3\cdot\underset{\sim}{e})$$

$$Y1 = \frac{1}{N}\sum_{\lambda} \frac{Y}{\gamma^2} (\mathbf{n}_1\cdot\mathbf{e})(\mathbf{n}_2\cdot\mathbf{e}) \quad ; \quad W4_\alpha = \frac{1}{N}\sum_{\lambda} \frac{W}{\gamma^2} (\mathbf{n}_1\cdot\mathbf{e})\, e_\alpha$$

$$Y2 = \frac{1}{N}\sum_{\lambda} \frac{Y}{\gamma^2} (\mathbf{n}_1\cdot\mathbf{e})(\mathbf{n}_3\cdot\mathbf{e}) \quad ; \quad W5_\alpha = \frac{1}{N}\sum_{\lambda} \frac{W}{\gamma^2} (\mathbf{n}_2\cdot\mathbf{e})\, e_\alpha$$

$$Y3 = \frac{1}{N}\sum_{\lambda} \frac{Y}{\gamma^2} (\mathbf{n}_2\cdot\mathbf{e})(\mathbf{n}_3\cdot\mathbf{e}) \quad ; \quad W6_\alpha = \frac{1}{N}\sum_{\lambda} \frac{W}{\gamma^2} (\mathbf{n}_3\cdot\mathbf{e})\, e_\alpha$$

$$X4_\alpha = \frac{1}{N}\sum_{\lambda} \frac{X}{\gamma^2} (\mathbf{n}_1\cdot\mathbf{e})\, e_\alpha \quad ; \quad Y4_\alpha = \frac{1}{N}\sum_{\lambda} \frac{Y}{\gamma^2} (\mathbf{n}_1\cdot\mathbf{e})\, e_\alpha$$

$$X5_\alpha = \frac{1}{N}\sum_{\lambda} \frac{X}{\gamma^2} (\mathbf{n}_2\cdot\mathbf{e})\, e_\alpha \quad ; \quad Y5_\alpha = \frac{1}{N}\sum_{\lambda} \frac{Y}{\gamma^2} (\mathbf{n}_2\cdot\mathbf{e})\, e_\alpha$$

$$X6_\alpha = \frac{1}{N}\sum_{\lambda} \frac{X}{\gamma^2} (\mathbf{n}_3\cdot\mathbf{e})\, e_\alpha \quad ; \quad Y6_\alpha = \frac{1}{N}\sum_{\lambda} \frac{Y}{\gamma^2} (\mathbf{n}_3\cdot\mathbf{e})\, e_\alpha$$

$$W_{\alpha\beta} = \frac{1}{N}\sum_{\lambda} \frac{W}{\gamma^2}\, e_\alpha e_\beta \quad ;$$

$$X_{\alpha\beta} = \frac{1}{N}\sum_{\lambda} \frac{X}{\gamma^2}\, e_\alpha e_\beta \quad ;$$

$$Y_{\alpha\beta} = \frac{1}{N}\sum_{\lambda} \frac{Y}{\gamma^2}\, e_\alpha e_\beta \quad ;$$

Using the above we get

$$S8A = \sum_{\mathbf{m}_1,\mathbf{m}_2} \sum_{\substack{\mathbf{n}_1\mathbf{n}_2\\ \mathbf{n}_3}} (W1)^2 (X3)(Y2)^2$$

$$S8B = \sum_{\mathbf{m}_1\mathbf{m}_2} \sum_{\substack{\mathbf{n}_1\mathbf{n}_2\\ \mathbf{n}_3}} \left[(W1)^2 (X3) \sum_{\alpha} (Y4_\alpha)^2 + 2(W1)^2 (Y2) \sum_{\alpha} (X5_\alpha)(Y4_\alpha) \right]$$

$$S8C = \sum_{\mathbf{m}_1\mathbf{m}_2} \sum_{\substack{\mathbf{n}_1\mathbf{n}_2\\ \mathbf{n}_3}} \Big[4(W1)(Y2) \sum_{\alpha,\beta} (W4_\alpha)(X_{\alpha\beta})(Y4_\beta)$$

$$+ 2(W1) \sum_{\alpha,\beta} (W4_\alpha)(X6_\alpha)(Y4_\beta)^2 + 2(Y2) \sum_{\alpha,\beta} (W4_\alpha)^2 (X5_\beta)(Y4_\beta)$$

$$+ (X3)\Big\{\sum_{\alpha}(W4_\alpha)^2\Big\}\Big\{\sum_{\alpha}(Y4_\alpha)^2\Big\} \Big]$$

