

AN ANHARMONIC CONTRIBUTION TO
THE HELMHOLTZ FREE ENERGY TO $O(\lambda^6)$

by

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ABSTRACT

The anharmonic contributions of order λ^6 to the Helmholtz free energy for a crystal in which every atom is on a site of inversion symmetry, have been evaluated. The corresponding diagrams in the various orders of the perturbation theory have been presented. The validity of the expressions given is for high temperatures. Numerical calculations for the diagrams which contribute to the free energy have been worked out for a nearest-neighbour central-force model of a face-centered cubic lattice in the high-temperature limit and in the leading term and the Ludwig approximations. The accuracy of the Ludwig approximation in evaluating the Brillouin-zone sums has been investigated. Expansion for all diagrams in the high-temperature limit has been carried out. The contribution to the specific heat involves a linear as well as cubic term. We have applied Lennard-Jones, Morse and Exponential 6 types of potentials. A comparison between the contribution to the free energy of order λ^6 to that of order λ^4 has been made.

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I. Introduction

The total potential energy of a crystal, which is a function of the atomic positions, can be expanded in powers of the displacements of the atoms from their equilibrium positions. Retaining the terms up to the quadratic (this is called the harmonic approximation) in the expansion, the motion of the atoms can be expressed as the vibration of independent harmonic oscillators, equal to the number of the degrees of freedom in the crystal. Each of these independent modes of vibration is characterized by a wave-vector \underline{k} , a polarization index j and a frequency $\omega(\underline{k}j)$.

Many properties of crystals cannot be described within the harmonic approximation. When the calculations are carried out, the crystal shows no thermal expansion and thermal conductivity. The specific heat at constant volume C_v becomes constant $3R$, at high temperatures but experimentally [1,2], C_v departs from $3R$ limit at high temperatures.

These properties can only be explained by the anharmonic theory which takes into account the terms higher than the quadratic in the expansion of the potential energy of a crystal.

Peierls [3] has discussed the anharmonic effect on the specific heat and has shown its deviation from the Dulong-Petit limit. He has also found that the thermal expansion is proportional to T^4 at low-temperatures and becomes linear in T at high-temperatures.

Van Hove [4] has introduced an ordering parameter, λ , equal in magnitude to a typical atomic displacement divided by the nearest neighbour distance. The lowest-order anharmonic contribution to the free energy are found to be of order λ^2 involving expressions which

consist of sums over three or less wave-vectors and a like number of polarization indices.

Ludwig [5] has given explicit expressions for the lowest-order contributions to the Helmholtz free energy in terms of sums over wave-vectors and polarizations for all temperatures. His calculations have involved the approximation of taking functions of the normal mode frequencies outside the summations and replacing them by some sort of averages.

Maradudin et al. [6] have calculated these contributions in the leading term approximation in which the highest ordered radial derivative of the interatomic potential is retained.

Klein et al. [7] have applied the lowest order perturbation theory to the calculation of the thermal properties of all rare gas solids except He. The agreement between the calculated and experimental values was good up to $T < \frac{1}{3} T_m$ (T_m is the melting temperature of a crystal). The contribution to the specific heat from λ^2 terms is found to be linear at high temperatures. Brooks [1] and Leadbetter [2] have experimentally found the presence of both linear and quadratic terms in the specific heat expression suggesting contributions from the anharmonic terms in higher orders.

The diagrammatic method has been applied in the calculation of the various thermodynamic properties of an anharmonic crystal. Van Hove [4] and Cowley [8] have applied it in calculating the lowest order terms of the anharmonic Helmholtz energy. Shukla and Cowley [9] have extended the calculations to the next higher order, λ^4 , of perturbation theory. They have shown that this order is responsible for the quadratic term in

the specific heat. Recently Wilk [10] and Aggrawal and Pathak [11] have analytically worked out the previous calculations using Ludwig's approximation(LA). It has been found that LA gives exact result for some simple sums, however most of the sums are underestimated by about 18% and the remaining sums are overestimated by about 20%.

Choquard [12] has introduced a new method called the self-consistent phonon theory. This method is based upon obtaining closed-form expressions for the free energies arising from different orders of perturbation theory (PT). The sum of the infinite series arising from the first order of PT is called the first order self-consistent field (SC1). All ring diagrams have been summed in this order. In the second order self-consistent equations (SC2), the first and second order contributions of PT are summed. The first calculation using SC1 theory has been done by Gillis et al. [13] on Ne. Goldman et al. [14] have carried out similar calculations for other rare gas crystals using SC1 theory and the cubic correction to the free energy missed out in the SC1 theory. This is called the improved self-consistent (ISC). Koehler [15] has carried out the calculation for another diagram which arises in SC2 theory from the quartic term. In the language of the PT, there are three other diagrams of this order [9] and it is unreasonable to add such diagram and neglect more important diagrams [9] in the same order.

An examination of the agreement between the ISC theory and the experiment appears to be poor beyond one-half of the melting temperature. It would be worth while going to the next higher order of PT, i.e. $O(\lambda^6)$, to give light to some other important diagrams to be included in the free energy calculations. It is the aim of the present thesis to study this point. All diagrams arising from this order, $O(\lambda^6)$, have been generated. Explicit expressions for the diagrams contributing to the

Helmholtz free energy have been worked out. The high-temperature expansions for these diagrams have been carried out. Numerical calculations have been performed for all the diagrams for a nearest-neighbour central force model of a face-centered-cubic lattice in the high-temperature limit and in the leading-term and the Ludwig approximation (LA). We have applied three different types of potentials: Lennard-Jones, Morse, and Buckingham (Exp. 6). A comparison between the contribution to the free energy of order λ^6 to that of order λ^4 has been made. We have been able to carry out the calculations for twenty-four out of the forty-three diagrams contributing to the free energy without using the LA and found that in LA most diagrams were underestimated by about 20%; one gave exact result and the rest were overestimated by about 37%.

In grouping the diagrams according to SC1, ISC and SC2, we have found that $F(\text{ISC})$ to $O(\lambda^6)$ did not agree with the final $F(\lambda^6)$ in contrast to the findings of Shukla and Cowley [9] which probably may be due to the inaccuracies in using LA to $O(\lambda^6)$. The plan of this thesis is as follows. The derivation of the anharmonic hamiltonian is presented in section (II), followed by the diagrammatic method and the high-temperature expansion in sections (III) and (IV) respectively. In section (V) we have outlined the numerical calculations, followed by the discussion and the conclusion in sections (VI) and (VII) respectively.

II. The Anharmonic Hamiltonian

The equilibrium position of the ℓ th unit cell in a crystal is defined by

$$\underline{x}(\ell) = \ell_1 \underline{a}_1 + \ell_2 \underline{a}_2 + \ell_3 \underline{a}_3 \quad (2.1)$$

where $\underline{a}_1, \underline{a}_2, \underline{a}_3$ are three non-coplanar vectors called the primitive translation vectors of the lattice. ℓ_1, ℓ_2, ℓ_3 are any three integers called the cell indices.

The displacement from equilibrium of the ℓ th atom in a monatomic crystal is denoted by $u(\ell)$. The total kinetic energy of the lattice is given by:

$$T = \frac{1}{2} M \sum_{\ell, \alpha} \dot{u}_{\alpha}^2(\ell) \quad (2.2)$$

where M is the mass of the atom and α denotes the cartesian coordinates x, y, z .

The total potential energy of the crystal is a function of the instantaneous atomic positions of the atoms. It can be expanded in a Taylor's series in powers of the displacement to give:

$$\begin{aligned} \Phi = \Phi_0 &+ \sum_{\ell, \alpha} \phi_{\alpha}(\ell) u_{\alpha}(\ell) + \frac{1}{2!} \sum_{\substack{\ell_1, \alpha_1 \\ \ell_2, \alpha_2}} \phi_{\alpha_1 \alpha_2}(\ell_1, \ell_2) u_{\alpha_1}(\ell_1) u_{\alpha_2}(\ell_2) \\ &+ \sum_{n=3}^{\infty} \frac{1}{n!} \sum_{\substack{\ell_1, \alpha_1 \\ \ell_n, \alpha_n}} \phi_{\alpha_1 \alpha_2 \dots \alpha_n}(\ell_1, \dots, \ell_n) u_{\alpha_1}(\ell_1) \dots u_{\alpha_n}(\ell_n) \end{aligned} \quad (2.3)$$

where Φ_0 is the static potential energy of the crystal. The n^{th} force constant $\phi_{\alpha_1 \dots \alpha_n}(\ell_1, \dots, \ell_n)$ represents the force exerted on the atom at $\underline{x}(\ell_1)$ in the α_1 direction when the atoms $\underline{x}(\ell_2), \underline{x}(\ell_3), \dots, \underline{x}(\ell_n)$ are displaced by unit distances in the directions $\alpha_2, \dots, \alpha_n$ respectively. It is given by:

$$\phi_{\alpha_1, \dots, \alpha_n}(\ell_1, \dots, \ell_n) = \left. \frac{\partial^n \Phi}{\partial u_{\alpha_1}(\ell_1) \dots \partial u_{\alpha_n}(\ell_n)} \right|_{\text{equilibrium}} \quad (2.4)$$

$\phi_{\alpha}(\ell)$ denoting the negative force acting in the α -direction on the atom

at $\underline{x}(\ell)$ at equilibrium. The net force on any particle vanishes at equilibrium, thus

$$\phi_{\alpha}(\ell) = 0 \quad (2.5)$$

The Hamiltonian of the system is given by:

$$H = T + \phi \quad (2.6)$$

In order to diagonalize the harmonic part of the hamiltonian, a transformation can be generated in the form: Born and Huang [16], Maradudin [17]

$$u_{\alpha}(\ell) = \left(\frac{\hbar}{2NM}\right)^{1/2} \sum_{\underline{kj}} \frac{e_{\alpha}(\underline{kj})}{\sqrt{\omega(\underline{kj})}} e^{2\pi i \underline{k} \cdot \underline{x}(\ell)} (a_{\underline{kj}} + a_{-\underline{kj}}^+) \quad (2.7a)$$

$$u_{\alpha}(\ell) = i \left(\frac{\hbar}{2NM}\right)^{1/2} \sum_{\underline{kj}} e_{\alpha}(\underline{kj}) \sqrt{\omega(\underline{kj})} e^{2\pi i \underline{k} \cdot \underline{x}(\ell)} (a_{\underline{kj}} - a_{-\underline{kj}}^+) \quad (2.7b)$$

where N is the number of the unit cells in the lattice. The wave vector \underline{k} is equal in magnitude to the reciprocal of the wavelength of the lattice-wave. The allowed values of \underline{k} depend on the boundary conditions of the lattice. These values are uniformly distributed throughout one unit cell of the reciprocal lattice.

For each value of \underline{k} , there are $3r$ eigenvalues $\omega(\underline{kj})$ and $3r$ eigenvectors $e(\underline{kj})$ where $j = 1, 2, \dots, 3r$. r is the number of atoms per unit cell. For monatomic crystal $r = 1$. The eigenvalue and the eigenvector are defined by

$$\omega^2(\underline{kj}) e_{\alpha}(\underline{kj}) = \sum_{\beta} D_{\alpha\beta}(\underline{k}) e_{\beta}(\underline{kj}) \quad (2.8)$$

where,

$$D_{\alpha\beta}(\underline{k}) = \frac{1}{M} \sum_{\ell} \phi_{\alpha\beta}(\ell) e^{-2\pi i \underline{k} \cdot \underline{x}(\ell)} \quad (2.9)$$

The eigenvectors can always be chosen to satisfy the conditions:

$$\sum_{\alpha} e_{\alpha}(\underline{kj}) e_{\alpha}(\underline{kj}') = \delta_{jj'} \quad (2.10a)$$

$$\sum_j e_{\alpha}(\underline{kj}) e_{\beta}(\underline{kj}) = \delta_{\alpha\beta} \quad (2.10b)$$

The reality condition on this transformation requires that:

$$e_{\alpha}(\underline{k}j) = e_{\alpha}^{*}(-\underline{k}j) \quad (2.11a)$$

$$\omega(\underline{k}j) = \omega(-\underline{k}j) \quad (2.11b)$$

$a_{\underline{k}j}$, $a_{\underline{k}j}^{+}$ in eq. (2.7) are the usual annihilation and creation operators.

Van Hove [4] has introduced the idea that in general the expectation value of the n^{th} order potential energy term in the anharmonic crystal hamiltonian is of the order of magnitude of $\hbar\omega(u/r_0)^{n/2}$ per unit volume, where ω is the mean vibrational frequency of the crystal, u is a root mean square atomic displacement and r_0 is the nearest neighbour distance in the crystal. We denote u/r_0 by λ in the Hamiltonian. This is mainly because of the relation between the force constants

$$\begin{aligned} \phi_{\alpha_1\alpha_2}(l_1, l_2) &\sim \frac{\phi}{\alpha_1\alpha_2}, \quad \phi_{\alpha_1\alpha_2\alpha_3}(l_1, l_2, l_3) \sim \frac{\phi}{\alpha_1\alpha_2\alpha_3}, \\ \phi_{\alpha_1\alpha_2\alpha_3\alpha_4}(l_1, l_2, l_3, l_4) &\sim \frac{\phi}{\alpha_1\alpha_2\alpha_3\alpha_4} \dots \text{etc. which gives} \\ \phi_{\alpha_1\alpha_2}(l_1, l_2) &\sim a_0 \phi_{\alpha_1\alpha_2\alpha_3}(l_1, l_2, l_3) \sim a_0^2 \phi_{\alpha_1\alpha_2\alpha_3\alpha_4}(l_1, l_2, l_3, l_4) \dots \end{aligned} \quad (2.12)$$

where a_0 is the lattice parameter.

Since the lattice is periodic, then, adding the same set of integers to all the cell indices in the n^{th} force constant keeps the value of this force-constant unchanged. In other words

$$\phi_{\alpha}(l) = \phi_{\alpha}(0), \quad \phi_{\alpha_1\alpha_2}(l_1, l_2) = \phi_{\alpha_1\alpha_2}(0, l_2 - l_1), \dots$$

$$\phi_{\alpha_1\alpha_2 \dots \alpha_n}(l_1, l_2 \dots l_n) = \phi_{\alpha_1\alpha_2 \dots \alpha_n}(0, l_2 - l_1 \dots l_n - l_1) \quad (2.13)$$

It is reasonable to make use of the transformation given by eq. (2.7) in the anharmonic hamiltonian as well as the harmonic part since, to our knowledge, there is no transformation diagonalizing the whole

hamiltonian.

The hamiltonian can then be written as

$$H = H_0 + V \quad (2.14)$$

where,

$$H_0 = \sum_{\underline{k}} \hbar \omega(\underline{k}) \left(a_{\underline{k}}^+ a_{\underline{k}} + \frac{1}{2} \right) \quad (2.15)$$

$$V = \sum_{n=3}^{\infty} \lambda^{n-2} \sum_{\substack{\underline{k}_1, \dots, \underline{k}_n \\ \underline{k}_1 + \dots + \underline{k}_n = 0}} V(\underline{k}_1, \dots, \underline{k}_n) A_{\underline{k}_1} \dots A_{\underline{k}_n} \quad (2.16)$$

where,

$$A_{\underline{k}} = a_{\underline{k}} + a_{-\underline{k}}^+$$

$$V(\underline{k}_1, \underline{k}_2, \dots, \underline{k}_n) = \frac{1}{n!} \left(\frac{\hbar}{2NM} \right)^{n/2} \sum_{\substack{\ell_1, \ell_2, \dots, \ell_n \\ \alpha_1, \alpha_2, \dots, \alpha_n}} \phi(\ell_1, \ell_2, \dots, \ell_n) \quad (2.17)$$

$$= \frac{e_{\alpha_1}(\underline{k}_1) e_{\alpha_2}(\underline{k}_2) \dots e_{\alpha_n}(\underline{k}_n)}{\sqrt{\omega(\underline{k}_1) \omega(\underline{k}_2) \dots \omega(\underline{k}_n)}} e^{2\pi i \underline{k}_1 \cdot \underline{x}(\ell_1)} \dots e^{2\pi i \underline{k}_n \cdot \underline{x}(\ell_n)} \quad (2.17)$$

Substituting, $\ell_2 = \ell_2 - \ell_1$, $\ell_3 = \ell_3 - \ell_1$, ..., $\ell_n = \ell_n - \ell_1$,

and knowing that

$$\underline{x}(\ell_2 + \ell_1) = \underline{x}(\ell_2) + \underline{x}(\ell_1) \quad (2.18)$$

The sum over ℓ_1 can then be carried out with the aid of the fact that:

$$\sum_{\ell_1} e^{2\pi i (\underline{k}_1 + \underline{k}_2 + \dots + \underline{k}_n) \cdot \underline{x}(\ell_1)} = N \Delta(\underline{k}_1 + \underline{k}_2 + \dots + \underline{k}_n) \quad (2.19)$$

where $\Delta(\underline{k}) = 1$

if \underline{k} = vector of reciprocal lattice

= 0

otherwise

Eq. (2.16) can be written as

$$V(\underline{k}_1, \underline{k}_2, \dots, \underline{k}_n) = \frac{1}{n!} N^{1-\frac{n}{2}} \Delta(\underline{k}_1 + \underline{k}_2 + \dots + \underline{k}_n)$$

$$= \left\{ \frac{\hbar^n}{2^n \omega(\underline{k}_1) \omega(\underline{k}_2) \dots \omega(\underline{k}_n)} \right\}^{\frac{1}{2}} \phi(\underline{k}_1, \dots, \underline{k}_n) \quad (2.20)$$

where,

$$\phi(\underline{k}_1, \underline{k}_2, \dots, \underline{k}_n) = \frac{1}{M^{n/2}} \sum_{\substack{\ell_1, \dots, \ell_n \\ \alpha_1, \alpha_2, \dots, \alpha_n}} \phi_{\alpha_1, \dots, \alpha_n}(\ell_1, \ell_2, \dots, \ell_n) \\ \times e_{\alpha_1}(\underline{k}_1) \dots e_{\alpha_n}(\underline{k}_n) e^{2\pi i \underline{k}_2 \cdot \underline{\ell}_2} \dots e^{2\pi i \underline{k}_n \cdot \underline{\ell}_n} \quad (2.21)$$

The translational invariance of the crystal leads to the condition that (Leibfried and Ludwig [18])

$$\sum_{\ell_1} \phi_{\alpha_1, \alpha_2, \alpha_3}(\ell_1, \ell_2, \ell_3) = 0 \quad (2.22a)$$

and

$$\phi_{\alpha_1, \alpha_2, \alpha_3}(\ell_1, 0, 0) = -\phi_{\alpha_1, \alpha_2, \alpha_3}(-\ell_1, 0, 0) \quad (2.22b)$$

Separating the ℓ 's sums in eq. (2.20) in all possible ways (i.e. when all ℓ 's are zeros and when one of the ℓ 's is not zero, two of the ℓ 's are not zeros and so on, making use of eq. (2.22), and assuming the two body interactions (i.e. ℓ 's take the value zero or all equal to each other) we can rewrite eq. (2.21) in the following form: (Appendix A)

$$\phi(\underline{k}_1 j_1, \underline{k}_2 j_2, \dots, \underline{k}_n j_n) = \frac{1}{2M^{n/2}} \sum'_{\alpha_1, \alpha_2, \dots, \alpha_n} \sum_{\ell} \phi_{\alpha_1, \alpha_2, \dots, \alpha_n}(\ell) e_{\alpha_1}(\underline{k}_1 j_1) \dots e_{\alpha_n}(\underline{k}_n j_n) \prod_{p=1}^n \left(1 - e^{-2\pi i \underline{k}_p \cdot \underline{x}(\ell)} \right) \quad (2.23)$$

where the prime on the summation excludes $\ell = 0$.

Assuming central force-potential (i.e. the interaction energy is a function of the distance between two atoms) we can write the coefficients

$$\phi_{\alpha_1, \dots, \alpha_n}(\bar{\ell}) \text{ as}$$

$$\phi_{\alpha_1}(\bar{\ell}) = \frac{\partial \phi(r)}{\partial u_{\alpha_1}^{\bar{\ell}}} \Big|_0 = \frac{\alpha_1}{r} \phi'(r) \Big|_0 \quad (2.24)$$

$$\phi_{\alpha_1 \alpha_2}(\bar{\ell}) = \frac{\partial^2 \phi(r)}{\partial u_{\alpha_1}^{\bar{\ell}} \partial u_{\alpha_2}^{\bar{\ell}}} \Big|_0 = \left\{ \frac{\alpha_1 \alpha_2}{r^2} \left[\phi''(r) - \frac{1}{r} \phi'(r) \right] + \frac{\delta_{\alpha_1 \alpha_2}}{r} \phi'(r) \right\} \Big|_0 \quad (2.25)$$

where the subscript 0 denotes that the derivatives are evaluated in the equilibrium configuration of the lattice. If we consider only the highest ordered radial derivative, we are dealing with the leading term approximation.

In general we can write the derivatives as:

$$\phi_{\alpha_1 \alpha_2 \dots \alpha_n}(\bar{\ell}) \approx \frac{\alpha_1 \alpha_2 \dots \alpha_n}{r^n} \phi^{(n)}(r) \Big|_0 \quad (2.26)$$

For the nearest neighbour of a face-centered cubic lattice, we have

$$\underline{x}(\ell) = \frac{a_0}{2} \underline{n} \quad (2.27a)$$

$$\alpha_n \underline{x}(\bar{\ell}) = \frac{a_0}{2} n_{\alpha_n} \quad (2.27b)$$

$$v_0 = a_0 / \sqrt{2} \quad (2.27c)$$

where, a_0 is the lattice parameter.

Making use of the relation,

$$\sum_{\alpha_1} n_{\alpha_1} e_{\alpha_1}(\underline{\kappa}_1, \underline{t}_1) = [\underline{n}_1 \cdot e(\underline{\kappa}_1, \underline{t}_1)] \quad (2.28)$$

In the light of equations (2.23), (2.26), (2.27) and (2.28) we can write,

$$\begin{aligned} \Phi(\underline{\kappa}_1, \underline{t}_1, \underline{\kappa}_2, \underline{t}_2, \dots, \underline{\kappa}_n, \underline{t}_n) &= \frac{\phi^{(n)}(r)}{2 (2M)^{n/2}} \sum_{\underline{n}} [\underline{n} \cdot e(\underline{\kappa}_1, \underline{t}_1)] \\ &\quad [\underline{n} \cdot e(\underline{\kappa}_2, \underline{t}_2)] \dots [\underline{n} \cdot e(\underline{\kappa}_n, \underline{t}_n)] \prod_{p=1}^{\infty} (1 - e^{-\pi i a_0 \underline{\kappa}_p \cdot \underline{n}}) \quad (2.29) \end{aligned}$$

III. The Diagrammatic Method

The Helmholtz free energy is given in terms of the partition function z by

$$F = -\frac{1}{\beta} \ln z \quad (3.1)$$

where

$$Z = \text{Tr} \exp(-\beta H) \quad (3.2)$$

H has been defined by equation (2.14) and $\beta = 1/K_B T$; K_B is the Boltzmann constant. Tr denotes the trace of the operator inside the braces.

Substituting $H = H_0 + V$ in equation (3.1) we find

$$Z = \text{Tr} \exp[-\beta(H_0 + V)] \quad (3.3)$$

The exponential operator cannot be factorized since the operators H_0 and V do not commute. However, it can be expanded in powers of the interaction V (Rickayzen [19] and Shukla and Muller [20]).

Therefore, the partition function can be written in the form:

$$Z = Z_0 \left[1 + \sum_{t=1}^{\infty} \frac{(-V)^t}{t!} \int_0^{\beta} ds_1 \dots \int_0^{\beta} ds_t \langle T \{ \tilde{V}(s_1) \dots \tilde{V}(s_t) \} \rangle_0 \right] \quad (3.4)$$

where

$$Z_0 = \text{Tr} \exp(-\beta H_0),$$

T is Dyson ordering operator which acts on the arguments of functions

$\tilde{V}(s_1)$ and $\tilde{V}(s_2)$ in the following manner:

$$\begin{aligned} T[\tilde{V}(s_1)\tilde{V}(s_2)] &= \tilde{V}(s_1)\tilde{V}(s_2) & \text{if} & \quad s_1 > s_2 \\ &= \tilde{V}(s_2)\tilde{V}(s_1) & \text{if} & \quad s_1 < s_2 \end{aligned} \quad (3.5)$$

$\tilde{V}(s)$ is defined by

$$\tilde{V}(s) = \exp(sH_0) V \exp(-sH_0) \quad (3.6)$$

The angular brackets $\langle \rangle_0$ represent the thermal average for an operator O defined by:

$$\langle O \rangle_0 = \frac{\text{Tr} \{ \exp(-\beta H_0) O \}}{\text{Tr} \{ \exp(-\beta H_0) \}} \quad (3.7)$$

The difficulty in evaluating expression (3.4) is that it involves an infinite series in the perturbing potential while the perturbation is itself an infinite series expansion of the cubic, quartic and higher order terms in the Taylor expansion of the potential energy of the crystal. The expression is most easily evaluated by means of diagrams. In order to show the procedure used, $\tilde{V}(s)_s$ are to be expressed in terms of A_{kj} by substituting for V from eq. (2.16) and then making use of the Wick's theorem [21] which states that "The average of an ordered product is equal to the sum of the products of all possible contractions." A contraction means the unperturbed thermal average of the ordered product of two operators and it can be defined as:

$$\begin{aligned} G(\underline{k}, \underline{k}', s) &= \langle T \tilde{A}_{\underline{k}, j}^+(s) \tilde{A}_{\underline{k}', j'}(0) \rangle_0 \\ &= \langle T \tilde{A}_{\underline{k}, j}(s) \tilde{A}_{\underline{k}', j'}^+(0) \rangle_0 \end{aligned} \quad (3.8)$$

If the two operators are of the same type, the contraction is zero.

From equation (2.16) we can write $\tilde{V}(s)$ as

$$\tilde{V}(s) = \sum_{n=3}^{\infty} \lambda^{n-2} \sum_{\underline{k}_1, \dots, \underline{k}_n} V(\underline{k}_1, \dots, \underline{k}_n) \tilde{A}_{\underline{k}_1}^+(s) \dots \tilde{A}_{\underline{k}_n}^-(s) \quad (3.9)$$

where

$$\tilde{A}_{\underline{k}, j}^-(s) = \exp(s H_0) \tilde{A}_{\underline{k}, j}^-(0) \exp(-s H_0) \quad (3.10)$$

Substituting for $\tilde{A}_{kj}(s)$ and $\tilde{A}_{kj}^+(s)$ in equation (3.8) and using the cyclic property of trace, it can be shown that (Appendix B)

$$G(\tilde{k}j, \tilde{k}'j', s+\beta) = G(\tilde{k}j, \tilde{k}'j', s) \quad -\beta < s < 0 \quad (3.11)$$

Therefore Green's function (contraction) can be expanded in a Fourier series with period β . The Fourier coefficients can be expressed in the following form (Appendix B)

$$G(\tilde{k}j, \tilde{k}'j', i\omega_n) = \frac{2\omega(\tilde{k}j)}{\beta\hbar} \frac{1}{\omega^2(\tilde{k}j) + \omega_n^2} \delta_{\tilde{k}\tilde{k}'} \delta_{jj'} \quad (3.12)$$

where

$$\omega_n = \frac{2\pi n}{\beta\hbar} \quad ; \quad n \text{ is an integer} \quad (3.13)$$

In expression (3.4), the phonon interactions V'_p can be represented by a dot. A contraction, equation (3.8), is represented by a solid phonon line joining two dots.

There are two types of diagrams: connected and disconnected. A diagram is connected if it has this property: one must be able to get from any vertex to any other vertex by staying on the line of the diagram; otherwise it is disconnected.

There is no contribution to the partition function from the odd powers of λ since the matrix elements always contain an odd number of operators \tilde{A}_{kj} i.e. in pairing such operators we are to be left with an unpaired operator which produces orthogonal states.

The contributions to the partition function can be evaluated following certain rules given by Cowley [8], Shukla and Muller [20] and Rickayzen [19].

These rules are:

1. Draw all topologically distinct diagrams with n vertices and the appropriate phonon lines.

2. Associate a factor $G(\underline{k}_j, i\omega_n)$ with each phonon lines where \underline{k} , j are the wave vector and the branch indices.
3. Conserve energy and momentum at each vertex and sum over all independent \underline{k}'_s and ω'_s .
4. Multiply by the number of pairing schemes and the topologically equivalent factors.
5. Insert a factor $\frac{(-\beta)^n}{n!}$
6. Insert the appropriate interaction coefficients at each vertex.

The contribution to Helmholtz free energy is given by [8], [19] and [20].

$$F = F_0 - \frac{1}{\beta} \sum^c$$

where F_0 represents the free energy of the non-interacting system and \sum^c represents the contribution from all connected diagrams i.e. only the connected diagrams contribute to the free energy [Appendix B].

(i) Diagrams of order λ^2 :

Peierls [3], Ludwig [5], Maradudin [6] and Cowley [8] have derived and evaluated the diagrams which contribute to the free energy of this order. All diagrams are presented in Fig. (1).

(ii) Diagrams of order λ^4 :

All of the diagrams contributing to the Helmholtz free energy to $O(\lambda^4)$ have been evaluated by Shukla and Cowley [9]. In Fig. (2), we have presented all diagrams of this order along with the corresponding pairing schemes and topologically equivalent diagrams.

(iii) Diagrams of order λ^6 :

The first contribution to the partition function can be derived from expression (3.4) by putting $t = 1$, thus

$$L_1 = \frac{(-1)^1}{1!} \int_0^\beta ds_1 \langle T \tilde{V}(s_1) \rangle. \quad (3.14)$$

Substituting for $\tilde{V}(s)$ from eq. (3.9), retaining the λ^6 -term, making use of Wick's theorem and the following relation

$$\tilde{A}_{-\tilde{\kappa}j}(s) = \tilde{A}_{\tilde{\kappa}j}^+(s) \quad (3.15)$$

Eq. (3.14) becomes:

$$L_1 = \frac{(-\beta)^1}{1!} \times 105 \times 1 \sum_{\substack{n_1 n_2 n_3 n_4 \\ 1 2 3 4}} \sum_{\substack{\tilde{\kappa}_1 j_1, \tilde{\kappa}_2 j_2, \\ \tilde{\kappa}_3 j_3, \tilde{\kappa}_4 j_4}} V(\tilde{\kappa}_1 j_1, -\tilde{\kappa}_1 j_1, \tilde{\kappa}_2 j_2, -\tilde{\kappa}_2 j_2, \tilde{\kappa}_3 j_3, -\tilde{\kappa}_3 j_3, \tilde{\kappa}_4 j_4, -\tilde{\kappa}_4 j_4) \\ \times G(\tilde{\kappa}_1 j_1, \eta_1) G(\tilde{\kappa}_2 j_2, \eta_2) G(\tilde{\kappa}_3 j_3, \eta_3) G(\tilde{\kappa}_4 j_4, \eta_4) \quad (3.16)$$

This equation is represented by diagram F(3.1) in Fig. (3). The vertex corresponds to the eight phonon interactions

$$V_8 \{ V(\tilde{\kappa}_1 j_1, -\tilde{\kappa}_1 j_1, \tilde{\kappa}_2 j_2, -\tilde{\kappa}_2 j_2, \tilde{\kappa}_3 j_3, -\tilde{\kappa}_3 j_3, \tilde{\kappa}_4 j_4, -\tilde{\kappa}_4 j_4) \}$$

The factor, 105, represents the pairing scheme and refers to the number of equivalent ways of pairing the operators. The constant, 1, is the topologically equivalent diagram (referring to the number of ways we can permute the vertices to get different shapes of a diagram).

As an example, the number of ways of pairing the eight lines in diagram (3.1)

$$= \frac{8c_2}{4} \times \frac{6c_2}{3} \times \frac{4c_2}{2} \times \frac{2c_2}{1} = 105,$$

where,

$$n_{c_r} = \frac{n!}{r! (n-r)!}$$

There is only one way of drawing diagram F(3.1), i.e. the number of topologically equivalent diagram is 1.

Generally, the pairing schemes arising from pairing $2\mathcal{V}$ modes into 2 independent modes is equal to

$$\frac{2^{\nu} c_2}{\nu} \times \frac{2^{\nu-2} c_2}{\nu-1} \times \frac{2^{\nu-4} c_2}{\nu-2} \times \dots \times \frac{2 c_2}{1} = \frac{(2\nu)!}{2^{\nu} \nu!} \quad (3.16)$$

The second contribution can be worked out by putting, $t = 2$, in expression (3.4). All diagrams arise from three different terms in this order each of which involves ten modes, i.e. the total number of pairing schemes is 945.

a. Diagrams from $V_3 - V_7$ term.

This term gives rise to two diagrams presented in Fig. (3). The second diagram does not contribute to the free energy since the coefficient V involves delta function, $\Delta(\underline{K})$, which implies that \underline{K} is zero or a vector of reciprocal lattice and in either case, the anharmonic coefficient V is zero [22]. All such diagrams give zero contribution for the same reason.

b. Diagrams from $V_4 - V_6$ term.

The three diagrams arising from this term are presented in Fig. (3) along with the corresponding pairing schemes and topologically equivalent diagrams.

c. Diagrams from $V_5 - V_5$ term.

One diagram does not contribute to the partition function for the reason mentioned above. The remaining two contribute. All diagrams are presented in Fig. (3).

The third contribution to the partition function can be obtained by substituting, $t = 3$, in expression (3.4). There are three different terms $[V_4 - V_4 - V_4 \& V_3 - V_4 - V_5 \& V_3 - V_3 - V_6]$ arising from this order. The total number of pairing schemes (for each term) is 10,395.

In Fig. [3], we have presented the corresponding diagrams.

Two terms $[V_3 - V_3 - V_3 - V_5 \text{ \& } V_3 - V_3 - V_4 - V_4]$ arise from the fourth order contribution; the equivalent diagrams are presented in Fig. (3).

There is one term $[V_3 - V_3 - V_3 - V_3 - V_4]$ arising from the fifth order. Forty eight diagrams correspond to this term; all of them have been presented in Fig. (3).

The last contribution of $O(\lambda^6)$ can be obtained by substituting $t = 6$ in expression (3.4). This gives rise to one term $[V_3 - V_3 - V_3 - V_3 - V_3 - V_3]$

We have considered diagram F(3.39) in order to illustrate the method used in finding the pairing schemes and topologically equivalent diagrams.

$$\begin{aligned} \text{The pairing scheme} &= \left({}^3C_1 \times {}^3C_1 \right)^3 \quad [\text{joining the vertices 1 and 2,} \\ &\quad \text{and 3 and 4, and 5 and 6}] \times \\ &\quad \left(\frac{{}^2C_1 \times {}^2C_1}{2} \right)^3 \quad [\text{joining the} \\ &\quad \text{vertices 2 and 3, and 4 and 5, and} \\ &\quad \text{6 and 1}]. \\ &= 5832 \end{aligned}$$

The topologically equivalent diagrams = $5! = 120$ [fixing a vertex and permuting the other five].

IV. The High-Temperature Limit

The computation of those diagrams that contribute to the free energy can be considerably simplified if the high-temperature limit is considered. Maradudin et al. [6] have worked out the expansion to the lowest order contribution. Maradudin and Melngailis [23] have used the high temperature expansion of the propagator in obtaining expressions for the mean-square velocity and mean-square amplitude of an atom in the surface layers of a crystal. They have expanded the Green function in powers of T^{-1} . Shukla and Cowley [9] have worked out the high temperature expansion for the various contributions of order λ^4 in the leading term of temperature. Our aim is to derive the high temperature expressions for all diagrams contributing to the free energy to order λ^6 in order to examine the convergence of the temperature-expansion and to compare the coefficient of T^2 term with that of order λ^2 .

We have considered the following two examples to illustrate the technique used in deriving the high-temperature expressions.