$$S8D = \sum_{\underset{\sim}{m_1}\,\underset{\sim}{m_2}} \sum_{\substack{\underset{\sim}{n_1}\,\underset{\sim}{n_2}\\ \underset{\sim}{n_3}}} \Big[2(W1)^2(X3)\sum_{\alpha}(Y6_\alpha)^2 + 4(W1)(X3)(Y2)$$

$$\times \sum_{\alpha}(W5_\alpha)(Y6_\alpha) \Big]$$

$$S8E = \sum_{\underset{\sim}{m_1}\,\underset{\sim}{m_2}} \sum_{\substack{\underset{\sim}{n_1}\,\underset{\sim}{n_2}\\ \underset{\sim}{n_3}}} \Big[(W1)^2(X3)\sum_{\alpha,\beta}(Y_{\alpha\beta})^2 + (X3)\sum_{\alpha,\beta}(W5_\alpha)^2(Y4_\beta)^2$$

$$+ 4(W1)(X3)\sum_{\alpha,\beta}(W5_\alpha)(Y_{\alpha\beta})(Y4_\beta) + 2(W1)^2\sum_{\alpha\beta}(X5_\beta)(Y_{\alpha\beta})(Y6_\alpha)$$

$$+ 2\Big\{\sum_{\alpha}(W5_\alpha)^2\Big\}\Big\{\sum_{\alpha}(X5_\alpha)(Y4_\alpha)\Big\}(Y2) + 4(W1)(Y2)$$

$$\times \sum_{\alpha,\beta}(W5_\alpha)(X5_\beta)(Y_{\alpha\beta}) + 4(W1)\Big\{\sum_{\alpha}(W5_\alpha)(Y6_\alpha)\Big\}\Big\{\sum_{\alpha}(X5_\alpha)(Y4_\alpha)\Big\}\Big]$$

$$S8F = \sum_{\underset{\sim}{m_1}\,\underset{\sim}{m_2}} \sum_{\substack{\underset{\sim}{n_1}\,\underset{\sim}{n_2}\\ \underset{\sim}{n_3}}} \Big[2\Big\{\sum_{\alpha}(W4_\alpha)^2\Big\}(X3)\Big\{\sum_{\alpha,\beta}(Y_{\alpha\beta})^2\Big\}$$

$$+ 4\Big\{\sum_{\alpha}(W4_\alpha)^2\Big\}\sum_{\alpha\beta}(X5_\beta)(Y_{\alpha\beta})(Y6_\alpha) + 4(W1)\Big\{\sum_{\alpha}(W4_\alpha)(X6_\alpha)\Big\}$$

$$\times \sum_{\alpha,\beta}(Y_{\alpha\beta})^2 + 8\sum_{\alpha,\beta,\gamma}(W4_\beta)(W1)(X_{\beta\gamma})(Y_{\alpha\gamma})(Y6_\alpha)$$

$$+ 4\sum_{\alpha,\beta,\gamma}(W4_\beta)(W_{\alpha\beta})(X5_\gamma)(Y_{\alpha\gamma})(Y2) + 4\sum_{\alpha\beta\gamma}(W4_\beta)(W_{\alpha\beta})(X3)(Y_{\alpha\gamma})(Y4_\gamma)$$

$$+ 4\sum_{\alpha,\beta,\gamma}(W4_\beta)(W_{\alpha\beta})(X5_\gamma)(Y6_\alpha)(Y4_\gamma) + 4\sum_{\alpha\beta\gamma}(W1)(W_{\alpha\beta})(X_{\beta\gamma})(Y_{\alpha\gamma})(Y2)$$

$$+ 4(W1)\sum_{\alpha\beta\gamma}(W_{\alpha\beta})(X6_\beta)(Y_{\alpha\gamma})(Y4_\gamma) + 4(W1)\sum_{\alpha\beta\gamma}(W_{\alpha\beta})(X_{\beta\gamma})(Y6_\alpha)(Y4_\gamma)$$

$$+ 4\sum_{\alpha\beta\gamma}(W4_\beta)(W5_\alpha)(X_{\beta\gamma})(Y_{\alpha\gamma})(Y2) + 4\sum_{\alpha\beta\gamma}(W4_\beta)(W5_\alpha)(X6_\beta)(Y_{\alpha\gamma})(Y4_\gamma)$$

$$+ 4\sum_{\alpha\beta\gamma}(W4_\beta)(W5_\alpha)(X_{\beta\gamma})(Y6_\alpha)(Y4_\gamma) \Big]$$