The free energy expression of diagram (1.1) is given by:

$$F(1.1) = -\frac{1}{\beta} \frac{(-\beta)^1}{1!} \times 3 \times 1 \sum_{\eta_1, \eta_2} \sum_{l, 2} V(l, -1, 2, -2) G(1, i\omega_{\eta_1}) G(2, i\omega_{\eta_2}) \quad (4.1)$$

where the factors 3 and 1 are respectively the pairing schemes and the topologically equivalent diagrams. For simplicity of notation, the following convention will be made unless otherwise specified that:

$$\underline{K}_1 \dot{t}_1 \equiv 1 \quad ; \quad \omega(\underline{K}_1 \dot{t}_1) \equiv \omega_1$$

The propagator is defined by:

$$G(1, i\omega_{\eta_1}) = \frac{2\omega_1}{\beta\hbar} \frac{1}{\omega_1^2 + \omega_{\eta_1}^2} \quad (4.2)$$

where

$$\beta = \frac{1}{K_B T}$$

$$\omega_{n_i} = 2\pi n_i / \beta \hbar \quad \text{and } n_i \text{ is an integer number.}$$

Equations (4.1) and (4.2) lead to:

$$F(1,1) = \frac{12}{(\beta \hbar)^2} \sum_{1,2} \omega_1 \omega_2 V(1,-1,2,-2) \sum_{n_1, n_2} \frac{1}{\omega_1^2 + \omega_{n_1}^2} \frac{1}{\omega_2^2 + \omega_{n_2}^2} \quad (4.3)$$

Putting n_1 , or n_2 or both equal to zero and using the symmetry (interchanging n by $-n$ will not change the expression), expression (4.3) becomes:

$$\begin{aligned} F(1,1) = \frac{12}{(\beta \hbar)^2} \sum_{1,2} \omega_1 \omega_2 V(1,-1,2,-2) & \left[\frac{1}{\omega_1^2 \omega_2^2} + \frac{1}{\omega_2^2} \sum_{n_1=1}^{\infty} \frac{1}{\omega_{n_1}^2} \left(1 + \frac{\omega_1^2}{\omega_{n_1}^2}\right)^{-1} \right. \\ & \left. + \frac{1}{\omega_1^2} \sum_{n_2=1}^{\infty} \frac{1}{\omega_{n_2}^2} \left(1 + \frac{\omega_2^2}{\omega_{n_2}^2}\right)^{-1} + \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{1}{\omega_{n_1}^2 \omega_{n_2}^2} \left(1 + \frac{\omega_1^2}{\omega_{n_1}^2}\right)^{-1} \left(1 + \frac{\omega_2^2}{\omega_{n_2}^2}\right)^{-1} \right] \end{aligned} \quad (4.4)$$

Assuming that $\omega_1 < \omega_{n_1}$, we can apply the binomial series to give:

$$\begin{aligned} F(1,1) = \frac{12}{(\beta \hbar)^2} \sum_{1,2} \omega_1 \omega_2 V(1,-1,2,-2) & \left[\frac{1}{\omega_1^2 \omega_2^2} \right. \\ & + \frac{2}{\omega_2^2} \sum_{n_1=1}^{\infty} \frac{1}{\omega_{n_1}^2} \left(1 - \frac{\omega_1^2}{\omega_{n_1}^2} + \frac{\omega_1^4}{\omega_{n_1}^4} - \frac{\omega_1^6}{\omega_{n_1}^6} + \dots\right) \\ & + \frac{2}{\omega_1^2} \sum_{n_2=1}^{\infty} \frac{1}{\omega_{n_2}^2} \left(1 - \frac{\omega_2^2}{\omega_{n_2}^2} + \frac{\omega_2^4}{\omega_{n_2}^4} - \frac{\omega_2^6}{\omega_{n_2}^6} + \dots\right) \\ & \left. + 4 \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{1}{\omega_{n_1}^2 \omega_{n_2}^2} \left(1 - \frac{\omega_1^2}{\omega_{n_1}^2} - \frac{\omega_2^2}{\omega_{n_2}^2} + \frac{\omega_1^4}{\omega_{n_1}^4} + \frac{\omega_1^2 \omega_2^2}{\omega_{n_1}^2 \omega_{n_2}^2} + \frac{\omega_2^4}{\omega_{n_2}^4} - \dots\right) \right] \end{aligned}$$

We have used the symmetry of n_1, n_2 , i.e. by changing n_1 by $-n_1$ we get the same expression.

Substituting for ω_{η} we get:

$$\begin{aligned}
 F(1,1) = & \frac{12}{(\beta\hbar)^2} \sum_{1,2} \omega_1 \omega_2 V(1,-1,2,-2) \left[\frac{1}{\omega_1^2 \omega_2^2} \right. \\
 & + \frac{2}{\omega_1^2} \left\{ \left(\frac{\beta\hbar}{2\pi} \right)^2 \sum_{\eta_1=1}^{\infty} \frac{1}{\eta_1^2} - \left(\frac{\beta\hbar}{2\pi} \right)^4 \omega_1^2 \sum_{\eta_1=1}^{\infty} \frac{1}{\eta_1^4} + \left(\frac{\beta\hbar}{2\pi} \right)^6 \omega_1^4 \sum_{\eta_1=1}^{\infty} \frac{1}{\eta_1^6} \right. \\
 & \left. - \left(\frac{\beta\hbar}{2\pi} \right)^8 \omega_1^6 \sum_{\eta_1=1}^{\infty} \frac{1}{\eta_1^8} + \dots \right\} + \frac{2}{\omega_2^2} \left\{ \left(\frac{\beta\hbar}{2\pi} \right)^2 \sum_{\eta_2=1}^{\infty} \frac{1}{\eta_2^2} - \left(\frac{\beta\hbar}{2\pi} \right)^4 \omega_2^2 \sum_{\eta_2=1}^{\infty} \frac{1}{\eta_2^4} \right. \\
 & + \left(\frac{\beta\hbar}{2\pi} \right)^6 \omega_2^4 \sum_{\eta_2=1}^{\infty} \frac{1}{\eta_2^6} - \left(\frac{\beta\hbar}{2\pi} \right)^8 \omega_2^6 \sum_{\eta_2=1}^{\infty} \frac{1}{\eta_2^8} + \dots \left. \right\} \\
 & + 4 \left\{ \left(\frac{\beta\hbar}{2\pi} \right)^4 \sum_{\eta_1=1}^{\infty} \frac{1}{\eta_1^2} \sum_{\eta_2=1}^{\infty} \frac{1}{\eta_2^2} - \omega_1^2 \left(\frac{\beta\hbar}{2\pi} \right)^6 \sum_{\eta_1=1}^{\infty} \frac{1}{\eta_1^4} \sum_{\eta_2=1}^{\infty} \frac{1}{\eta_2^2} \right. \\
 & - \omega_2^2 \left(\frac{\beta\hbar}{2\pi} \right)^6 \sum_{\eta_2=1}^{\infty} \frac{1}{\eta_2^4} \sum_{\eta_1=1}^{\infty} \frac{1}{\eta_1^2} + \left(\frac{\beta\hbar}{2\pi} \right)^8 \left[\omega_1^4 \sum_{\eta_1=1}^{\infty} \frac{1}{\eta_1^6} \sum_{\eta_2=1}^{\infty} \frac{1}{\eta_2^2} \right. \\
 & \left. \left. + \omega_2^4 \sum_{\eta_2=1}^{\infty} \frac{1}{\eta_2^6} \sum_{\eta_1=1}^{\infty} \frac{1}{\eta_1^2} \right] + \dots \right\}
 \end{aligned}$$

It has been shown by Reif [24] Morse and Feshbach [25] that:

$$\begin{aligned}
 \sum_{\eta=1}^{\infty} \frac{1}{\eta^2} &= \frac{\pi^2}{6}, \quad \sum_{\eta=1}^{\infty} \frac{1}{\eta^4} = \frac{\pi^4}{90}, \quad \sum_{\eta=1}^{\infty} \frac{1}{\eta^6} = \frac{\pi^6}{945}, \\
 \sum_{\eta=1}^{\infty} \frac{1}{\eta^8} &= \frac{\pi^8}{9450}
 \end{aligned} \tag{4.5}$$

Making use of these facts and equation (2.20)

$$F(1,1) = \frac{(\kappa_B T)^2}{8N} \sum_{\substack{\kappa_1 \delta_1 \\ \kappa_2 \delta_2}} \frac{\phi(\kappa_1 \delta_1, -\kappa_1 \delta_1, \kappa_2 \delta_2, -\kappa_2 \delta_2)}{\omega_1^2 \omega_2^2}$$

$$\begin{aligned}
& \left[1 + \frac{\hbar^2}{6 (K_B T)^2} \omega_1^2 + \frac{\hbar^4}{720 (K_B T)^4} (2 \omega_1^2 + 5 \omega_1^2 \omega_2^2) \right. \\
& + \frac{\hbar^6}{60480 (K_B T)^6} (4 \omega_1^6 + 14 \omega_1^4 \omega_2^2) \\
& + \frac{\hbar^8}{725760 (K_B T)^8} (12 \omega_1^8 + 20 \omega_1^6 \omega_2^2 + 7 \omega_1^4 \omega_2^4) \\
& \left. + \dots \right] \quad (4.6)
\end{aligned}$$

We have considered diagram (1.2) as the second example. Its expression is given by:

$$\begin{aligned}
F(1,2) = & -\frac{1}{\beta} \frac{(-\beta)^2}{2!} \times 6 \times 1 \sum_{1,2,3} V(1,2,3) V(-1,-2,-3) \\
& \sum_{\eta_1, \eta_2} G(1, i\omega_{\eta_1}) G(2, i\omega_{\eta_2}) G(3, -i\omega_{\eta_1} - i\omega_{\eta_2}) \quad (4.7)
\end{aligned}$$

The factors 6 and 1 are the pairing schemes and topologically equivalent diagrams respectively.

Substituting for the propagators and V'_β from eq. (4.2) and (2.20), respectively, putting each of the η'_β equal to zero, using the symmetry and expanding the expression using the binomial series we get:

$$\begin{aligned}
F(1,2) = & -\frac{(K_B T)^2}{12N} \sum_{1,2,3} \Delta(K_1 + K_2 + K_3) \phi(1,2,3) \phi(-1,-2,-3) \\
& \left[\frac{1}{\omega_1^2 \omega_2^2 \omega_3^2} + \sum_{\substack{i,j,k=1 \\ i \neq j \neq k}}^3 \frac{2}{\omega_i^2} \sum_{\eta=1}^{\infty} \frac{1}{\omega_\eta^4} \left(1 - \frac{\omega_i^2}{\omega_\eta^2} + \frac{\omega_i^4}{\omega_\eta^4} - \dots \right) \right]
\end{aligned}$$

$$\begin{aligned}
& \left(1 - \frac{\omega_k^2}{\omega_\eta^2} + \frac{\omega_k^4}{\omega_\eta^4} - \dots\right) + 2 \sum_{\eta=1}^{\infty} \frac{1}{4 \omega_\eta^6} \left(1 - \frac{\omega_1^2}{\omega_\eta^2} + \dots\right) \left(1 - \frac{\omega_2^2}{\omega_\eta^2} + \dots\right) \\
& \left(1 - \frac{\omega_3^2}{4 \omega_\eta^2} + \dots\right) + \sum_{\substack{\eta_1=-\infty \\ \eta_1 \neq \pm \eta_2 \neq 0}}^{\infty} \sum_{\substack{\eta_2=-\infty \\ \eta_2 \neq 0}}^{\infty} \frac{1}{\omega_{\eta_1}^2 \omega_{\eta_2}^2 (\omega_{\eta_1} + \omega_{\eta_2})^2} \left(1 - \frac{\omega_1^2}{\omega_{\eta_1}^2} + \dots\right) \\
& \left(1 - \frac{\omega_2^2}{\omega_{\eta_2}^2} + \dots\right) \left(1 - \frac{\omega_3^2}{(\omega_{\eta_1} + \omega_{\eta_2})^2} + \dots\right) \Big] \quad (4.8)
\end{aligned}$$

Substituting for ω_η and making use of the relations (4.5), we can get the following (we have carried out the calculation for the last term in expression (4.8) as an example in Appendix D)

$$\begin{aligned}
F(1.2) = & - \frac{(K_B T)^2}{12 N} \sum_{1,2,3} \frac{\Delta(K_1 + K_2 + K_3) \phi(1,2,3) \phi(-1,-2,-3)}{\omega_1^2 \omega_2^2 \omega_3^2} \left[1 \right. \\
& \left. + \frac{\hbar^4}{240 (K_B T)^4} \omega_1^2 \omega_2^2 + \frac{\hbar^6}{30240 (K_B T)^6} \left\{ 3 \omega_1^4 (\omega_1^2 + \omega_2^2) + \frac{57}{4} \omega_1^2 \omega_2^2 \omega_3^2 \right\} + \dots \right] \quad (4.9)
\end{aligned}$$

Following the same procedure, the high temperature expressions for all diagrams which contribute to the free energy of order λ^4 can be worked out. The general corresponding expressions have been given by Shukla and Cowley [9]. These expressions are:

$$\begin{aligned}
F(2.1) = & \frac{(K_B T)^3}{48 N^2} \sum_{1,2,3} \frac{\phi(1,-1,2,-2,3,-3)}{\omega_1^2 \omega_2^2 \omega_3^2} \left[1 + \frac{\hbar^2}{8 (K_B T)^2} \omega_1^2 \right. \\
& \left. + X(2.1) + \dots \right] \quad (4.10)
\end{aligned}$$

where, $X(2.1)$ is the next order in the expression (4.10). Its full expression has been given in appendix E along with all the following

expressions.

$$F(2.2) = -\frac{(K_B T)^3}{16 N^2} \sum_{\substack{\vec{k}_1, \vec{k}_2, \vec{k}_4 \\ \vec{d}_1, \vec{d}_2, \vec{d}_3}} \frac{\phi(\vec{k}_1 \vec{d}_1, -\vec{k}_1 \vec{d}_1, \vec{k}_2 \vec{d}_2, -\vec{k}_2 \vec{d}_2) \phi(\vec{k}_4 \vec{d}_4, -\vec{k}_4 \vec{d}_4, -\vec{k}_2 \vec{d}_2, \vec{k}_2 \vec{d}_2)}{\omega^2(\vec{k}_1 \vec{d}_1) \omega^2(\vec{k}_2 \vec{d}_2) \omega^2(\vec{k}_2 \vec{d}_2) \omega^2(\vec{k}_4 \vec{d}_4)}$$

$$\left[1 + \frac{\hbar^2}{6 (K_B T)^2} \omega^2(\vec{k}_1 \vec{d}_1) + X(2.2)_k \right] \quad (4.11)$$

$$F(2.3) = -\frac{(K_B T)^3}{3 N^2} \sum_{\substack{\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4 \\ \vec{d}_1, \vec{d}_2, \vec{d}_3, \vec{d}_4}} \frac{\Delta(\vec{k}_1 + \vec{k}_2 + \vec{k}_3) \phi(\vec{k}_1 \vec{d}_1, \vec{k}_2 \vec{d}_2, \vec{k}_3 \vec{d}_3) \phi(-\vec{k}_1 \vec{d}_1, -\vec{k}_2 \vec{d}_2, -\vec{k}_3 \vec{d}_3, \vec{k}_4 \vec{d}_4, -\vec{k}_4 \vec{d}_4)}{\omega^2(\vec{k}_1 \vec{d}_1) \omega^2(\vec{k}_2 \vec{d}_2) \omega^2(\vec{k}_3 \vec{d}_3) \omega^2(\vec{k}_4 \vec{d}_4)}$$

$$\left[1 + \frac{\hbar^2}{12 (K_B T)^2} \omega^2(\vec{k}_4 \vec{d}_4) + X(2.3) + \dots \right] \quad (4.12)$$

$$F(2.4) = \frac{(K_B T)^3}{8 N^2} \sum_{\substack{\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4, \vec{k}_5 \\ \vec{d}_1, \vec{d}_2, \vec{d}_3, \vec{d}_4, \vec{d}_5}} \frac{\phi(\vec{k}_1 \vec{d}_1, \vec{k}_3 \vec{d}_3, \vec{k}_4 \vec{d}_4) \phi(-\vec{k}_1 \vec{d}_1, -\vec{k}_3 \vec{d}_3, -\vec{k}_4 \vec{d}_4) \phi(-\vec{k}_1 \vec{d}_1, \vec{k}_2 \vec{d}_2, \vec{k}_5 \vec{d}_5, -\vec{k}_5 \vec{d}_5)}{\omega^2(\vec{k}_1 \vec{d}_1) \omega^2(\vec{k}_2 \vec{d}_2) \omega^2(\vec{k}_3 \vec{d}_3) \omega^2(\vec{k}_4 \vec{d}_4) \omega^2(\vec{k}_5 \vec{d}_5)}$$

$$\left[1 + \frac{\hbar^2}{12 (K_B T)^2} \omega^2(\vec{k}_5 \vec{d}_5) + X(2.4) + \dots \right] \quad (4.13)$$

$$F(2.5) = -\frac{(K_B T)^3}{48 N^2} \sum_{\substack{\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4 \\ \vec{d}_1, \vec{d}_2, \vec{d}_3, \vec{d}_4}} \frac{\Delta(\vec{k}_1 + \vec{k}_2 + \vec{k}_3 + \vec{k}_4) \phi(\vec{k}_1 \vec{d}_1, \vec{k}_2 \vec{d}_2, \vec{k}_3 \vec{d}_3, \vec{k}_4 \vec{d}_4) \phi(-\vec{k}_1 \vec{d}_1, -\vec{k}_2 \vec{d}_2, -\vec{k}_3 \vec{d}_3, -\vec{k}_4 \vec{d}_4)}{\omega^2(\vec{k}_1 \vec{d}_1) \omega^2(\vec{k}_2 \vec{d}_2) \omega^2(\vec{k}_3 \vec{d}_3) \omega^2(\vec{k}_4 \vec{d}_4)}$$

$$\left[1 + X(2.5) + \dots \right] \quad (4.14)$$

$$F(2.6) = -\frac{(K_B T)^3}{16 N^2} \sum_{\substack{\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4, \vec{k}_5, \vec{k}_6 \\ \vec{d}_1, \vec{d}_2, \vec{d}_3, \vec{d}_4, \vec{d}_5, \vec{d}_6}} \frac{\Delta(\vec{k}_1 + \vec{k}_3 + \vec{k}_4) \Delta(\vec{k}_1 - \vec{k}_5 - \vec{k}_6) \phi(-\vec{k}_1 \vec{d}_1, \vec{k}_5 \vec{d}_5, \vec{k}_6 \vec{d}_6) \phi(\vec{k}_1 \vec{d}_1, \vec{k}_3 \vec{d}_3, \vec{k}_4 \vec{d}_4)}{\omega^2(\vec{k}_1 \vec{d}_1) \omega^2(\vec{k}_2 \vec{d}_2) \omega^2(\vec{k}_3 \vec{d}_3) \omega^2(\vec{k}_4 \vec{d}_4) \omega^2(\vec{k}_5 \vec{d}_5) \omega^2(\vec{k}_6 \vec{d}_6)} \\ \phi(\vec{k}_1 \vec{d}_1, -\vec{k}_3 \vec{d}_3, -\vec{k}_4 \vec{d}_4) \phi(-\vec{k}_1 \vec{d}_1, -\vec{k}_5 \vec{d}_5, -\vec{k}_6 \vec{d}_6)$$

$$\left[1 + X(2.6) + \dots \right] \quad (4.15)$$

$$F(2.7) = \frac{(K_8 T)^3}{8 N^2} \sum_{\substack{\tilde{K}_1 \tilde{K}_2 \tilde{K}_3 \tilde{K}_4 \tilde{K}_5 \\ \tilde{d}_1 \tilde{d}_2 \tilde{d}_3 \tilde{d}_4 \tilde{d}_5}} \frac{\Delta(\tilde{K}_1 + \tilde{K}_2 + \tilde{K}_3) \Delta(\tilde{K}_3 + \tilde{K}_4 + \tilde{K}_5) \phi(\tilde{K}_1 \tilde{d}_1, \tilde{K}_2 \tilde{d}_2, \tilde{K}_3 \tilde{d}_3) \phi(-\tilde{K}_3 \tilde{d}_3, -\tilde{K}_4 \tilde{d}_4, -\tilde{K}_5 \tilde{d}_5)}{\omega^2(\tilde{K}_1 \tilde{d}_1) \omega^2(\tilde{K}_2 \tilde{d}_2) \omega^2(\tilde{K}_3 \tilde{d}_3) \omega^2(\tilde{K}_4 \tilde{d}_4) \omega^2(\tilde{K}_5 \tilde{d}_5)} \\ \phi(\tilde{K}_1 \tilde{d}_1, -\tilde{K}_2 \tilde{d}_2, \tilde{K}_4 \tilde{d}_4, \tilde{K}_5 \tilde{d}_5)$$