$$S8G = \sum_{\underset{\sim}{m_1}\,\underset{\sim}{m_2}} \sum_{\substack{\underset{\sim}{n_1}\,\underset{\sim}{n_2}\\ \underset{\sim}{n_3}}} \Big[(X3)\Big\{\sum_{\alpha} (W5_\alpha)^2\Big\}\Big\{\sum_{\alpha} (Y6_\alpha)^2\Big\} + 2(X3)\Big\{\sum_{\alpha} (W5_\alpha)(Y6_\alpha)\Big\}^2 \Big]$$

$$\begin{aligned} S8H = \sum_{\underset{\sim}{m_1}\,\underset{\sim}{m_2}} \sum_{\substack{\underset{\sim}{n_1}\,\underset{\sim}{n_2}\\ \underset{\sim}{n_3}}} \Big[& (X3)\Big\{\sum_{\alpha} (W5_\alpha)^2\Big\}\Big\{\sum_{\alpha,\beta} (Y_{\alpha\beta})^2\Big\} \\ & + 2\Big\{\sum_{\alpha} (W5_\alpha)^2\Big\}\Big\{\sum_{\alpha\beta} (X5_\alpha)(Y_{\alpha\beta})(Y6_\beta)\Big\} + 2\sum_{\alpha\beta\gamma} (W5_\alpha)(W5_\beta) \\ & \times (X3)(Y_{\alpha\gamma})(Y_{\beta\gamma}) + 4\Big\{\sum_{\alpha\beta} (W5_\alpha)(X5_\beta)(Y_{\alpha\beta})\Big\} \\ & \times \Big\{\sum_{\alpha} (W5_\alpha)(Y6_\alpha)\Big\} \Big] \end{aligned}$$

$$\begin{aligned} S8I = \sum_{\underset{\sim}{m_1}\,\underset{\sim}{m_2}} \sum_{\substack{\underset{\sim}{n_1}\,\underset{\sim}{n_2}\\ \underset{\sim}{n_3}}} \Big[& (X3)\Big\{\sum_{\alpha\beta} (W_{\alpha\beta})^2\Big\}\Big\{\sum_{\alpha\beta} (Y_{\alpha\beta})^2\Big\} \\ & + 4\Big\{\sum_{\alpha\beta} (W_{\alpha\beta})^2\Big\}\Big\{\sum_{\alpha\beta} (X5_\beta)(Y_{\alpha\beta})(Y6_\alpha)\Big\} + 4\sum_{\substack{\alpha\beta\\ \gamma\delta}} (W5_\alpha)(W_{\alpha\gamma})(X_{\gamma\delta})(Y_{\beta\delta})(Y6_\beta) \\ & + 2\sum_{\substack{\alpha\beta\\ \gamma\delta}} (W_{\alpha\gamma})(W_{\beta\gamma})(X3)(Y_{\alpha\delta})(Y_{\beta\delta}) + 4\sum_{\substack{\alpha\beta\\ \gamma\delta}} (W_{\alpha\gamma})(W_{\beta\gamma})(X5_\delta)(Y_{\alpha\delta})(Y6_\beta) \\ & + 4\sum_{\substack{\alpha\beta\\ \gamma\delta}} (W5_\alpha)(W_{\beta\gamma})(X_{\gamma\delta})(Y_{\alpha\delta})(Y6_\beta) + 4\sum_{\substack{\alpha\beta\\ \gamma\delta}} (W5_\alpha)(W_{\beta\gamma})(X6_\gamma)(Y_{\alpha\delta})(Y_{\beta\delta}) \\ & + 4\sum_{\substack{\alpha\beta\\ \gamma\delta}} (W5_\alpha)(W_{\beta\gamma})(X_{\gamma\delta})(Y6_\alpha)(Y_{\beta\delta}) \Big] \end{aligned}$$

APPENDIX G

First we define the following:

$$\langle A B C \ldots Z \rangle = \frac{\mathrm{Tr}\, e^{-\beta H_0} A B C \ldots Z}{\mathrm{Tr}\, e^{-\beta H_0}} = \frac{1}{Z_0} \mathrm{Tr}\, e^{-\beta H_0} A B C \ldots Z$$

for operators A,B,C,...Z. Then we can write (see(22))

$$\frac{Z_5}{Z_0} = \frac{\beta^2}{2!} \int_0^1 ds_1 \int_0^1 ds_2 \, \langle T \tilde{H}_4(s_1) \tilde{H}_4(s_2) \rangle$$

where the Dyson chronological operator T orders a set of operators from right to left in order of increasing argument and where

$$\tilde{H}_i(s) = e^{s\beta H_0} H_i \, e^{-s\beta H_0}$$

Substituting for H_4 from page 7 get

$$\frac{Z_5}{Z_0} = \frac{\beta^2}{2!} \sum_{\substack{\lambda_1\lambda_2 \\ \lambda_3\lambda_4}} \sum_{\substack{\lambda_5\lambda_6 \\ \lambda_7\lambda_8}} V(\lambda_1\lambda_2\lambda_3\lambda_4) V(\lambda_5\lambda_6\lambda_7\lambda_8) \int_0^1 ds_1 \int_0^1 ds_2 \langle T \tilde{A}_{\lambda_1}(s_1) \ldots \tilde{A}_{\lambda_4}(s_1) \tilde{A}_{\lambda_5}(s_2) \ldots \tilde{A}_{\lambda_8}(s_2) \rangle$$

where $\quad \tilde{A}_{\lambda_i}(s) = e^{s\beta H_0} A_{\lambda_i} e^{-s\beta H_0}$

In the terminology of ref(22) the contribution to $\frac{Z_5}{Z_0}$ from unlinked clusters is

$$\left(\frac{Z_5}{Z_0}\right)_{\text{unlinked}} = \frac{\beta^2}{2!} \sum_{\substack{\lambda_1\lambda_2 \\ \lambda_3\lambda_4}} V(\lambda_1 -\lambda_1\, \lambda_2 -\lambda_2) V(\lambda_3 -\lambda_3\, \lambda_4 -\lambda_4) \int_0^1 ds_1 \int_0^1 ds_2$$

$$\times \; 9 \; \langle T \tilde{A}_{\lambda_1}(s_1) \tilde{A}_{-\lambda_1}(s_1) \rangle \langle T \tilde{A}_{\lambda_2}(s_1) \tilde{A}_{-\lambda_2}(s_1) \rangle \langle T \tilde{A}_{\lambda_3}(s_2) \tilde{A}_{-\lambda_3}(s_2) \rangle \langle T \tilde{A}_{\lambda_4}(s_2) \tilde{A}_{-\lambda_4}(s_2) \rangle$$

where the factor 9 arises when we interchange indices and combine terms.

$$\left(\frac{Z_5}{Z_0}\right)_{unlinked} = \frac{1}{2}\left\{-\beta\sum_{\lambda_1\lambda_2} V(\lambda_1 -\lambda_1\, \lambda_2 -\lambda_2)\int_0^1 ds_1\,(3)\langle T\tilde{A}_{\lambda_1}(s_1)\tilde{A}_{-\lambda_1}(s_1)\rangle\langle T\tilde{A}_{\lambda_2}(s_1)A_{-\lambda_2}(s_1)\rangle\right\}^2$$

But

$$\frac{Z_1}{Z_0} = -\beta\int_0^1 ds_1\ \langle T\tilde{H}_4(s_1)\rangle = -\beta\sum_{\substack{\lambda_1\lambda_2\\ \lambda_3\lambda_4}} V(\lambda_1\lambda_2\lambda_3\lambda_4)\int_0^1 ds_1\,\langle T\tilde{A}_{\lambda_1}(s_1)\tilde{A}_{\lambda_2}(s_1)\tilde{A}_{\lambda_3}(s_1)\tilde{A}_{\lambda_4}(s_1)\rangle$$

Again from ref(22)

$$\frac{Z_1}{Z_0} = -\beta\sum_{\lambda_1\lambda_2} V(\lambda_1 -\lambda_1\, \lambda_2 -\lambda_2)\int_0^1 ds_1\,(3)\langle T\tilde{A}_{\lambda_1}(s_1)\tilde{A}_{-\lambda_1}(s_1)\rangle\langle T\tilde{A}_{\lambda_2}(s_1)\tilde{A}_{-\lambda_2}(s_1)\rangle$$

Thus we have

$$\left(\frac{Z_5}{Z_0}\right)_{unlinked} = \frac{1}{2}\left(\frac{Z_1}{Z_0}\right)^2$$

Consider now

$$\frac{Z_{10}}{Z_0} = \frac{\beta^4}{4!}\int_0^1 ds_1\int_0^1 ds_2\int_0^1 ds_3\int_0^1 ds_4\ \langle T H_3(s_1)H_3(s_2)H_3(s_3)H_3(s_4)\rangle$$