$$\left[1 + X(2.7) + \dots \right] \quad (4.16)$$

$$F(2.8) = -\frac{(K_8 T)^3}{24 N^3} \sum_{\substack{\tilde{K}_1 \tilde{K}_2 \tilde{K}_3 \tilde{K}_4 \tilde{K}_5 \tilde{K}_6 \\ \tilde{d}_1 \tilde{d}_2 \tilde{d}_3 \tilde{d}_4 \tilde{d}_5 \tilde{d}_6}} \frac{\Delta(\tilde{K}_1 + \tilde{K}_2 + \tilde{K}_3) \Delta(-\tilde{K}_1 + \tilde{K}_4 + \tilde{K}_5) \Delta(\tilde{K}_2 + \tilde{K}_5 - \tilde{K}_6) \phi(\tilde{K}_1 \tilde{d}_1, \tilde{K}_2 \tilde{d}_2, \tilde{K}_3 \tilde{d}_3)}{\omega^2(\tilde{K}_1 \tilde{d}_1) \omega^2(\tilde{K}_2 \tilde{d}_2) \omega^2(\tilde{K}_3 \tilde{d}_3) \omega^2(\tilde{K}_4 \tilde{d}_4) \omega^2(\tilde{K}_5 \tilde{d}_5) \omega^2(\tilde{K}_6 \tilde{d}_6)} \\ \phi(-\tilde{K}_1 \tilde{d}_1, \tilde{K}_4 \tilde{d}_4, \tilde{K}_5 \tilde{d}_5) \phi(\tilde{K}_2 \tilde{d}_2, -\tilde{K}_5 \tilde{d}_5, \tilde{K}_6 \tilde{d}_6) \phi(-\tilde{K}_3 \tilde{d}_3, -\tilde{K}_4 \tilde{d}_4, -\tilde{K}_6 \tilde{d}_6)$$

$$\left[1 + X(2.8) + \dots \right] \quad (4.17)$$

For all diagrams of order λ^6 contributing to the free energy, we have set up the corresponding expressions from which we have substituted for the propagators and performed the summation over η' applying the previous technique. There is only one diagram of first-order perturbation (3.1) and its contribution to the free energy is:

$$F(3.1) = -\frac{1}{\beta} \frac{(-\beta)'_{105}}{1'} \sum_{1,2,3,4} V(1, -1, 2, -2, 3, -3, 4, -4) \sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(1, i\omega_{\eta_1}) \\ G(2, i\omega_{\eta_2}) G(3, i\omega_{\eta_3}) G(4, i\omega_{\eta_4})$$

The factors 105 and 1 are the pairing schemes and the topologically equivalent diagrams respectively. Substituting for the propagators,

expanding and performing the summations over $\eta_1, \eta_2, \eta_3, \eta_4$ we get

$$F(3.1) = \frac{(K_B T)^4}{384 N^3} \sum_{1,2,3,4} \frac{\phi(1, -1, 2, -2, 3, -3, 4, -4)}{\omega_1^2 \omega_2^2 \omega_3^2 \omega_4^2} \left[1 + \frac{\hbar^2}{3 (K_B T)^2} \omega_1^2 + X(3.1) + \dots \right] \quad (4.18)$$

Corresponding to the second order, there are five diagrams. The contribution from diagram (3.2) is given by:

$$F(3.2) = -\frac{1}{\beta} \frac{(-\beta)^2}{2!} \times 630 \times 2 \sum_{1,2,3,4,5} V(1,2,3) V(-1,-2,-3,4,-4,5,-5) \sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(1, i\omega_{\eta_1}) G(2, i\omega_{\eta_2}) G(3, -i\omega_{\eta_1} - i\omega_{\eta_2}) G(4, i\omega_{\eta_3}) G(5, i\omega_{\eta_4})$$

where the factors 630 and 2 are the pairing schemes and the topologically equivalent factor.

Performing the summations we find

$$F(3.2) = -\frac{(K_B T)^4}{48 N^3} \sum_{1,2,3,4,5} \frac{\Delta(K_1 + K_2 + K_3) \phi(1,2,3) \phi(-1,-2,-3,4,-4,5,-5)}{\omega_1^2 \omega_2^2 \omega_3^2 \omega_4^2 \omega_5^2} \left[1 + \frac{\hbar^2}{6 (K_B T)^2} \omega_4^2 + X(3.2) + \dots \right] \quad (4.19)$$

Diagram (3.3) has the same structure as diagram (3.2). The general expression is:

$$F(3.3) = -\frac{1}{\beta} \frac{(-\beta)^2}{2!} \times 360 \times 2 \sum_{1,2,3,4,5} V(2,3,4,5) V(1,-1,-2,-3,-4,-5) \sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(1, i\omega_{\eta_1}) G(2, i\omega_{\eta_2}) G(3, i\omega_{\eta_3}) G(4, i\omega_{\eta_4}) G(5, -i\omega_{\eta_2} - i\omega_{\eta_3} - i\omega_{\eta_4})$$

Making use of eq. (4.2), binomial series and performing the summations over η we get:

$$F(3.3) = -\frac{(K_B T)^4}{48 N^3} \sum_{1,2,3,4,5} \frac{\Delta(K_2 + K_3 + K_4 + K_5) \phi(2,3,4,5) \phi(1,-1,-2,-3,-4,-5)}{\omega_1^2 \omega_2^2 \omega_3^2 \omega_4^2 \omega_5^2}$$

$$\left[1 + \frac{\hbar^2}{12 (K_B T)^2} \omega_1^2 + X(3.3) + \dots \right] \quad (4.20)$$

The contribution of the third diagram containing two vertex is given by:

$$F(3.4) = -\frac{1}{\beta} \frac{(-\beta)^2}{2!} \times 5 \times 4 \times 2 \sum_{\substack{K_1^j, K_2^j, K_3^j, K_4^j, K_5^j \\ j_1, j_2, j_3, j_4, j_5}} V(K_1^j, -K_1^j, K_2^j, -K_2^j) V(-K_2^j, K_2^j, K_4^j, -K_4^j, K_5^j, -K_5^j)$$

$$\sum_{\eta_1, \eta_2, \eta_3, \eta_4} G(K_1^j, i\omega_{\eta_1}) G(K_2^j, i\omega_{\eta_2}) G(K_3^j, i\omega_{\eta_3}) G(K_4^j, i\omega_{\eta_4}) G(K_5^j, i\omega_{\eta_5})$$

Where wave-vector conservation has been satisfied. The expansion for diagram (3.4) is given by:

$$F(3.4) = -\frac{(K_B T)^4}{32 N^3} \sum_{\substack{K_1^j, K_2^j, K_3^j, K_4^j, K_5^j \\ j_1, j_2, j_3, j_4, j_5}} \frac{\phi(K_1^j, -K_1^j, K_2^j, -K_2^j) \phi(-K_2^j, K_2^j, K_4^j, -K_4^j, K_5^j, -K_5^j)}{\omega^2(K_1^j) \omega^2(K_2^j) \omega^2(K_3^j) \omega^2(K_4^j) \omega^2(K_5^j)}$$

$$\left[1 + \frac{\hbar^2}{12 (K_B T)^2} \{ \omega^2(K_1^j) + 2\omega^2(K_4^j) \} + X(3.4) + \dots \right] \quad (4.21)$$

There are two diagrams of two vertices each containing five phonons.

The expression of Diagram (3.5) is

$$F(3.5) = -\frac{1}{\beta} \frac{(-\beta)^2}{2!} \times 120 \times 1 \sum_{1,2,3,4,5} V(1,2,3,4,5) V(-1,-2,-3,-4,-5)$$

$$\sum_{\eta_1, \eta_2, \eta_3, \eta_4} G(1, i\omega_{\eta_1}) G(2, i\omega_{\eta_2}) G(3, i\omega_{\eta_3}) G(4, i\omega_{\eta_4}) G(5, -i\omega_{\eta_1} - i\omega_{\eta_2} - i\omega_{\eta_3} - i\omega_{\eta_4})$$

The high temperature limit expression is:

$$F(3.5) = -\frac{(K_B T)^4}{240 N^3} \sum_{1,2,3,4,5} \frac{\Delta(K_1+K_2+K_3+K_4+K_5) \phi(1,2,3,4,5) \phi(-1,-2,-3,-4,-5)}{\omega_1^2 \omega_2^2 \omega_3^2 \omega_4^2 \omega_5^2}$$

$$\left[1 + \chi(3.5) + \dots \right] \quad (4.22)$$

The contribution of the last of the two vertex diagrams (3.6) is given by:

$$F(3.6) = -\frac{1}{\beta} \frac{(-\beta)^2}{2!} \times 600 \times 1 \sum_{1,2,3,4,5} V(1,-1,3,4,5) V(2,-2,-3,-4,-5)$$

$$\sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(1, i\omega_{\eta_1}) G(2, i\omega_{\eta_2}) G(3, i\omega_{\eta_3}) G(4, i\omega_{\eta_4}) G(5, -i\omega_{\eta_3} - i\omega_{\eta_4})$$

The high temperature limit is:

$$F(3.6) = -\frac{(K_B T)^4}{48 N^3} \sum_{1,2,3,4,5} \frac{\Delta(K_3+K_4+K_5) \phi(1,-1,3,4,5) \phi(2,-2,-3,-4,-5)}{\omega_1^2 \omega_2^2 \omega_3^2 \omega_4^2 \omega_5^2}$$

$$\left[1 + \frac{\hbar^2}{6(K_B T)^2} \omega_1^2 + \chi(3.6) + \dots \right] \quad (4.23)$$

The eleven diagrams which contribute to the third order can be evaluated similarly. There are four of the three-vertex diagrams each containing four phonons. The contribution of diagram (3.7) is:

$$F(3.7) = -\frac{1}{\beta} \frac{(-\beta)^3}{3!} \times 1728 \times 1 \sum_{\substack{K_1, K_2, K_3, K_4 \\ j_1, j_2, j_3, j_4, j_5, j_6}} V(K_1 j_1, -K_1 j_1, -K_4 j_4, K_4 j_5)$$

$$V(K_2 j_2, -K_2 j_2, -K_4 j_5, +K_4 j_6) V(K_3 j_3, -K_3 j_3, -K_4 j_6, -K_4 j_4)$$

$$\sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(\underline{k}_1 \dot{\eta}_1, i\omega_{\eta_1}) G(\underline{k}_2 \dot{\eta}_2, i\omega_{\eta_2}) G(\underline{k}_3 \dot{\eta}_3, i\omega_{\eta_3})$$

$$G(\underline{k}_4 \dot{\eta}_4, i\omega_{\eta_4}) G(\underline{k}_5 \dot{\eta}_5, i\omega_{\eta_5}) G(\underline{k}_6 \dot{\eta}_6, i\omega_{\eta_6})$$

After substituting for the propagators, expanding the result and performing the summations of η we find

$$F(3.7) = \frac{(K_B T)^4}{48 N^3} \sum_{\substack{\underline{k}_1 \underline{k}_2 \underline{k}_3 \underline{k}_4 \\ \dot{\eta}_1 \dot{\eta}_2 \dot{\eta}_3 \dot{\eta}_4 \dot{\eta}_5 \dot{\eta}_6}} \frac{\phi(\underline{k}_1 \dot{\eta}_1, -\underline{k}_1 \dot{\eta}_1, -\underline{k}_4 \dot{\eta}_4, \underline{k}_4 \dot{\eta}_5) \phi(\underline{k}_2 \dot{\eta}_2, -\underline{k}_2 \dot{\eta}_2, -\underline{k}_4 \dot{\eta}_5, \underline{k}_4 \dot{\eta}_6)}{\omega^2(\underline{k}_1 \dot{\eta}_1) \omega^2(\underline{k}_2 \dot{\eta}_2) \omega^2(\underline{k}_3 \dot{\eta}_3) \omega^2(\underline{k}_4 \dot{\eta}_4) \omega^2(\underline{k}_5 \dot{\eta}_5) \omega^2(\underline{k}_6 \dot{\eta}_6)} \\ \phi(\underline{k}_3 \dot{\eta}_3, -\underline{k}_3 \dot{\eta}_3, -\underline{k}_4 \dot{\eta}_6, \underline{k}_4 \dot{\eta}_4) \\ \left[1 + \frac{\hbar^2}{4 (K_B T)^2} \omega^2(\underline{k}_1 \dot{\eta}_1) + X(3.7) + \dots \right] \quad (4.24)$$

From diagram (3.8), its contribution has been found as:

$$F(3.8) = -\frac{1}{\beta} \frac{(-\beta)^3}{3!} \times 864 \times 3 \sum_{\substack{\underline{k}_1 \underline{k}_2 \underline{k}_3 \underline{k}_4 \\ \dot{\eta}_1 \dot{\eta}_2 \dot{\eta}_3 \dot{\eta}_4 \dot{\eta}_5 \dot{\eta}_6}} V(\underline{k}_1 \dot{\eta}_1, -\underline{k}_1 \dot{\eta}_1, \underline{k}_2 \dot{\eta}_2, -\underline{k}_2 \dot{\eta}_3) V(-\underline{k}_2 \dot{\eta}_2, \underline{k}_2 \dot{\eta}_3, \underline{k}_4 \dot{\eta}_4, -\underline{k}_4 \dot{\eta}_5) \\ V(-\underline{k}_4 \dot{\eta}_4, \underline{k}_4 \dot{\eta}_5, \underline{k}_6 \dot{\eta}_6, -\underline{k}_6 \dot{\eta}_6)$$

$$\sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(\underline{k}_1 \dot{\eta}_1, i\omega_{\eta_1}) G(\underline{k}_2 \dot{\eta}_2, i\omega_{\eta_2}) G(\underline{k}_3 \dot{\eta}_3, -i\omega_{\eta_2}) G(\underline{k}_4 \dot{\eta}_4, i\omega_{\eta_3}) \\ G(\underline{k}_5 \dot{\eta}_5, -i\omega_{\eta_3}) G(\underline{k}_6 \dot{\eta}_6, i\omega_{\eta_4})$$

The factors 864 and 3 denote the number of pairing schemes and the topologically equivalent diagrams. Substituting for the propagators and performing the summations in exactly the same manner as in the previous diagrams, we find:

$$F(3.8) = \frac{(K_B T)^4}{32 N^3} \sum_{\substack{K_1 K_2 K_4 K_6 \\ j_1 j_2 j_3 j_4 j_5 j_6}} \frac{\phi(K_{j_1}, -K_{j_1}, K_{j_2}, -K_{j_2}, K_{j_3}, -K_{j_3}) \phi(-K_{j_2}, K_{j_2}, K_{j_4}, -K_{j_4}) \phi(-K_{j_4}, K_{j_4}, K_{j_5}, -K_{j_5}) \phi(-K_{j_5}, K_{j_5}, K_{j_6}, -K_{j_6})}{\omega^2(K_{j_1}) \omega^2(K_{j_2}) \omega^2(K_{j_3}) \omega^2(K_{j_4}) \omega^2(K_{j_5}) \omega^2(K_{j_6})} \\ \left[1 + \frac{\hbar^2}{6(K_B T)^2} \omega^2(K_{j_1}) + X(3.8) + \dots \right] \quad (4.25)$$

The corresponding contribution to the free energy for diagram (3.9) is:

$$F(3.9) = -\frac{1}{\beta} \frac{(-\beta)^3}{3!} \times 1152 \times 3 \sum_{\substack{K_1 K_2 K_4 K_5 K_6 \\ j_1 j_2 j_3 j_4 j_5 j_6}} V(K_{j_1}, -K_{j_1}, K_{j_2}, -K_{j_2}, K_{j_3}, -K_{j_3}) V(-K_{j_2}, K_{j_2}, K_{j_4}, -K_{j_4}, K_{j_5}, -K_{j_5}) \\ V(K_{j_3}, -K_{j_3}, K_{j_4}, -K_{j_4}, K_{j_5}, -K_{j_5}, K_{j_6}, -K_{j_6}) \\ \sum_{i_1 i_2 i_3 i_4} G(K_{j_1}, i_1, i_1, \omega_{i_1}) G(K_{j_2}, i_2, i_2, \omega_{i_2}) G(K_{j_4}, i_4, i_4, \omega_{i_4}) G(K_{j_5}, i_5, i_5, \omega_{i_5}) G(K_{j_6}, i_6, i_6, -i\omega_{i_2} - i\omega_{i_3} - i\omega_{i_4}) \\ G(K_{j_3}, -i\omega_{i_2})$$

Following the same procedure, we can write the high temperature expression as:

$$F(3.9) = \frac{(K_B T)^4}{24 N^3} \sum_{\substack{K_1 K_2 K_4 K_5 K_6 \\ j_1 j_2 j_3 j_4 j_5 j_6}} \frac{\Delta(-K_{j_2} + K_{j_4} + K_{j_5} + K_{j_6}) \phi(K_{j_1}, -K_{j_1}, K_{j_2}, -K_{j_2}, K_{j_3}, -K_{j_3}) \phi(-K_{j_2}, K_{j_2}, K_{j_4}, -K_{j_4}, K_{j_5}, -K_{j_5}) \phi(K_{j_3}, -K_{j_3}, K_{j_4}, -K_{j_4}, K_{j_5}, -K_{j_5}, K_{j_6}, -K_{j_6})}{\omega^2(K_{j_1}) \omega^2(K_{j_2}) \omega^2(K_{j_3}) \omega^2(K_{j_4}) \omega^2(K_{j_5}) \omega^2(K_{j_6})} \\ \phi(K_{j_3}, -K_{j_3}, -K_{j_4}, -K_{j_4}, -K_{j_5}, -K_{j_5}, -K_{j_6}, -K_{j_6}) \\ \left[1 + \frac{\hbar^2}{12(K_B T)^2} \omega^2(K_{j_1}) + X(3.9) + \dots \right] \quad (4.26)$$

The contribution from the fourth of the three-vertex diagram is:

$$F(3.10) = -\frac{1}{\beta} \frac{(-\beta)^3}{3!} \times 1728 \times 1 \sum_{1,2,3,4,5,6} V(1,-2,3,-4) V(-1,2,-5,6) V(-3,4,5,-6)$$

$$\sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(1, i\omega_{\eta_1}) G(2, i\omega_{\eta_2}) G(3, i\omega_{\eta_3}) G(4, i\omega_{\eta_1} - i\omega_{\eta_2} + i\omega_{\eta_3})$$

$$G(5, i\omega_{\eta_4}) G(6, i\omega_{\eta_1} - i\omega_{\eta_2} + i\omega_{\eta_4})$$