As above we can expand the integrand and interchange summation indices, getting the unlinked contribution

$$\left(\frac{Z_{10}}{Z_0}\right)_{unlinked} = \frac{\beta^4}{4!}\sum_{\lambda_1\lambda_2\lambda_3}\sum_{\lambda_4\lambda_5\lambda_6}\int_0^1 ds_1\int_0^1 ds_2\int_0^1 ds_3\int_0^1 ds_4\quad V(\lambda_1\lambda_2\lambda_3)V(-\lambda_1 -\lambda_2 -\lambda_3)V(\lambda_4\lambda_5\lambda_6)$$

$$\times V(-\lambda_4 -\lambda_5 -\lambda_6)\times(108)\langle T\tilde{A}_{\lambda_1}(s_1)\tilde{A}_{-\lambda_1}(s_2)\rangle\langle T\tilde{A}_{\lambda_2}(s_1)\tilde{A}_{-\lambda_2}(s_2)\rangle\langle T\tilde{A}_{\lambda_3}(s_1)\tilde{A}_{-\lambda_3}(s_2)\rangle$$

$$\times\ \langle T\tilde{A}_{\lambda_4}(s_3)\tilde{A}_{-\lambda_4}(s_4)\rangle\langle T\tilde{A}_{\lambda_5}(s_3)\tilde{A}_{-\lambda_5}(s_4)\rangle\langle T\tilde{A}_{\lambda_6}(s_3)\tilde{A}_{-\lambda_6}(s_4)\rangle$$

i.e.
$$\left(\frac{Z_{10}}{Z_0}\right)_{unlinked} = \frac{1}{2}\left\{\frac{\beta^2}{2!}\sum_{\lambda_1\lambda_2\lambda_3} V(\lambda_1\lambda_2\lambda_3)V(-\lambda_1-\lambda_2-\lambda_3)\int_0^1 ds_1\int_0^1 ds_2\,(6) \times\langle T\widetilde{A}_{\lambda_1}(s_1)\widetilde{A}_{-\lambda_1}(s_2)\rangle\langle T\widetilde{A}_{\lambda_2}(s_1)\widetilde{A}_{-\lambda_2}(s_2)\rangle\langle T\widetilde{A}_{\lambda_3}(s_1)A_{-\lambda_3}(s_2)\rangle\right\}^2$$

But

$$\frac{Z_2}{Z_0} = \frac{\beta^2}{2!}\int_0^1 ds_1\int_0^1 ds_2\,\langle T\widetilde{H}_3(s_1)\widetilde{H}_3(s_2)\rangle$$

$$= \frac{\beta^2}{2!}\sum_{\lambda_1\lambda_2\lambda_3}\sum_{\lambda_4\lambda_5\lambda_6} V(\lambda_1\lambda_2\lambda_3)V(\lambda_4\lambda_5\lambda_6)\int_0^1 ds_1\int_0^1 ds_2\langle T\widetilde{A}_{\lambda_1}(s_1)\widetilde{A}_{\lambda_2}(s_1)\widetilde{A}_{\lambda_3}(s_1)$$
$$\times\widetilde{A}_{\lambda_4}(s_2)\widetilde{A}_{\lambda_5}(s_2)\widetilde{A}_{\lambda_6}(s_2)\rangle$$

$$= \frac{\beta^2}{2!}\sum_{\lambda_1\lambda_2\lambda_3} V(\lambda_1\lambda_2\lambda_3)V(-\lambda_1-\lambda_2-\lambda_3)\int_0^1 ds_1\int_0^1 ds_2\,(6)\,\langle T\widetilde{A}_{\lambda_1}(s_1)\widetilde{A}_{-\lambda_1}(s_2)\rangle$$
$$\times\langle T\widetilde{A}_{\lambda_2}(s_1)\widetilde{A}_{-\lambda_2}(s_2)\rangle\langle T\widetilde{A}_{\lambda_3}(s_1)\widetilde{A}_{-\lambda_3}(s_2)\rangle$$

Thus

$$\left(\frac{Z_{10}}{Z_0}\right)_{unlinked} = \frac{1}{2}\left(\frac{Z_2}{Z_0}\right)^2$$

Next consider

$$\left(\frac{Z_7}{Z_0}\right) = -\frac{\beta^3}{3!}\int_0^1 ds_1\int_0^1 ds_2\int_0^1 ds_3\,\langle T\widetilde{H}_3(s_1)\widetilde{H}_3(s_2)\widetilde{H}_4(s_3)\rangle$$

$$= -\frac{\beta^3}{3!}\sum_{\lambda_1\lambda_2\lambda_3}\sum_{\lambda_4\lambda_5\lambda_6}\sum_{\substack{\lambda_7\lambda_8\\ \lambda_9\lambda_{10}}} V(\lambda_1\lambda_2\lambda_3)V(\lambda_4\lambda_5\lambda_6)V(\lambda_7\lambda_8\lambda_9\lambda_{10})$$
$$\times\int_0^1 ds_1\int_0^1 ds_2\int_0^1 ds_3\,\langle T\widetilde{A}_{\lambda_1}(s_1)\widetilde{A}_{\lambda_2}(s_1)\widetilde{A}_{\lambda_3}(s_1)\widetilde{A}_{\lambda_4}(s_2)\widetilde{A}_{\lambda_5}(s_2)\widetilde{A}_{\lambda_6}(s_2)$$
$$\times\widetilde{A}_{\lambda_7}(s_3)\ldots\widetilde{A}_{\lambda_{10}}(s_3)\rangle$$

$$\left(\frac{Z_7}{Z_0}\right)_{unlinked} = -\frac{\beta^3}{3!}\sum_{\lambda_1\lambda_2\lambda_3}\sum_{\lambda_4\lambda_5} V(\lambda_1\lambda_2\lambda_3)\,V(-\lambda_1-\lambda_2-\lambda_3)\,V(\lambda_4-\lambda_4\lambda_5-\lambda_5)$$

$$\times\int_0^1 ds_1\int_0^1 ds_2\int_0^1 ds_3\,(18)\langle T\tilde{A}_{\lambda_1}(s_1)\tilde{A}_{-\lambda_1}(s_2)\rangle\langle T\tilde{A}_{\lambda_2}(s_1)\tilde{A}_{-\lambda_2}(s_2)\rangle$$

$$\times\langle T\tilde{A}_{\lambda_3}(s_1)\tilde{A}_{-\lambda_3}(s_2)\rangle\,\langle T\tilde{A}_{\lambda_4}(s_3)\tilde{A}_{-\lambda_4}(s_3)\rangle\langle T\tilde{A}_{\lambda_5}(s_3)\tilde{A}_{-\lambda_5}(s_3)\rangle$$

$$= \frac{1}{3}\left\{\frac{\beta^2}{2!}\sum_{\lambda_1\lambda_2\lambda_3} V(\lambda_1\lambda_2\lambda_3)\,V(-\lambda_1-\lambda_2-\lambda_3)\int_0^1 ds_1\int_0^1 ds_2\,(6)\,\langle T\tilde{A}_{\lambda_1}(s_1)\tilde{A}_{-\lambda_1}(s_2)\rangle\right.$$

$$\left.\times\langle T\tilde{A}_{\lambda_2}(s_1)\tilde{A}_{-\lambda_2}(s_2)\rangle\langle T\tilde{A}_{\lambda_3}(s_1)\tilde{A}_{-\lambda_3}(s_2)\rangle\right\}$$

$$\times\left\{-\beta\sum_{\lambda_1\lambda_2}\int_0^1 ds_1\quad V(\lambda_1-\lambda_1\,\lambda_2-\lambda_2)\,(3)\,\langle T\tilde{A}_{\lambda_1}(s_1)\tilde{A}_{-\lambda_1}(s_1)\rangle\langle T\tilde{A}_{\lambda_2}(s_1)\tilde{A}_{-\lambda_2}(s_1)\rangle\right\}$$

$$= \frac{1}{3}\left(\frac{Z_1}{Z_0}\right)\left(\frac{Z_2}{Z_0}\right)$$

But

$$\left(\frac{Z_7}{Z_0}\right)_{unlinked} = \left(\frac{Z_8}{Z_0}\right)_{unlinked} = \left(\frac{Z_9}{Z_0}\right)_{unlinked}$$

$$\therefore\left(\frac{Z_7}{Z_0}+\frac{Z_8}{Z_0}+\frac{Z_9}{Z_0}\right)_{unlinked} = \left(\frac{Z_1}{Z_0}\right)\left(\frac{Z_2}{Z_0}\right)$$

and the total free energy is

$$F = F_{linked} + F_{unlinked} + \frac{1}{2\beta}\lambda^4\left(\frac{Z_1}{Z_0}+\frac{Z_2}{Z_0}\right)^2$$

$$= F_{linked} - \frac{1}{\beta}\left[\frac{Z_5}{Z_0}+\frac{Z_7}{Z_0}+\frac{Z_8}{Z_0}+\frac{Z_9}{Z_0}+\frac{Z_0}{Z_0}\right]_{unlinked} + \frac{1}{\beta}\,\frac{1}{2}\left(\frac{Z_1}{Z_0}+\frac{Z_2}{Z_0}\right)^2$$

$$= F_{linked}$$

where F_{linked} denotes the contribution to F from "linked clusters" only.