The factors 1728 and 1 are the pairing schemes and topologically equivalent factor. Performing the summations over $\eta_1, \eta_2, \eta_3, \eta_4$ we find

$$F(3.10) = \frac{(k_B T)^4}{48 N^3} \sum_{1,2,3,4,5,6} \frac{\Delta(k_1 - k_2 + k_3 - k_4) \Delta(-k_1 + k_2 - k_5 + k_6) \phi(1, -2, 3, -4) \phi(-1, 2, -5, 6)}{\omega_1^2 \omega_2^2 \omega_3^2 \omega_4^2 \omega_5^2 \omega_6^2} \phi(-3, 4, 5, -6)$$

$$\left[1 + X(3.10) + \dots \right] \quad (4.27)$$

There are four diagrams from the $V_3 - V_4 - V_5$ term contribute to the free energy. The contribution from diagram (3.11) is given by:

$$F(3.11) = -\frac{1}{\beta} \frac{(-\beta)^3}{3!} \times 720 \times 6 \sum_{\substack{k_1, k_2, k_4, k_5, k_6 \\ j_1, j_2, j_3, j_4, j_5, j_6}} V(k_1 j_1, -k_1 j_1, k_2 j_2, -k_2 j_2) V(-k_2 j_2, k_2 j_2, k_4 j_4, -k_4 j_4) V(k_5 j_5, -k_5 j_5, k_6 j_6, -k_6 j_6)$$

$$\sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(k_1 j_1, i\omega_{\eta_1}) G(k_2 j_2, i\omega_{\eta_2}) G(k_2 j_3, -i\omega_{\eta_2}) G(k_4 j_4, i\omega_{\eta_3})$$

$$G(k_5 j_5, i\omega_{\eta_4}) G(k_6 j_6, -i\omega_{\eta_3} - i\omega_{\eta_4})$$

The pairing schemes and the topologically equivalent diagrams are 720 and 6, respectively. Substituting from the Fourier coefficients and expanding the series performing the summations over η we get:

$$F(3.11) = \frac{(K_B T)^4}{24 N^3} \sum_{\substack{K_1 K_2 K_4 K_5 K_6 \\ j_1 j_2 j_3 j_4 j_5 j_6}} \frac{\Delta(K_4 + K_5 + K_6) \phi(K_1 j_1, -K_1 j_1, K_2 j_2, -K_2 j_2) \phi(-K_2 j_2, K_2 j_2, K_4 j_4, K_5 j_5, K_6 j_6)}{\omega^2(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_2 j_3) \omega^2(K_4 j_4) \omega^2(K_5 j_5) \omega^2(K_6 j_6)} \phi(-K_4 j_4, -K_5 j_5, -K_6 j_6)$$

$$\left[1 + \frac{\hbar^2}{12 (K_B T)^2} \omega^2(K_1 j_1) + \chi(3.11) + \dots \right] \quad (4.28)$$

Evaluating the contributions coming from diagram (3.12) we find

$$F(3.12) = -\frac{1}{\beta} \frac{(\beta)^3}{3!} \times 2160 \times 6 \sum_{\substack{K_1 K_2 K_4 K_5 K_6 \\ j_1 j_2 j_3 j_4 j_5 j_6}} V(K_1 j_1, K_2 j_2, -K_2 j_3, -K_1 j_1) V(-K_2 j_2, K_4 j_4, K_5 j_5) V(-K_2 j_3, -K_4 j_4, -K_5 j_5, K_6 j_6, -K_6 j_6)$$

$$\sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(K_1 j_1, i\omega_{\eta_1}) G(K_2 j_2, i\omega_{\eta_2}) G(K_2 j_3, -i\omega_{\eta_2}) G(K_4 j_4, i\omega_{\eta_3})$$

$$G(K_5 j_5, -i\omega_{\eta_2} - i\omega_{\eta_3}) G(K_6 j_6, i\omega_{\eta_4})$$

We can perform the summations as before and the result is:

$$F(3.12) = \frac{(K_B T)^4}{8 N^3} \sum_{\substack{K_1 K_2 K_4 K_5 K_6 \\ j_1 j_2 j_3 j_4 j_5 j_6}} \frac{\Delta(K_2 + K_4 + K_5) \phi(K_1 j_1, -K_1 j_1, K_2 j_2, -K_2 j_3) \phi(-K_2 j_2, K_4 j_4, K_5 j_5)}{\omega^2(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_2 j_3) \omega^2(K_4 j_4) \omega^2(K_5 j_5) \omega^2(K_6 j_6)} \phi(-K_2 j_3, -K_4 j_4, -K_5 j_5, K_6 j_6, -K_6 j_6)$$

$$\left[1 + \frac{\hbar^2}{12 (K_B T)^2} \{ \omega^2(K_1 j_1) + \omega^2(K_6 j_6) \} + \chi(3.12) + \dots \right] \quad (4.29)$$

It can be shown that the contribution for diagram (3.13) is:

$$F(3.13) = -\frac{1}{\beta} \frac{(-\beta)^3}{3!} \times 2160 \times 6 \sum_{1,2,3,4,5,6} V(1,-1,2,3,4) V(-2,-3,5,6) V(-4,-5,-6)$$

$$\sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(1, i\omega_{\eta_1}) G(2, i\omega_{\eta_2}) G(3, i\omega_{\eta_3}) G(4, -i\omega_{\eta_2} - i\omega_{\eta_3})$$

$$G(5, i\omega_{\eta_4}) G(6, i\omega_{\eta_2} + i\omega_{\eta_3} - i\omega_{\eta_4})$$

Performing the summations over η we find:

$$F(3.13) = \frac{(K_B T)^4}{8N^3} \sum_{1,2,3,4,5,6} \frac{\Delta(K_2+K_3+K_4) \Delta(K_4+K_5+K_6) \phi(1,-1,2,3,4) \phi(-2,-3,5,6) \phi(-4,-5,-6)}{\omega_1^2 \omega_2^2 \omega_3^2 \omega_4^2 \omega_5^2 \omega_6^2}$$

$$\left[1 + \frac{\hbar^2}{12(K_B T)^2} \omega_1^2 + X(3.13) + \dots \right] \quad (4.30)$$

The expression corresponding to diagram (3.14) can be worked out to give:

$$F(3.14) = -\frac{1}{\beta} \frac{(-\beta)^3}{3!} \times 1440 \times 6 \sum_{1,2,3,4,5,6} V(1,2,3) V(-1,-2,4,5,6) V(-3,-4,-5,-6)$$

$$\sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(1, i\omega_{\eta_1}) G(2, i\omega_{\eta_2}) G(3, -i\omega_{\eta_1} - i\omega_{\eta_2}) G(4, i\omega_{\eta_3})$$

$$G(5, i\omega_{\eta_4}) G(6, i\omega_{\eta_1} + i\omega_{\eta_2} - i\omega_{\eta_3} - i\omega_{\eta_4})$$

Substituting for Green's functions, expanding the resultant series and summing over η we find:

$$F(3.14) = \frac{(k_B T)^4}{12 N^3} \sum_{1,2,3,4,5,6} \frac{\Delta(k_1+k_2+k_3) \Delta(k_3+k_4+k_5+k_6) \phi(1,2,3) \phi(-1,-2,4,5,6) \phi(-3,-4,-5,-6)}{\omega_1^2 \omega_2^2 \omega_3^2 \omega_4^2 \omega_5^2 \omega_6^2}$$

$$\left[1 + X(3.14) + \dots \right] \quad (4.31)$$

Each of the remaining three-vertex diagrams contains two vertices with three phonons each and one with six phonons. The contribution to the free energy of the first diagram of these is given by:

$$F(3.15) = -\frac{1}{\beta} \frac{(-\beta)^3}{3!} \times 720 \times 3 \sum_{1,2,3,4,5,6} V(1,2,3) V(-1,-2,-3,4,5,6) V(-4,-5,-6)$$

$$\sum_{n_1 n_2 n_3 n_4} G(1, i\omega_{n_1}) G(2, i\omega_{n_2}) G(3, -i\omega_{n_1} - i\omega_{n_2}) G(4, i\omega_{n_3}) \\ G(5, i\omega_{n_4}) G(6, -i\omega_{n_3} - i\omega_{n_4})$$

The factors 720 and 3 are as usual the pairing schemes and the topological factor. Performing the summations, we get:

$$F(3.15) = \frac{(k_B T)^4}{72 N^3} \sum_{1,2,3,4,5,6} \frac{\Delta(k_1+k_2+k_3) \Delta(k_4+k_5+k_6) \phi(1,2,3) \phi(-1,-2,-3,4,5,6) \phi(-4,-5,-6)}{\omega_1^2 \omega_2^2 \omega_3^2 \omega_4^2 \omega_5^2 \omega_6^2}$$

$$\left[1 + X(3.15) + \dots \right] \quad (4.32)$$

The contributions from diagram (3.16) can be carried out to give the following expression:

$$F(3.16) = -\frac{1}{\beta} \frac{(-\beta)^3}{3!} \times 1620 \times 3 \sum_{\substack{K_1 K_2 K_3 K_5 K_6 \\ i_1 i_2 i_3 i_4 i_5 i_6}} V(K_1 i_1, -K_1 i_1, K_2 i_2, -K_2 i_2, K_3 i_3, -K_3 i_3, K_4 i_4, -K_4 i_4) \\ V(K_3 i_3, K_5 i_5, K_6 i_6) V(-K_3 i_4, -K_5 i_5, -K_6 i_6) \\ \sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(K_1 i_1, i\omega_{\eta_1}) G(K_2 i_2, i\omega_{\eta_2}) G(K_3 i_3, i\omega_{\eta_3}) G(K_4 i_4, i\omega_{\eta_4}) \\ G(K_5 i_5, i\omega_{\eta_5}) G(K_6 i_6, -i\omega_{\eta_2} - i\omega_{\eta_3})$$

Carrying out the summations over η 's we get:

$$F(3.16) = \frac{(K_B T)^4}{32 N^3} \sum_{\substack{K_1 K_2 K_3 K_5 K_6 \\ i_1 i_2 i_3 i_4 i_5 i_6}} \frac{\Delta(K_3 + K_4 + K_5) \phi(K_1 i_1, -K_1 i_1, K_2 i_2, -K_2 i_2, K_3 i_3, -K_3 i_3, K_4 i_4, -K_4 i_4)}{\omega^2(K_1 i_1) \omega^2(K_2 i_2) \omega^2(K_3 i_3) \omega^2(K_4 i_4) \omega^2(K_5 i_5) \omega^2(K_6 i_6)} \\ \phi(K_3 i_3, K_5 i_5, K_6 i_6) \phi(-K_3 i_4, -K_5 i_5, -K_6 i_6) \\ \left[1 + \frac{\hbar^2}{6 (K_B T)^2} \omega^2(K_1 i_1) + X(3.16) + \dots \right] \quad (4.33)$$

The contribution of the last of the three-vertex diagrams is given by:

$$F(3.17) = -\frac{1}{\beta} \frac{(-\beta)^3}{3!} \times 3240 \times 3 \sum_{1,2,3,4,5,6} V(1, -1, -2, -3, 4, 5) V(2, 3, 6) V(-4, -5, -6) \\ \sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(1, i\omega_{\eta_1}) G(2, i\omega_{\eta_2}) G(3, i\omega_{\eta_3}) G(4, i\omega_{\eta_4}) G(5, i\omega_{\eta_2} + i\omega_{\eta_3} - i\omega_{\eta_4}) \\ G(6, -i\omega_{\eta_2} - i\omega_{\eta_3})$$

Substituting for the various propagators appearing in the above equation, expanding the expression and performing the summations over η 's we get:

$$F(3.17) = \frac{(k_B T)^4}{16N^3} \sum_{1,2,3,4,5,6} \frac{\Delta(\underline{k}_2 + \underline{k}_3 + \underline{k}_6) \Delta(\underline{k}_4 + \underline{k}_5 + \underline{k}_6) \phi(1, -1, -2, -3, 4, 5) \phi(2, 3, 6)}{\omega_1^2 \omega_2^2 \omega_3^2 \omega_4^2 \omega_5^2 \omega_6^2} \phi(-4, -5, -6)$$

$$\left[1 + \frac{\hbar^2}{12 (k_B T)^2} \omega_1^2 + X(3.17) + \dots \right] \quad (4.34)$$

There are thirteen diagrams of the fourth order. Four of them contain three vertices each with three phonons and one vertex with five phonons.

The contribution of the first diagram is given by:

$$F(3.18) = -\frac{1}{\beta} \frac{(-\beta)^4}{4!} \times 3240 \times 24 \sum_{\substack{\underline{k}_1, \underline{k}_2, \underline{k}_3, \underline{k}_4, \underline{k}_5, \underline{k}_6, \underline{k}_7 \\ j_1, j_2, j_3, j_4, j_5, j_6, j_7}} V(\underline{k}_1^{j_1}, -\underline{k}_1^{j_1}, \underline{k}_2^{j_2}, \underline{k}_3^{j_3}, \underline{k}_4^{j_4}) \\ V(-\underline{k}_3^{j_3}, -\underline{k}_4^{j_4}, -\underline{k}_2^{j_2}) V(-\underline{k}_2^{j_2}, -\underline{k}_6^{j_6}, -\underline{k}_7^{j_7}) V(\underline{k}_2^{j_2}, \underline{k}_6^{j_6}, \underline{k}_7^{j_7}) \\ \sum_{\eta_1, \eta_2, \eta_3, \eta_4} G(\underline{k}_1^{j_1}, i\omega_{\eta_1}) G(\underline{k}_2^{j_2}, i\omega_{\eta_2}) G(\underline{k}_3^{j_3}, i\omega_{\eta_3}) G(\underline{k}_4^{j_4}, -i\omega_{\eta_2} - i\omega_{\eta_3}) \\ G(\underline{k}_5^{j_5}, i\omega_{\eta_2}) G(\underline{k}_6^{j_6}, i\omega_{\eta_4}) G(\underline{k}_7^{j_7}, -i\omega_{\eta_2} - i\omega_{\eta_4})$$

Where the factors 3240 and 24 are the pairing schemes and the topologically equivalent factor. When eq. (4.2) is substituted for the various propagators appearing in the above equation with different arguments and the product is resolved into partial fractions, a total of thirty terms have to be summed over η_1, η_2, η_3 and η_4 . Expanding each term and performing the summations we find:

$$\begin{aligned}
F(3.18) = & -\frac{(K_B T)^4}{8N^3} \sum_{\substack{K_1 K_2 K_3 K_4 K_6 K_7 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7}} \frac{\Delta(K_1 + K_2 + K_3) \Delta(K_4 + K_6 + K_7) \phi(K_1 j_1, -K_1 j_1, K_2 j_2, K_3 j_3, K_4 j_4)}{\omega(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_3 j_3) \omega^2(K_4 j_4) \omega^2(K_5 j_5) \omega^2(K_6 j_6) \omega^2(K_7 j_7)} \\
& \phi(-K_3 j_3, -K_4 j_4, -K_5 j_5) \phi(-K_2 j_2, -K_6 j_6, -K_7 j_7) \phi(K_2 j_5, K_6 j_6, K_7 j_7) \\
& \left[1 + \frac{\hbar^2}{12(K_B T)^2} \omega^2(K_1 j_1) + \chi(3.18) + \dots \right] \quad (4.35)
\end{aligned}$$

The contribution from the second four-vertex diagrams is:

$$\begin{aligned}
F(3.19) = & -\frac{1}{\beta} \frac{(-\beta)^4}{4!} \times 2160 \times 12 \sum_{\substack{K_1 K_2 K_3 K_4 K_6 K_7 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7}} V(K_1 j_1, K_2 j_2, K_3 j_3) V(-K_1 j_1, -K_2 j_2, -K_3 j_3, K_4 j_4, -K_4 j_4) \\
& V(K_4 j_5, K_6 j_6, K_7 j_7) V(-K_4 j_4, -K_6 j_6, -K_7 j_7) \\
& \sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(K_1 j_1, i\omega_{\eta_1}) G(K_2 j_2, i\omega_{\eta_2}) G(K_3 j_3, -i\omega_{\eta_1} - i\omega_{\eta_2}) G(K_4 j_4, i\omega_{\eta_3}) \\
& G(K_4 j_5, i\omega_{\eta_3}) G(K_6 j_6, i\omega_{\eta_4}) G(K_7 j_7, -i\omega_{\eta_3} - i\omega_{\eta_4})
\end{aligned}$$

Performing the summations over η 's we find:

$$\begin{aligned}
F(3.19) = & -\frac{(K_B T)^4}{24N^3} \sum_{\substack{K_1 K_2 K_3 K_4 K_6 K_7 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7}} \frac{\Delta(K_1 + K_2 + K_3) \Delta(K_4 + K_6 + K_7) \phi(K_1 j_1, K_2 j_2, K_3 j_3) \phi(-K_1 j_1, -K_2 j_2, -K_3 j_3, K_4 j_4, K_4 j_5)}{\omega^2(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_3 j_3) \omega^2(K_4 j_4) \omega^2(K_4 j_5) \omega^2(K_6 j_6) \omega^2(K_7 j_7)} \\
& \phi(K_4 j_5, K_6 j_6, K_7 j_7) \phi(-K_4 j_4, -K_6 j_6, -K_7 j_7) \\
& \left[1 + \chi(3.19) + \dots \right] \quad (4.36)
\end{aligned}$$

The contribution from diagram (3.20) is given by:

$$\begin{aligned}
F(3.20) = & -\frac{1}{\beta} \frac{(-\beta)^4}{4!} \times 6480 \times 12 \sum_{1,2,3,4,5,6,7} V(1,2,5) V(-5,6,7) V(-1,-2,-7,3,4) \\
& V(-3,-4,-6)
\end{aligned}$$

$$\sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(1, i\omega_{\eta_1}) G(2, i\omega_{\eta_2}) G(3, i\omega_{\eta_3}) G(4, i\omega_{\eta_4}) G(5, -i\omega_{\eta_1} - i\omega_{\eta_2}) \\ G(6, -i\omega_{\eta_3} - i\omega_{\eta_4}) G(7, -i\omega_{\eta_1} - i\omega_{\eta_2} + i\omega_{\eta_3} + i\omega_{\eta_4})$$

The high temperature expansion is:

$$F(3.20) = -\frac{(K_B T)^4}{16 N^3} \sum_{1,2,3,4,5,6,7} \frac{\Delta(K_1 + K_2 + K_5) \Delta(K_3 + K_4 + K_6) \Delta(-K_5 + K_6 + K_7) \phi(1,2,5) \phi(-5,6,7)}{\omega_1^2 \omega_2^2 \omega_3^2 \omega_4^2 \omega_5^2 \omega_6^2 \omega_7^2} \\ \phi(-1,-2,3,4,-7) \phi(-3,-4,-6) \\ [1 + X(3.20) + \dots] \quad (4.37)$$

For diagram (3.21), the contribution is:

$$F(3.21) = -\frac{1}{\beta} \frac{(K_B T)^4}{4!} \times 12960 \times 4 \sum_{1,2,3,4,5,6,7} V(1,-1,2,3,4) V(-2,5,6) V(-3,-5,7) V(-4,-6,-7) \\ \sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(1, i\omega_{\eta_1}) G(2, i\omega_{\eta_2}) G(3, i\omega_{\eta_3}) G(4, -i\omega_{\eta_2} - i\omega_{\eta_3}) G(5, i\omega_{\eta_4}) \\ G(6, -i\omega_{\eta_2} - i\omega_{\eta_4}) G(7, i\omega_{\eta_3} + i\omega_{\eta_4})$$

Substituting for the propagators and performing the summations we get:

$$F(3.21) = -\frac{(K_B T)^4}{12 N^3} \sum_{1,2,3,4,5,6,7} \frac{\Delta(K_2 + K_3 + K_7) \Delta(-K_2 + K_5 + K_6) \Delta(-K_3 - K_5 + K_7) \phi(1,-1,2,3,4)}{\omega_1^2 \omega_2^2 \omega_3^2 \omega_4^2 \omega_5^2 \omega_6^2 \omega_7^2} \\ \phi(-2,5,6) \phi(-3,-5,7) \phi(-4,-6,-7) \\ [1 + \frac{\hbar^2}{12 (K_B T)^2} \omega_1^2 + X(3.21) + \dots] \quad (4.38)$$

Nine diagrams from $V_3 - V_3 - V_4 - V_4$ term contribute. The contribution from diagram F(3.22) is given by:

$$\begin{aligned}
 F(3.22) = & -\frac{1}{\beta} \frac{(-\beta)^4}{4!} \times 2592 \times 12 \sum_{\substack{\vec{k}_1, \vec{k}_2, \vec{k}_4, \vec{k}_6, \vec{k}_7 \\ \vec{d}_1, \vec{d}_2, \vec{d}_3, \vec{d}_4, \vec{d}_5, \vec{d}_6, \vec{d}_7}} V(\vec{k}_1 \vec{d}_1, -\vec{k}_1 \vec{d}_1, \vec{k}_2 \vec{d}_2, -\vec{k}_2 \vec{d}_2) \\
 & V(-\vec{k}_2 \vec{d}_2, \vec{k}_2 \vec{d}_3, \vec{k}_4 \vec{d}_4, -\vec{k}_4 \vec{d}_5) V(\vec{k}_4 \vec{d}_5, \vec{k}_6 \vec{d}_6, \vec{k}_7 \vec{d}_7) V(-\vec{k}_4 \vec{d}_4, -\vec{k}_6 \vec{d}_6, -\vec{k}_7 \vec{d}_7) \\
 & \sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(\vec{k}_1 \vec{d}_1, i\omega_{\eta_1}) G(\vec{k}_2 \vec{d}_2, i\omega_{\eta_2}) G(\vec{k}_3 \vec{d}_3, i\omega_{\eta_2}) G(\vec{k}_4 \vec{d}_4, i\omega_{\eta_3}) \\
 & G(\vec{k}_4 \vec{d}_5, i\omega_{\eta_3}) G(\vec{k}_6 \vec{d}_6, i\omega_{\eta_4}) G(\vec{k}_7 \vec{d}_7, -i\omega_{\eta_3} - i\omega_{\eta_4})
 \end{aligned}$$

The pairing schemes and the topologically equivalent factors are 2592 and 12 respectively. Resolving the product into partial functions, we find a total of twenty terms which can be expanded and summed over all η . Finally we find:

$$\begin{aligned}
 F(3.22) = & -\frac{(k_B T)^4}{16N^3} \sum_{\substack{\vec{k}_1, \vec{k}_2, \vec{k}_4, \vec{k}_6, \vec{k}_7 \\ \vec{d}_1, \vec{d}_2, \vec{d}_3, \vec{d}_4, \vec{d}_5, \vec{d}_6, \vec{d}_7}} \frac{\Delta(\vec{k}_4 + \vec{k}_6 + \vec{k}_7) \phi(\vec{k}_1 \vec{d}_1, -\vec{k}_1 \vec{d}_1, \vec{k}_2 \vec{d}_2, -\vec{k}_2 \vec{d}_3) \phi(-\vec{k}_2 \vec{d}_2, \vec{k}_2 \vec{d}_3, \vec{k}_4 \vec{d}_4, -\vec{k}_4 \vec{d}_5)}{\omega^2(\vec{k}_1 \vec{d}_1) \omega^2(\vec{k}_2 \vec{d}_2) \omega^2(\vec{k}_2 \vec{d}_3) \omega^2(\vec{k}_4 \vec{d}_4) \omega^2(\vec{k}_4 \vec{d}_5) \omega^2(\vec{k}_6 \vec{d}_6) \omega^2(\vec{k}_7 \vec{d}_7)} \\
 & \phi(\vec{k}_4 \vec{d}_5, \vec{k}_6 \vec{d}_6, \vec{k}_7 \vec{d}_7) \phi(-\vec{k}_4 \vec{d}_4, -\vec{k}_6 \vec{d}_6, -\vec{k}_7 \vec{d}_7)
 \end{aligned}$$

$$\left[1 + \frac{\hbar^2}{12 (k_B T)^2} \omega^2(\vec{k}_1 \vec{d}_1) + \chi(3.22) + \dots \right] \quad (4.39)$$

The contribution from diagram (3.23) is given by:

$$\begin{aligned}
 F(3.23) = & -\frac{1}{\beta} \frac{(-\beta)^4}{4!} \times 2592 \sum_{\substack{\tilde{\kappa}_1, \tilde{\kappa}_2, \tilde{\kappa}_4, \tilde{\kappa}_5, \tilde{\kappa}_6, \tilde{\kappa}_7 \\ j_1, j_2, j_3, j_4, j_5, j_6, j_7}} V(\tilde{\kappa}_1 j_1, -\tilde{\kappa}_1 j_1, \tilde{\kappa}_2 j_2, -\tilde{\kappa}_2 j_2) V(\tilde{\kappa}_3 j_3, \tilde{\kappa}_4 j_4, \tilde{\kappa}_5 j_5) \\
 & V(-\tilde{\kappa}_2 j_2, -\tilde{\kappa}_6 j_6, -\tilde{\kappa}_7 j_7) V(-\tilde{\kappa}_4 j_4, -\tilde{\kappa}_5 j_5, \tilde{\kappa}_6 j_6, \tilde{\kappa}_7 j_7) \\
 & \sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(\tilde{\kappa}_1 j_1, i\omega_{\eta_1}) G(\tilde{\kappa}_2 j_2, i\omega_{\eta_2}) G(\tilde{\kappa}_3 j_3, i\omega_{\eta_2}) G(\tilde{\kappa}_4 j_4, i\omega_{\eta_3}) \\
 & G(\tilde{\kappa}_5 j_5, -i\omega_{\eta_2} - i\omega_{\eta_3}) G(\tilde{\kappa}_6 j_6, i\omega_{\eta_4}) G(\tilde{\kappa}_7 j_7, -i\omega_{\eta_2} - i\omega_{\eta_4})
 \end{aligned}$$

The high temperature expansion has been derived in the following form:

$$\begin{aligned}
 F(3.23) = & -\frac{(k_B T)^4}{16 \omega^3} \sum_{\substack{\tilde{\kappa}_1, \tilde{\kappa}_2, \tilde{\kappa}_4, \tilde{\kappa}_5, \tilde{\kappa}_6, \tilde{\kappa}_7 \\ j_1, j_2, j_3, j_4, j_5, j_6, j_7}} \frac{\Delta(\tilde{\kappa}_2 + \tilde{\kappa}_4 + \tilde{\kappa}_5) \Delta(\tilde{\kappa}_2 + \tilde{\kappa}_6 + \tilde{\kappa}_7) \phi(\tilde{\kappa}_1 j_1, -\tilde{\kappa}_1 j_1, \tilde{\kappa}_2 j_2, -\tilde{\kappa}_2 j_2)}{\omega^2(\tilde{\kappa}_1 j_1) \omega^2(\tilde{\kappa}_2 j_2) \omega^2(\tilde{\kappa}_3 j_3) \omega^2(\tilde{\kappa}_4 j_4) \omega^2(\tilde{\kappa}_5 j_5) \omega^2(\tilde{\kappa}_6 j_6) \omega^2(\tilde{\kappa}_7 j_7)} \\
 & \phi(\tilde{\kappa}_2 j_3, \tilde{\kappa}_4 j_4, \tilde{\kappa}_5 j_5) \phi(\tilde{\kappa}_2 j_2, -\tilde{\kappa}_6 j_6, -\tilde{\kappa}_7 j_7) \phi(\tilde{\kappa}_4 j_4, -\tilde{\kappa}_5 j_5, \tilde{\kappa}_6 j_6, \tilde{\kappa}_7 j_7) \\
 & \left[1 + \frac{\hbar^2}{12 (k_B T)^2} \omega^2(\tilde{\kappa}_1 j_1) + X(3.23) + \dots \right] \quad (4.40)
 \end{aligned}$$

The general expression for the contribution to the free energy from diagram (3.24) can be written as:

$$F(3.24) = -\frac{1}{\beta} \frac{(-\beta)^4}{4!} \times 5184 \times 6 \sum_{\substack{K_1 K_2 K_4 K_5 K_7 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7}} V(K_1 j_1, -K_1 j_1, -K_2 j_2, K_2 j_3) V(K_2 j_2, K_4 j_4, K_5 j_5)$$

$$V(-K_2 j_3, -K_4 j_4, -K_5 j_6) V(-K_5 j_5, K_5 j_6, K_7 j_7, -K_7 j_7)$$

$$\sum_{\substack{\eta_1 \eta_2 \eta_3 \eta_4 \\ i_1 i_2 i_3 i_4}} G(K_1 j_1, i\omega_{\eta_1}) G(K_2 j_2, i\omega_{\eta_2}) G(K_2 j_3, i\omega_{\eta_2}) G(K_4 j_4, i\omega_{\eta_3}) \\ G(K_5 j_5, -i\omega_{\eta_2} - i\omega_{\eta_3}) G(K_5 j_6, -i\omega_{\eta_2} - i\omega_{\eta_3}) G(K_7 j_7, i\omega_{\eta_4})$$

Working out the summations over η 's we find:

$$F(3.24) = -\frac{(K_B T)^4}{16N^3} \sum_{\substack{K_1 K_2 K_4 K_5 K_7 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7}} \frac{\Delta(K_2 + K_4 + K_5) \phi(K_1 j_1, -K_1 j_1, -K_2 j_2, K_2 j_3) \phi(K_2 j_2, K_4 j_4, K_5 j_5)}{\omega^2(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_2 j_3) \omega^2(K_4 j_4) \omega^2(K_5 j_5) \omega^2(K_5 j_6) \omega^2(K_7 j_7)}$$

$$\phi(-K_2 j_3, -K_4 j_4, -K_5 j_6) \phi(-K_5 j_5, K_5 j_6, K_7 j_7, -K_7 j_7)$$

$$\left[1 + \frac{\hbar^2}{6 (K_B T)^2} \omega^2(K_1 j_1) + \chi(3.24) + \dots \right] \quad (4.41)$$

Similarly, the contribution from diagram (3.25) is:

$$F(3.25) = -\frac{1}{\beta} \frac{(-\beta)^4}{4!} \times 2592 \times 12 \sum_{\substack{K_1 K_2 K_3 K_6 K_7 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7}} V(K_1 j_1, -K_1 j_1, -K_3 j_3, K_3 j_4) V(K_3 j_3, K_6 j_6, K_7 j_7)$$

$$V(K_2 j_2, -K_2 j_2, -K_3 j_4, K_3 j_5) V(-K_3 j_5, -K_6 j_6, -K_7 j_7)$$

$$\sum_{\substack{\eta_1 \eta_2 \eta_3 \eta_4 \\ i_1 i_2 i_3 i_4}} G(K_1 j_1, i\omega_{\eta_1}) G(K_2 j_2, i\omega_{\eta_2}) G(K_3 j_3, i\omega_{\eta_3}) G(K_3 j_4, i\omega_{\eta_3})$$

$$G(K_3 j_5, i\omega_{\eta_3}) G(K_6 j_6, i\omega_{\eta_4}) G(K_7 j_7, -i\omega_{\eta_3} - i\omega_{\eta_4})$$

Performing the summations we get:

$$F(3.25) = -\frac{(K_8 T)^4}{16N^3} \sum_{\substack{K_1 K_2 K_3 K_4 K_5 K_6 K_7 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7}} \frac{\Delta(K_3 + K_6 + K_7) \phi(K_1 j_1, -K_1 j_1, -K_3 j_3, K_3 j_4) \phi(K_3 j_3, K_6 j_6, K_7 j_7)}{\omega^2(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_3 j_3) \omega^2(K_4 j_4) \omega^2(K_5 j_5) \omega^2(K_6 j_6) \omega^2(K_7 j_7)} \\ \phi(K_2 j_2, K_2 j_2 - K_3 j_4, K_3 j_5) \phi(-K_3 j_5, -K_6 j_6, -K_7 j_7)$$

$$\left[1 + \frac{t^2}{6(K_8 T)^2} \omega^2(K_1 j_1) + X(3.25) + \dots \right] \quad (4.42)$$

The contribution from diagram (3.26) is given by:

$$F(3.26) = -\frac{1}{\beta} \frac{(-\beta)^4}{4!} \times 5184 \times 12 \sum_{\substack{K_1 K_2 K_3 K_4 K_5 K_6 K_7 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7}} V(K_1 j_1, -K_1 j_1, K_2 j_2, -K_2 j_3) V(-K_2 j_2, -K_4 j_4, K_5 j_5, K_6 j_6) \\ V(K_2 j_3, K_4 j_4, K_7 j_7) V(-K_5 j_5, -K_6 j_6, -K_7 j_7)$$

$$\sum_{\substack{n_1 n_2 n_3 n_4 \\ 1 2 3 4}} G(K_1 j_1, i\omega_{n_1}) G(K_2 j_2, i\omega_{n_2}) G(K_2 j_3, i\omega_{n_2}) G(K_4 j_4, i\omega_{n_3})$$

$$G(K_5 j_5, i\omega_{n_4}) G(K_6 j_6, i\omega_{n_2} + i\omega_{n_3} - i\omega_{n_4})$$

$$G(K_7 j_7, -i\omega_{n_2} - i\omega_{n_3})$$

Substituting for the propagators and performing the summations we find:

$$F(3.26) = -\frac{(K_B T)^4}{4N^3} \sum_{\substack{K_1 K_2 K_4 K_5 K_6 K_7 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7}} \frac{\Delta(K_2 + K_4 + K_7) \Delta(K_5 + K_6 + K_7) \phi(K_1 j_1, -K_1 j_1, K_2 j_2, -K_2 j_2) \phi(K_3 j_3, K_4 j_4, K_7 j_7)}{\omega^2(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_3 j_3) \omega^2(K_4 j_4) \omega^2(K_5 j_5) \omega^2(K_6 j_6) \omega^2(K_7 j_7)} \\ \phi(-K_2 j_2, -K_4 j_4, K_5 j_5, K_6 j_6) \phi(-K_5 j_5, -K_6 j_6, -K_7 j_7) \\ \left[1 + \frac{\hbar^2}{12(K_B T)^2} \omega^2(K_1 j_1) + \chi(3.26) + \dots \right] \quad (4.43)$$

The free energy expression arising from diagram (3.27) is:

$$F(3.27) = -\frac{1}{\beta} \frac{(\beta)^4}{4!} \times 1728 \times 12 \sum_{\substack{K_1 K_2 K_3 K_5 K_6 K_7 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7}} V(K_1 j_1, K_2 j_2, K_3 j_3) V(-K_1 j_1, -K_2 j_2, -K_3 j_3) \\ V(K_3 j_4, K_5 j_5, K_6 j_6, K_7 j_7) V(-K_3 j_3, -K_5 j_5, -K_6 j_6, -K_7 j_7) \\ \sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(K_1 j_1, i\omega_{\eta_1}) G(K_2 j_2, -i\omega_{\eta_1} - i\omega_{\eta_2}) G(K_3 j_3, i\omega_{\eta_2}) \\ G(K_3 j_4, i\omega_{\eta_2}) G(K_5 j_5, i\omega_{\eta_3}) G(K_6 j_6, i\omega_{\eta_4}) \\ G(K_7 j_7, -i\omega_{\eta_2} - i\omega_{\eta_3} - i\omega_{\eta_4})$$

Making use of the propagators and performing the summations over η we get:

$$F(3.27) = -\frac{(K_B T)^4}{24N^3} \sum_{\substack{K_1 K_2 K_3 K_5 K_6 K_7 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7}} \frac{\Delta(K_1 + K_2 + K_3) \Delta(K_3 + K_5 + K_6 + K_7) \phi(K_1 j_1, K_2 j_2, K_3 j_3) \phi(-K_1 j_1, -K_2 j_2, -K_3 j_3)}{\omega^2(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_3 j_3) \omega^2(K_4 j_4) \omega^2(K_5 j_5) \omega^2(K_6 j_6) \omega^2(K_7 j_7)} \\ \phi(K_3 j_4, K_5 j_5, K_6 j_6, K_7 j_7) \phi(-K_3 j_3, -K_5 j_5, -K_6 j_6, -K_7 j_7) \\ \left[1 + \chi(3.27) + \dots \right] \quad (4.44)$$

The contribution from diagram (3.28) is:

$$F(3.28) = -\frac{1}{\beta} \frac{(-\beta)^4}{4!} \times 2592 \times 12 \sum_{1,2,3,4,5,6,7} V(1,2,6,7) V(-1,-2,-5) V(-3,-4,-5) \\ V(3,4,-6,-7) \\ \sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(1, i\omega_{\eta_1}) G(2, -i\omega_{\eta_1} + i\omega_{\eta_2}) G(3, i\omega_{\eta_3}) G(4, -i\omega_{\eta_2} - i\omega_{\eta_3}) \\ G(5, i\omega_{\eta_2}) G(6, i\omega_{\eta_4}) G(7, -i\omega_{\eta_2} - i\omega_{\eta_4})$$

Performing the summations over η 's we find:

$$F(3.28) = -\frac{(k_B T)^4}{16 N^3} \frac{\sum_{1,2,3,4,5,6,7} \Delta(K_1 + K_2 - K_5) \Delta(K_3 + K_4 + K_5) \Delta(K_1 + K_2 + K_6 + K_7) \phi(1,2,6,7)}{\omega_1^2 \omega_2^2 \omega_3^2 \omega_4^2 \omega_5^2 \omega_6^2 \omega_7^2} \\ \phi(-1,-2,5) \phi(-3,-4,-5) \phi(3,4,-6,-7) \\ \left[1 + \chi(3.28) + \dots \right] \quad (4.45)$$