APPENDIX H

In Equations(24) we have defined

$$Z' = \frac{e^{-\beta(E_m - E_n)} - 1}{\beta(E_m - E_n)}$$

We now define the quantity

$$T = \beta \sum_{m,n} e^{-\beta E_n} \frac{1}{E_m - E_n} \langle n|H_\alpha|m\rangle\langle m|H_\beta|n\rangle Z'$$

$$= T_m - T_n$$

where $T_i = \sum_{m,n} \frac{\langle n|H_\alpha|m\rangle\langle m|H_\beta|n\rangle}{(E_m - E_n)^2} e^{-\beta E_i}$

Interchanging the labels m and n and using the fact that $\langle m|H_\alpha|n\rangle = (-1)^\alpha \langle n|H_\alpha|m\rangle$ (see APPENDIX D), we get

$$T_n = \sum_{m,n} \langle n|H_\alpha|m\rangle\langle m|H_\beta|n\rangle \frac{1}{(E_m - E_n)^2} e^{-\beta E_n}$$

$$= \sum_{m,n} \langle n|H_\alpha|m\rangle\langle m|H_\beta|n\rangle \frac{1}{(E_m - E_n)^2} e^{-\beta E_m} = T_m$$

if $\alpha+\beta$ is an even integer. Hence Z' makes no contribution to Z_2, Z_4, Z_5, or Z_6. Consider now Z'' where

$$Z'' = \frac{e^{-\beta(E_m - E_n)} - 1}{\beta(E_m - E_n)} - \frac{[e^{\beta(E_n - E_p)} - 1](E_m - E_n)}{\beta(E_m - E_p)(E_n - E_p)} - \frac{e^{\beta(E_n - E_m)} - 1}{\beta(E_m - E_p)}$$

Writing $\langle m|H_\alpha|n\rangle = (H_\alpha)_{mn}$ the contribution of Z'' to Z_7 is T_7 where

$$T_7 = -\sum_{n,m,p} (H_3)_{nm}(H_3)_{mp}(H_4)_{pn} \Big[\frac{e^{-\beta E_m} - e^{-\beta E_n}}{E_{pn} E_{mn}^2} + \frac{e^{-\beta E_p} - e^{-\beta E_n}}{E_{mp} E_{pn}^2}$$

$$- \frac{e^{-\beta E_m} - e^{-\beta E_n}}{E_{pn} E_{mn} E_{mp}} \Big]$$

where $E_{mn} = E_m - E_n$, etc.

The contribution to Z_8 is

$$T_8 = -\sum_{n,m,p} (H_3)_{nm}(H_4)_{mp}(H_3)_{pn}\left[\frac{e^{-\beta E_m}-e^{-\beta E_n}}{E_{pn}E_{mn}^2}+\frac{e^{-\beta E_p}-e^{-\beta E_n}}{E_{mp}E_{pn}^2}-\frac{e^{-\beta E_m}-e^{-\beta E_n}}{E_{pn}E_{mn}E_{mp}}\right]$$

$$= -\sum_{n,m,p} (H_3)_{nm}(H_3)_{mp}(H_4)_{pn}\left[\frac{e^{-\beta E_n}-e^{-\beta E_m}}{E_{pm}E_{mn}^2}+\frac{e^{-\beta E_p}-e^{-\beta E_m}}{E_{np}E_{pm}^2}-\frac{e^{-\beta E_n}-e^{-\beta E_m}}{E_{pm}E_{nm}E_{np}}\right]$$

where in the last step the labels m and n have been interchanged and we have used $(H_\alpha)_{mn}=(-1)^\alpha(H_\alpha)_{nm}$. In a similar way the contribution to Z_9 becomes

$$T_9 = -\sum_{n,m,p} (H_3)_{nm}(H_3)_{mp}(H_4)_{pn}\left[\frac{e^{-\beta E_p}-e^{-\beta E_n}}{E_{mn}E_{pn}^2}+\frac{e^{-\beta E_m}-e^{-\beta E_n}}{E_{pm}E_{mn}^2}-\frac{e^{-\beta E_p}-e^{-\beta E_n}}{E_{mn}E_{pn}E_{pm}}\right]$$