The contribution from the eighth of the four-vertex diagrams is given by:

$$F(3.29) = -\frac{1}{\beta} \frac{(-\beta)^4}{4!} \times 10368 \times 6 \sum_{1,2,3,4,5,6,7} V(1,2,3) V(-3,4,-5) V(-2,-4,-6,-7) V(-1,5,6,7) \\ \sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(1, i\omega_{\eta_1}) G(2, i\omega_{\eta_2}) G(3, -i\omega_{\eta_1} - i\omega_{\eta_2}) G(4, i\omega_{\eta_3}) \\ G(5, i\omega_{\eta_1} + i\omega_{\eta_2} + i\omega_{\eta_3}) G(6, i\omega_{\eta_4}) G(7, -i\omega_{\eta_2} - i\omega_{\eta_3} - i\omega_{\eta_4})$$

When the summations over η 's is performed we find:

$$F(3.29) = -\frac{(k_B T)^4}{8N^3} \sum_{1,2,3,4,5,6,7} \frac{\Delta(k_1+k_2+k_3)\Delta(k_3-k_4+k_5)\Delta(-k_1+k_5+k_6+k_7)}{\omega_1^2 \omega_2^2 \omega_3^2 \omega_4^2 \omega_5^2 \omega_6^2 \omega_7^2} \phi(1,2,3)\phi(-3,4,-5) \\ \phi(-2,-4,-6,-7)\phi(-1,5,6,7) \\ \left[1 + \chi(3.29) + \dots \right] \quad (4.46)$$

The last of the four-vertex diagrams gives the following contribution to the free energy:

$$F(3.30) = -\frac{1}{\beta} \frac{(-\beta)^4}{4!} \times 5184 \times 12 \sum_{1,2,3,4,5,6,7} V(1,2,4,5)V(-1,-2,-3)V(3,-4,6,7)V(-5,-6,-7) \\ \sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(1, i\omega_{\eta_1}) G(2, i\omega_{\eta_2}) G(3, -i\omega_{\eta_1} - i\omega_{\eta_2}) G(4, i\omega_{\eta_3}) G(5, -i\omega_{\eta_1} - i\omega_{\eta_2} - i\omega_{\eta_3}) \\ G(6, i\omega_{\eta_4}) G(7, i\omega_{\eta_1} + i\omega_{\eta_2} + i\omega_{\eta_3} - i\omega_{\eta_4})$$

Substituting for the propagators and performing the summations over η 's we find:

$$F(3.30) = -\frac{(k_B T)^4}{8N^3} \sum_{1,2,3,4,5,6,7} \frac{\Delta(k_1+k_2+k_3)\Delta(k_1+k_2+k_4+k_5)\Delta(k_5+k_6+k_7)}{\omega_1^2 \omega_2^2 \omega_3^2 \omega_4^2 \omega_5^2 \omega_6^2 \omega_7^2} \phi(1,2,4,5)\phi(-1,-2,-3) \\ \phi(3,-4,6,7)\phi(-5,-6,-7) \\ \left[1 + \chi(3.30) + \dots \right] \quad (4.47)$$

There are eight diagrams of the fifth order perturbation. The contribution from the first one of them takes the form:

$$\begin{aligned}
F(3.31) = & -\frac{1}{\beta} \frac{(-\beta)^5}{5!} \times 7776 \times 15 \sum_{\substack{K_1 K_2 K_3 K_4 K_5 K_6 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7 j_8}} V(K_1 j_1, K_2 j_2, K_3 j_3) V(-K_1 j_1, -K_2 j_2, -K_3 j_3) \\
& V(-K_3 j_3, K_4 j_4, K_5 j_5, -K_5 j_6) V(K_5 j_6, K_7 j_7, K_8 j_8) V(-K_5 j_5, -K_7 j_7, -K_8 j_8) \\
& \sum_{\substack{\eta_1 \eta_2 \eta_3 \eta_4}} G(K_1 j_1, i\omega_{\eta_1}) G(K_2 j_2, i\omega_{\eta_2}) G(K_3 j_3, -i\omega_{\eta_1} - i\omega_{\eta_2}) G(K_4 j_4, -i\omega_{\eta_2} - i\omega_{\eta_3}) \\
& G(K_5 j_5, i\omega_{\eta_3}) G(K_6 j_6, i\omega_{\eta_3}) G(K_7 j_7, i\omega_{\eta_4}) G(K_8 j_8, i\omega_{\eta_3} - i\omega_{\eta_4})
\end{aligned}$$

Making use of eq. (4.2), expanding the result and performing the summations over η we find:

$$\begin{aligned}
F(3.31) = & \frac{(K_8 T)^4}{32 N^2} \sum_{\substack{K_1 K_2 K_3 K_4 K_5 K_6 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7 j_8}} \frac{\Delta(K_1 + K_2 + K_3) \Delta(K_5 + K_7 + K_8) \phi(K_1 j_1, K_2 j_2, K_3 j_3) \phi(-K_1 j_1, -K_2 j_2, -K_3 j_3)}{\omega^2(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_3 j_3) \omega^2(K_4 j_4) \omega^2(K_5 j_5) \omega^2(K_6 j_6) \omega^2(K_7 j_7) \omega^2(K_8 j_8)} \\
& \phi(-K_3 j_3, K_4 j_4, K_5 j_5, -K_5 j_6) \phi(K_5 j_6, K_7 j_7, K_8 j_8) \phi(-K_5 j_5, -K_7 j_7, -K_8 j_8) \\
& [1 + \chi(3.31) + \dots] \quad (4.48)
\end{aligned}$$

The contribution to the second of the five-vertex diagrams can be written as follows:

$$\begin{aligned}
F(3.32) = & -\frac{1}{\beta} \frac{(-\beta)^5}{5!} \times 7776 \times 60 \sum_{\substack{K_1 K_2 K_3 K_4 K_5 K_6 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7 j_8}} V(K_1 j_1, -K_1 j_1, K_2 j_2, -K_2 j_2) V(-K_2 j_2, -K_4 j_4, -K_5 j_5) \\
& V(K_2 j_2, K_4 j_4, K_5 j_5) V(K_5 j_5, K_7 j_7, K_8 j_8) V(-K_5 j_5, -K_7 j_7, -K_8 j_8) \\
& \sum_{\substack{\eta_1 \eta_2 \eta_3 \eta_4}} G(K_1 j_1, i\omega_{\eta_1}) G(K_2 j_2, i\omega_{\eta_2}) G(K_3 j_3, i\omega_{\eta_2}) G(K_4 j_4, -i\omega_{\eta_2} - i\omega_{\eta_3}) \\
& G(K_5 j_5, i\omega_{\eta_3}) G(K_6 j_6, i\omega_{\eta_3}) G(K_7 j_7, i\omega_{\eta_4}) G(K_8 j_8, -i\omega_{\eta_3} - i\omega_{\eta_4})
\end{aligned}$$

We have substituted for the propagators and resolved the product into partial fractions. We have obtained a total of nineteen terms. Expanding each term using the binomial series and performing the summations over η we find:

$$F(3.32) = \frac{(K_B T)^4}{8N^3} \sum_{\substack{K_1 K_2 K_4 K_5 K_7 K_8 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7 j_8}} \frac{\Delta(K_2 + K_4 + K_5) \Delta(K_5 + K_7 + K_8) \phi(K_1 j_1, -K_1 j_1, K_2 j_2, -K_2 j_2) \phi(-K_2 j_2, -K_4 j_4, -K_5 j_5)}{\omega^2(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_3 j_3) \omega^2(K_4 j_4) \omega^2(K_5 j_5) \omega^2(K_6 j_6) \omega^2(K_7 j_7) \omega^2(K_8 j_8)} \\ \phi(K_2 j_2, K_4 j_4, K_5 j_5) \phi(-K_5 j_5, -K_7 j_7, -K_8 j_8) \phi(K_5 j_5, K_7 j_7, K_8 j_8) \\ \left[1 + \frac{\hbar^2}{12 (K_B T)^2} \omega^2(K_1 j_1) + X(3.32) + \dots \right] \quad (4.49)$$

Diagram (3.33) gives:

$$F(3.33) = -\frac{1}{\beta} \frac{(-\beta)^5}{5!} \times 15552 \times 30 \sum_{\substack{K_1 K_2 K_4 K_5 K_6 K_7 K_8 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7 j_8}} V(K_1 j_1, -K_1 j_1, -K_2 j_2, K_2 j_2) V(-K_2 j_2, -K_4 j_4, -K_5 j_5) \\ V(K_2 j_2, -K_6 j_6, -K_8 j_8) V(K_5 j_5, K_6 j_6, K_7 j_7) V(K_4 j_4, -K_7 j_7, K_8 j_8) \\ \sum_{\substack{\eta_1 \eta_2 \eta_3 \eta_4 \\ 1 2 3 4}} G(K_1 j_1, i\omega_{\eta_1}) G(K_2 j_2, i\omega_{\eta_2}) G(K_2 j_2, i\omega_{\eta_2}) G(K_4 j_4, i\omega_{\eta_3}) \\ G(K_5 j_5, -i\omega_{\eta_2} - i\omega_{\eta_3}) G(K_6 j_6, i\omega_{\eta_4}) G(K_7 j_7, i\omega_{\eta_2} + i\omega_{\eta_3} - i\omega_{\eta_4}) \\ G(K_8 j_8, i\omega_{\eta_2} - i\omega_{\eta_4})$$

The factors 15552 and 30 are the pairing schemes and the topologically equivalent diagrams. Performing the summations over η' 's we get:

$$\begin{aligned}
 F(3.33) = & \frac{(K_B T)^4}{8N^3} \sum_{\substack{K_1, K_2, K_4, K_5, K_6, K_7, K_8 \\ j_1, j_2, j_3, j_4, j_5, j_6, j_7, j_8}} \frac{\Delta(K_2 + K_4 + K_5) \Delta(K_2 - K_6 - K_8) \Delta(K_5 + K_6 + K_7) \phi(K_1 j_1, -K_1 j_1, -K_2 j_2, K_2 j_2)}{\omega^2(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_3 j_3) \omega^2(K_4 j_4) \omega^2(K_5 j_5) \omega^2(K_6 j_6) \omega^2(K_7 j_7) \omega^2(K_8 j_8)} \\
 & \phi(-K_2 j_3, -K_4 j_4, -K_5 j_5) \phi(K_2 j_2, -K_6 j_6, -K_8 j_8) \phi(K_5 j_5, K_6 j_6, K_7 j_7) \\
 & \phi(K_4 j_4, -K_7 j_7, -K_8 j_8) \\
 & \left[1 + \frac{\hbar^2}{12 (K_B T)^2} \omega^2(K_1 j_1) + \chi(3.33) + \dots \right] \quad (4.50)
 \end{aligned}$$

The contribution from the fourth of the five-vertex diagrams is:

$$\begin{aligned}
 F(3.34) = & -\frac{1}{\beta} \frac{(-\beta)^5}{5!} \times 3888 \times 60 \sum_{\substack{K_1, K_2, K_4, K_5, K_6, K_7 \\ j_1, j_2, j_3, j_4, j_5, j_6, j_7, j_8}} V(K_1 j_1, -K_1 j_1, K_2 j_2, -K_2 j_3) \\
 & V(-K_2 j_2, -K_6 j_6, -K_7 j_7) V(K_2 j_3, K_4 j_4, K_5 j_5) V(-K_4 j_4, -K_5 j_5, -K_3 j_8) \\
 & V(K_6 j_6, K_7 j_7, K_3 j_8) \\
 & \sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(K_1 j_1, i\omega_{\eta_1}) G(K_2 j_2, i\omega_{\eta_2}) G(K_2 j_3, i\omega_{\eta_2}) G(K_4 j_4, i\omega_{\eta_3}) \\
 & G(K_5 j_5, -i\omega_{\eta_2} - i\omega_{\eta_3}) G(K_6 j_6, i\omega_{\eta_4}) G(K_7 j_7, -i\omega_{\eta_2} - i\omega_{\eta_4}) \\
 & G(K_3 j_8, i\omega_{\eta_2})
 \end{aligned}$$

Performing the η sums we get:

$$F(3.34) = \frac{(K_B T)^7}{16 N^3} \sum_{\substack{\vec{k}_1, \vec{k}_2, \vec{k}_4, \vec{k}_5, \vec{k}_6, \vec{k}_7 \\ \vec{j}_1, \vec{j}_2, \vec{j}_3, \vec{j}_4, \vec{j}_5, \vec{j}_6, \vec{j}_7, \vec{j}_8}} \frac{\Delta(\vec{k}_2 + \vec{k}_4 + \vec{k}_5) \Delta(\vec{k}_2 + \vec{k}_6 + \vec{k}_7) \phi(\vec{k}_1 \vec{j}_1, -\vec{k}_1 \vec{j}_1, \vec{k}_2 \vec{j}_2, -\vec{k}_2 \vec{j}_3)}{\omega^2(\vec{k}_1 \vec{j}_1) \omega^2(\vec{k}_2 \vec{j}_2) \omega^2(\vec{k}_2 \vec{j}_3) \omega^2(\vec{k}_4 \vec{j}_4) \omega^2(\vec{k}_5 \vec{j}_5) \omega^2(\vec{k}_6 \vec{j}_6) \omega^2(\vec{k}_7 \vec{j}_7) \omega^2(\vec{k}_8 \vec{j}_8)} \\ \phi(-\vec{k}_2 \vec{j}_2, -\vec{k}_6 \vec{j}_6, -\vec{k}_7 \vec{j}_7) \phi(\vec{k}_2 \vec{j}_3, \vec{k}_4 \vec{j}_4, \vec{k}_5 \vec{j}_5) \phi(-\vec{k}_4 \vec{j}_4, -\vec{k}_5 \vec{j}_5, -\vec{k}_8 \vec{j}_8) \phi(\vec{k}_6 \vec{j}_6, \vec{k}_7 \vec{j}_7, \vec{k}_8 \vec{j}_8) \\ \left[1 + \frac{\hbar^2}{12 (K_B T)^2} \omega^2(\vec{k}_1 \vec{j}_1) + X(3.34) + \dots \right] \quad (4.51)$$

We can write the contribution from diagram (3.35) in the form:

$$F(3.35) = -\frac{1}{\beta} \frac{(-\beta)^5}{5!} \times 7776 \times 120 \sum_{\substack{\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_5, \vec{k}_6, \vec{k}_7, \vec{k}_8 \\ \vec{j}_1, \vec{j}_2, \vec{j}_3, \vec{j}_4, \vec{j}_5, \vec{j}_6, \vec{j}_7, \vec{j}_8}} V(\vec{k}_1 \vec{j}_1, \vec{k}_2 \vec{j}_2, \vec{k}_3 \vec{j}_3) V(-\vec{k}_1 \vec{j}_1, -\vec{k}_2 \vec{j}_2, -\vec{k}_3 \vec{j}_3) \\ V(\vec{k}_3 \vec{j}_4, \vec{k}_5 \vec{j}_5, \vec{k}_8 \vec{j}_8) V(-\vec{k}_3 \vec{j}_4, -\vec{k}_5 \vec{j}_5, -\vec{k}_8 \vec{j}_8) V(\vec{k}_6 \vec{j}_6, \vec{k}_7 \vec{j}_7, -\vec{k}_8 \vec{j}_8) \\ \sum_{\substack{\eta_1 \eta_2 \eta_3 \eta_4 \\ 1, 2, 3, 4}} G(\vec{k}_1 \vec{j}_1, i\omega_{\eta_1}) G(\vec{k}_2 \vec{j}_2, -i\omega_{\eta_1} - i\omega_{\eta_2}) G(\vec{k}_3 \vec{j}_3, i\omega_{\eta_2}) G(\vec{k}_4 \vec{j}_4, i\omega_{\eta_2}) \\ G(\vec{k}_5 \vec{j}_5, i\omega_{\eta_3}) G(\vec{k}_6 \vec{j}_6, i\omega_{\eta_4}) G(\vec{k}_7 \vec{j}_7, -i\omega_{\eta_2} - i\omega_{\eta_3} - i\omega_{\eta_4}) \\ G(\vec{k}_8 \vec{j}_8, -i\omega_{\eta_2} - i\omega_{\eta_3})$$

Carrying out the summations over η/ρ we find:

$$F(3.35) = \frac{(K_8 T)^4}{4N^3} \sum_{\substack{K_1 K_2 K_3 K_4 K_5 K_6 K_7 K_8 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7 j_8}} \frac{\Delta(K_1 + K_2 + K_3) \Delta(K_3 + K_5 + K_8) \Delta(K_6 + K_7 - K_8) \phi(K_1 j_1, K_2 j_2, K_3 j_3)}{\omega^4(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_3 j_3) \omega^2(K_4 j_4) \omega^2(K_5 j_5) \omega^2(K_6 j_6) \omega^2(K_7 j_7) \omega^2(K_8 j_8)} \\ \phi(-K_1 j_1, -K_2 j_2, -K_3 j_4) \phi(K_3 j_4, K_5 j_5, K_8 j_8) \phi(K_3 j_3, -K_5 j_5, -K_6 j_6, -K_7 j_7) \phi(K_6 j_6, K_7 j_7, K_8 j_8) \\ \left[1 + \chi(3.35) + \dots \right] \quad (4.52)$$

The contribution from diagram (3.36) is:

$$F(3.36) = -\frac{1}{\beta} \frac{(-\beta)^5}{5!} \times 3888 \times 60 \sum_{\substack{K_1 K_2 K_3 K_4 K_5 K_6 K_7 K_8 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7 j_8}} V(K_1 j_1, K_2 j_2, K_5 j_5) V(-K_1 j_1, -K_2 j_2, K_3 j_3, K_4 j_4) V(-K_3 j_3, -K_4 j_4, -K_5 j_5) \\ V(K_5 j_5, -K_7 j_7, -K_8 j_8) V(K_5 j_6, K_7 j_7, K_8 j_8) \\ \sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(K_1 j_1, i\omega_{\eta_1}) G(K_2 j_2, -i\omega_{\eta_2} - i\omega_{\eta_1}) G(K_3 j_3, i\omega_{\eta_3}) G(K_4 j_4, -i\omega_{\eta_2} - i\omega_{\eta_3}) \\ G(K_5 j_5, i\omega_{\eta_2}) G(K_5 j_6, i\omega_{\eta_2}) G(K_7 j_7, i\omega_{\eta_4}) G(K_8 j_8, -i\omega_{\eta_2} - i\omega_{\eta_4})$$