The sum of these three contributions is

$$T_7+T_8+T_9 = -\sum_{n,m,p} (H_3)_{nm}(H_3)_{mp}(H_4)_{pn}\left[\frac{e^{-\beta E_m}-e^{-\beta E_n}}{E_{pn}E_{mn}^2}+\frac{e^{-\beta E_p}-e^{-\beta E_m}}{E_{np}E_{pm}^2}\right.$$
$$\left.+\frac{e^{-\beta E_p}-e^{-\beta E_n}}{E_{mp}E_{pn}^2}+\frac{e^{-\beta E_p}-e^{-\beta E_n}}{E_{mn}E_{pn}^2}-\frac{e^{-\beta E_m}-e^{-\beta E_n}}{E_{pn}E_{mn}E_{mp}}-\frac{e^{-\beta E_n}-e^{-\beta E_m}}{E_{pm}E_{nm}E_{np}}-\frac{e^{-\beta E_p}-e^{-\beta E_n}}{E_{mn}E_{pn}E_{pm}}\right]$$

The first and second <u>and</u> third and fourth terms cancel one another if we make use of the label interchange $p \rightleftharpoons n$. Hence we get from the last three

$$T_7+T_8+T_9 = \sum_{n,m,p} (H_3)_{nm}(H_3)_{mp}(H_4)_{pn}\frac{1}{E_{pn}E_{mn}E_{mp}}\left[(e^{-\beta E_m}-e^{-\beta E_n})+(e^{-\beta E_m}-e^{-\beta E_p})\right]$$

Again using the interchange $n \rightleftharpoons p$ we get finally

$$T_7+T_8+T_9=0$$

Finally consider Z'''. Using the expressions given in Eqs(24) we find that the contribution to Z_{10} from Z''' is Z'''_{10} where

$$Z'''_{10} = T_1 - T_2 + T_3 - T_4 + T_5 - T_6$$

$$T_i = \sum_{n,m,p,q} C_{nmpq} S_i$$

$$C_{nmpq} = \langle n|H_3|m\rangle\langle m|H_3|p\rangle\langle p|H_3|q\rangle\langle q|H_3|n\rangle$$

$$S_1 = \frac{e^{-\beta E_m}}{E_{pn}E_{qn}E_{mn}^2} + \frac{e^{-\beta E_m}}{E_{qn}E_{pn}E_{mp}E_{nm}} + \frac{e^{-\beta E_m}}{E_{qn}E_{pq}E_{mq}E_{nm}} + \frac{e^{-\beta E_m}}{E_{qn}E_{pq}E_{mp}E_{mn}}$$

$$S_2 = \frac{e^{-\beta E_n}}{E_{pq}E_{mq}E_{nq}^2} + \frac{e^{-\beta E_n}}{E_{qn}E_{pq}E_{mq}E_{nm}} + \frac{e^{-\beta E_n}}{E_{qn}E_{mp}E_{np}E_{pq}} + \frac{e^{-\beta E_n}}{E_{qn}E_{pq}E_{mp}E_{mn}}$$

$$S_3 = \frac{e^{-\beta E_p}}{E_{mp}E_{qn}E_{np}^2} + \frac{e^{-\beta E_p}}{E_{qn}E_{mp}E_{np}E_{pq}}$$

$$S_4 = \frac{e^{-\beta E_n}}{E_{mp}E_{qn}E_{np}^2} + \frac{e^{-\beta E_n}}{E_{qn}E_{pn}E_{mp}E_{nm}}$$

$$S_5 = \frac{e^{-\beta E_n}}{E_{pn}E_{qn}E_{mn}^2}$$

$$S_6 = \frac{e^{-\beta E_q}}{E_{pq}E_{mq}E_{nq}^2}$$

The coefficients C_{nmpq} are invariant under cyclic permutations of the set of summation indices n,m,p,q i.e.

$$C_{nmpq} = C_{mpqn} = C_{pqnm} = C_{qnmp}$$

Hence, cyclically permuting the summation indices of T_2 in the following way: $n \to m, m \to p, p \to q, q \to n$ we easily get

$$T_2 = T_1$$

Also, applying the cyclic permutation $n \to p, m \to q, p \to n, q \to m$ to T_4 we get

$$T_4 = T_3$$

and applying the permutation $n \to q, m \to n, p \to m, q \to p$ to T_6 get

$$T_6 = T_5$$

Thus we get the final result

$$Z_{10}''' = 0$$

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