Performing the η summations we find

$$F(3.36) = \frac{(K_8 T)^4}{16N^3} \sum_{\substack{K_1 K_2 K_3 K_4 K_5 K_6 K_7 K_8 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7 j_8}} \frac{\Delta(K_1 + K_2 + K_5) \Delta(K_3 + K_4 + K_5) \Delta(K_5 + K_7 + K_8) \phi(K_1 j_1, K_2 j_2, K_5 j_5) \phi(K_1 j_1, -K_2 j_2, K_3 j_3, K_4 j_4)}{\omega^2(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_3 j_3) \omega^2(K_4 j_4) \omega^2(K_5 j_5) \omega^2(K_6 j_6) \omega^2(K_7 j_7) \omega^2(K_8 j_8)} \\ \phi(-K_3 j_3, -K_4 j_4, -K_5 j_6) \phi(K_5 j_5, -K_7 j_7, K_8 j_8) \phi(K_5 j_6, K_7 j_7, K_8 j_8) \\ \left[1 + \chi(3.36) + \dots \right] \quad (4.53)$$

Similarly, the contribution from diagram (3.37) is:

$$F(3.37) = -\frac{1}{\beta} \frac{(-\beta)^5}{5!} \times 15552 \times 60 \sum_{1,2,3,4,5,6,7,8} V(1,2,3) V(-1,-7,-8) V(-2,-4,-5) V(-3,5,-6) V(4,6,7,8)$$

$$\sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(1, i\omega_{\eta_1}) G(2, i\omega_{\eta_2}) G(3, -i\omega_{\eta_1} - i\omega_{\eta_2}) G(4, i\omega_{\eta_3})$$

$$G(5, -i\omega_{\eta_2} - i\omega_{\eta_3}) G(6, i\omega_{\eta_1} - i\omega_{\eta_3}) G(7, i\omega_{\eta_4}) G(8, -i\omega_{\eta_1} - i\omega_{\eta_4})$$

The high temperature expression is:

$$F(3.37) = \frac{(k_B T)^4}{4N^3} \sum_{1,2,3,4,5,6,7,8} \frac{\Delta(K_1 + K_2 + K_3) \Delta(K_1 + K_7 + K_8) \Delta(K_2 + K_4 + K_5) \Delta(K_3 - K_5 + K_6) \phi(1,2,3)}{\omega_1^2 \omega_2^2 \omega_3^2 \omega_4^2 \omega_5^2 \omega_6^2 \omega_7^2 \omega_8^2}$$

$$\phi(-1,-7,-8) \phi(-2,-4,-5) \phi(-3,5,-6) \phi(4,6,7,8)$$

$$[1 + \chi(3.37) + \dots] \quad (4.54)$$

The contribution from the last of the five-vertex diagrams is given by:

$$F(3.38) = -\frac{1}{\beta} \frac{(-\beta)^5}{5!} \times 31104 \times 15 \sum_{1,2,3,4,5,6,7,8} V(1,2,3) V(-3,-4,-5) V(-2,4,-6,7) V(5,6,8) V(-1,7,-8)$$

$$\sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(1, i\omega_{\eta_1}) G(2, -i\omega_{\eta_1} - i\omega_{\eta_2}) G(3, i\omega_{\eta_2}) G(4, -i\omega_{\eta_2} - i\omega_{\eta_3})$$

$$G(5, i\omega_{\eta_3}) G(6, i\omega_{\eta_2} - i\omega_{\eta_4}) G(7, -i\omega_{\eta_1} - i\omega_{\eta_4}) G(8, i\omega_{\eta_4})$$

Performing the summations over η' we find:

$$F(3.38) = \frac{(K_B T)^4}{8\sqrt{3}} \sum_{1,2,3,4,5,6,7,8} \frac{\Delta(K_1+K_2+K_3)\Delta(K_3+K_4+K_5)\Delta(K_5+K_6+K_8)\Delta(K_1+K_7+K_8)\phi(1,2,3)}{\omega_1^2 \omega_2^2 \omega_3^2 \omega_4^2 \omega_5^2 \omega_6^2 \omega_7^2 \omega_8^2} \\ \phi(-3,-4,-5)\phi(-2,4,-6,7)\phi(5,6,8)\phi(-1,-7,-8) \\ \left[1 + X(3.38) + \dots \right] \quad (4.55)$$

There are five diagrams of the six order. The contribution from the first is given by:

$$F(3.39) = -\frac{1}{\beta} \frac{(-\beta)^6}{6!} \times 5832 \times 120 \sum_{\substack{K_1, K_2, K_3, K_4, K_5, K_6, K_7, K_8, K_9 \\ j_1, j_2, j_3, j_4, j_5, j_6, j_7, j_8, j_9}} V(K_1 j_1, K_2 j_2, K_3 j_3) V(-K_2 j_2, -K_3 j_3, -K_1 j_4) V(K_1 j_4, K_5 j_5, K_6 j_6) \\ V(-K_5 j_5, -K_6 j_6, -K_1 j_7) V(K_1 j_7, K_8 j_8, K_9 j_9) V(-K_1 j_1, K_8 j_8, -K_9 j_9) \\ \sum_{\substack{\eta_1 \eta_2 \eta_3 \eta_4 \\ 1, 2, 3, 4}} G(K_1 j_1, i\omega_{\eta_1}) G(K_2 j_2, -i\omega_{\eta_1} - i\omega_{\eta_2}) G(K_3 j_3, i\omega_{\eta_2}) G(K_1 j_4, i\omega_{\eta_1}) \\ G(K_5 j_5, -i\omega_{\eta_1} - i\omega_{\eta_3}) G(K_6 j_6, i\omega_{\eta_3}) G(K_1 j_7, i\omega_{\eta_1}) \\ G(K_8 j_8, -i\omega_{\eta_1} - i\omega_{\eta_4}) G(K_9 j_9, i\omega_{\eta_4})$$

Substituting for the propagators and resolving the product, we get a total of ten terms which can be expanded. Performing the summations over η' we get:

$$F(3.39) = \frac{(K_8 T)^4}{48 N^3} \sum_{\substack{K_1, K_2, K_3, K_4, K_5, K_6, K_7, K_8, K_9 \\ j_1, j_2, j_3, j_4, j_5, j_6, j_7, j_8, j_9}} \frac{\Delta(K_1 + K_2 + K_3) \Delta(K_4 + K_5 + K_6) \Delta(K_7 + K_8 + K_9) \phi(K_1 j_1, K_2 j_2, K_3 j_3) \phi(K_4 j_4, K_5 j_5, K_6 j_6)}{\omega^2(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_3 j_3) \omega^2(K_4 j_4) \omega^2(K_5 j_5) \omega^2(K_6 j_6) \omega^2(K_7 j_7) \omega^2(K_8 j_8) \omega^2(K_9 j_9)} \\ \phi(K_1 j_4, -K_2 j_2, -K_3 j_3) \phi(-K_1 j_7, -K_5 j_5, -K_6 j_6) \phi(K_1 j_7, K_8 j_8, K_9 j_9) \\ \phi(-K_1 j_1, -K_8 j_8, -K_9 j_9) \\ [1 + \chi(3.39) + \dots] \quad (4.56)$$

From the second of the six-vertex diagrams, the contribution is:

$$F(3.40) = -\frac{1}{\beta} \frac{(T\beta)^6}{6!} \times 23328 \times 180 \sum_{\substack{K_1, K_2, K_3, K_4, K_5, K_6, K_7, K_8, K_9 \\ j_1, j_2, j_3, j_4, j_5, j_6, j_7, j_8, j_9}} V(K_1 j_1, K_2 j_2, K_3 j_3) V(-K_1 j_1, -K_2 j_2, -K_3 j_3) \\ V(-K_3 j_3, -K_5 j_5, -K_6 j_6) V(K_6 j_6, K_7 j_7, K_8 j_8) V(K_3 j_3, -K_8 j_8, -K_9 j_9) V(K_5 j_5, -K_7 j_7, K_9 j_9) \\ \sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(K_1 j_1, i\omega_{\eta_1}) G(K_2 j_2, -i\omega_{\eta_1} - i\omega_{\eta_2}) G(K_3 j_3, i\omega_{\eta_2}) G(K_4 j_4, i\omega_{\eta_2}) \\ G(K_5 j_5, -i\omega_{\eta_2} - i\omega_{\eta_3}) G(K_6 j_6, i\omega_{\eta_3}) G(K_7 j_7, -i\omega_{\eta_3} - i\omega_{\eta_4}) \\ G(K_8 j_8, i\omega_{\eta_4}) G(K_9 j_9, i\omega_{\eta_4} - i\omega_{\eta_2})$$

Following the procedure used in deriving the high temperature limit for the previous diagrams, we find:

$$F(3.40) = -\frac{(K_B T)^4}{8N^3} \sum_{\substack{K_1, K_2, K_3, K_4, K_5, K_6, K_7, K_8, K_9 \\ j_1, j_2, j_3, j_4, j_5, j_6, j_7, j_8, j_9}} \frac{\Delta(K_1 + K_2 + K_3) \Delta(K_3 + K_5 + K_6) \Delta(K_6 + K_7 + K_8) \Delta(K_5 - K_7 + K_9) \phi(K_1 j_1, K_2 j_2, K_3 j_3)}{\omega^2(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_3 j_3) \omega^2(K_4 j_4) \omega^2(K_5 j_5) \omega^2(K_6 j_6) \omega^2(K_7 j_7) \omega^2(K_8 j_8) \omega^2(K_9 j_9)} \\ \phi(-K_1 j_1, -K_2 j_2, -K_3 j_3) \phi(-K_3 j_4, -K_5 j_5, -K_6 j_6) \phi(K_6 j_6, K_7 j_7, K_8 j_8) \\ \phi(K_3 j_3, K_8 j_8, -K_9 j_9) \phi(K_5 j_5, -K_7 j_7, K_9 j_9) \\ \left[1 + \chi(3.40) + \dots \right] \quad (4.57)$$

The contribution from diagram (3.41) is:

$$F(3.41) = -\frac{1}{\beta} \frac{(-\beta)^6}{6!} \times 46656 \times 60 \sum_{1,2,3,4,5,6,7,8,9} V(1,2,3) V(-3,-4,-5) V(-2,-6,-7) V(-1,7,9) \\ V(4,6,8) V(5,-8,-9) \\ \sum_{\substack{n_1 n_2 n_3 n_4 \\ 1,2,3,4}} G(1, i\omega_{n_1}) G(2, i\omega_{n_2}) G(3, -i\omega_{n_1} - i\omega_{n_2}) G(4, i\omega_{n_3}) \\ G(5, i\omega_{n_1} + i\omega_{n_2} - i\omega_{n_3}) G(6, i\omega_{n_4}) G(7, -i\omega_{n_2} - i\omega_{n_4}) G(8, -i\omega_{n_3} - i\omega_{n_4}) \\ G(9, i\omega_{n_1} + i\omega_{n_2} + i\omega_{n_4})$$

The high temperature expression of this diagram is

$$F(3.41) = -\frac{(K_B T)^4}{12N^3} \sum_{1,2,3,4,5,6,7,8,9} \frac{\Delta(K_1 + K_2 + K_3) \Delta(K_3 + K_4 + K_5) \Delta(K_2 + K_6 + K_7) \Delta(K_1 - K_7 - K_9) \Delta(K_4 + K_8 + K_9)}{\omega_1^2 \omega_2^2 \omega_3^2 \omega_4^2 \omega_5^2 \omega_6^2 \omega_7^2 \omega_8^2 \omega_9^2} \\ \phi(1,2,3) \phi(-3,-4,-5) \phi(-2,-6,-7) \phi(-1,7,9) \phi(4,6,8) \phi(5,-8,-9) \\ \left[1 + \chi(3.41) + \dots \right] \quad (4.58)$$

Diagram (3.42) gives the contribution as follows:

$$\begin{aligned}
 F(3.42) = & -\frac{1}{\beta} \frac{(-\beta)^6}{6!} \times 11664 \times 180 \sum_{\substack{\kappa_1 \kappa_2 \kappa_3 \kappa_4 \kappa_5 \kappa_6 \kappa_7 \kappa_8 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7 j_8}} V(\kappa_1 j_1, \kappa_2 j_2, \kappa_3 j_3) V(-\kappa_2 j_2, -\kappa_3 j_3, -\kappa_1 j_4) \\
 & V(\kappa_1 j_4, \kappa_5 j_5, \kappa_6 j_6) V(-\kappa_6 j_6, -\kappa_7 j_7, -\kappa_8 j_8) \\
 & V(\kappa_7 j_7, \kappa_8 j_8, \kappa_6 j_9) V(-\kappa_1 j_1, -\kappa_5 j_5, -\kappa_6 j_9) \\
 & \sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(\kappa_1 j_1, i\omega_{\eta_1}) G(\kappa_2 j_2, i\omega_{\eta_2}) G(\kappa_3 j_3, -i\omega_{\eta_1} - i\omega_{\eta_2}) \\
 & G(\kappa_4 j_4, i\omega_{\eta_1}) G(\kappa_5 j_5, -i\omega_{\eta_1} - i\omega_{\eta_3}) G(\kappa_6 j_6, i\omega_{\eta_3}) \\
 & G(\kappa_7 j_7, i\omega_{\eta_4}) G(\kappa_8 j_8, i\omega_{\eta_3} - i\omega_{\eta_4}) G(\kappa_6 j_9, i\omega_{\eta_3})
 \end{aligned}$$

Performing the summations over η' we find:

$$\begin{aligned}
 F(3.42) = & -\frac{(K_B T)^4}{16N^3} \sum_{\substack{\kappa_1 \kappa_2 \kappa_3 \kappa_4 \kappa_5 \kappa_6 \kappa_7 \kappa_8 \\ j_1 j_2 j_3 j_4 j_5 j_6 j_7 j_8 j_9}} \frac{\Delta(\kappa_1 + \kappa_2 + \kappa_3) \Delta(\kappa_6 + \kappa_7 + \kappa_8) \Delta(\kappa_1 + \kappa_5 + \kappa_6) \phi(\kappa_1 j_1, \kappa_2 j_2, \kappa_3 j_3)}{\omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) \omega^2(\kappa_7 j_7) \omega^2(\kappa_8 j_8) \omega^2(\kappa_6 j_9)} \\
 & \phi(-\kappa_2 j_2, -\kappa_3 j_3, -\kappa_1 j_4) \phi(\kappa_1 j_4, \kappa_5 j_5, \kappa_6 j_6) \phi(-\kappa_6 j_6, -\kappa_7 j_7, -\kappa_8 j_8) \\
 & \phi(\kappa_7 j_7, \kappa_8 j_8, \kappa_6 j_9) \phi(-\kappa_1 j_1, -\kappa_5 j_5, -\kappa_6 j_9) \\
 & [1 + \chi(3.42) + \dots]
 \end{aligned}$$

The contribution from the last of the six vertex diagrams is given by:

$$F(3.43) = -\frac{1}{\beta} \frac{(-\beta)^6}{6!} \times 46656 \times 10 \sum_{1,2,3,4,5,6,7,8,9} V(1,2,3) V(-2,-4,-5) V(5,6,7) V(-3,-7,-8) \\ V(4,8,9) V(-1,-6,-9)$$

$$\sum_{\eta_1 \eta_2 \eta_3 \eta_4} G(1, i\omega_{\eta_1}) G(2, -i\omega_{\eta_1} - i\omega_{\eta_2}) G(3, i\omega_{\eta_2}) G(4, i\omega_{\eta_3}) G(5, i\omega_{\eta_1} + i\omega_{\eta_2} - i\omega_{\eta_3})$$

$$G(6, i\omega_{\eta_4}) G(7, -i\omega_{\eta_1} - i\omega_{\eta_2} + i\omega_{\eta_3} - i\omega_{\eta_4}) G(8, i\omega_{\eta_1} - i\omega_{\eta_3} + i\omega_{\eta_4})$$

$$G(9, i\omega_{\eta_1} - i\omega_{\eta_4})$$

Substituting for the propagators and performing the summations we find:

$$F(3.43) = -\frac{(k_B T)^4}{72 N^3} \sum_{1,2,3,4,5,6,7,8,9} \frac{\Delta(k_1+k_2+k_3) \Delta(k_2+k_4+k_5) \Delta(k_5+k_6+k_7) \Delta(k_3+k_7+k_8) \Delta(k_4+k_8+k_9)}{\omega_1^2 \omega_2^2 \omega_3^2 \omega_4^2 \omega_5^2 \omega_6^2 \omega_7^2 \omega_8^2 \omega_9^2}$$

$$\phi(1,2,3) \phi(-2,-4,-5) \phi(5,6,7) \phi(-3,-7,-8) \phi(4,8,9) \phi(-1,-6,-9)$$

$$[1 + X(3.43) + \dots]$$

(4.60)

V. Numerical Calculations

The numerical work presented in this thesis has been done using the following four approximations.

1. High-temperature limit.
2. Central-force model.

These two assumptions have been discussed in the previous sections.

3. Leading-term approximation.

In this approximation only the highest ordered radial derivative of the interatomic potential is retained. Feldman and Horton [26] have evaluated the lowest-order contribution to the Helmholtz free energy without making this approximation. They have concluded that the leading-term approximation is unreliable. Leech and Reissland [27] have shown that the error for diagram F(1.2) is about 4% whereas for diagram F(1.1) the error is about 32%. Wilk [10] has carried out the calculations of free energy to $O(\lambda^4)$ without making the leading term approximation. He has found that the variation in numbers from the leading-term approximation range from 0.3% to 47%. However, the ratio of the total contributions to $O(\lambda^4)$ and $O(\lambda^2)$ have yielded same value as obtained by Shukla and Cowley [9] in the leading term approximation, showing that this approximation is not too bad.

4. The Ludwig Approximation.

In this approximation, Ludwig [5] has replaced each factor $1/\omega^2(Kj)$ appearing in the free energy sums by a kind of average $[1/\langle\omega^2\rangle]$ independent of K and j . Such factors can be taken outside the summations. $\langle\omega^2\rangle$ is defined by

$$\langle\omega^2\rangle = \frac{1}{3N} \sum_{Kj} \omega^2(Kj) \quad (5.1)$$

It can be shown (for the model we have used here) that

$$\langle \omega^2 \rangle = \frac{4 \phi''(r_0)}{M} \quad (5.2)$$

The physical idea behind the Ludwig approximation is essentially the same as in Einstein model of a solid.

The diagrams containing closed loops can be evaluated with the help of the following expression [6]

$$\sum_{\alpha \beta} \sum_{\underline{k} j} \frac{e_{\alpha}(\underline{k} j) e_{\beta}(\underline{k} j) n_{\alpha} n_{\beta} (1 - c_0 \pi a_0 \underline{k} \cdot \underline{n})}{\omega^2(\underline{k} j)} = \frac{NM}{2 \phi''(r_0)} \quad (5.3)$$

where $(n_{\alpha}, n_{\beta}, n_{\gamma})$ is a vector separating an atom from one of its nearest neighbours.

In order to carry out the sums over \underline{k} and j which appear in the different expressions of the free energy, it is convenient to introduce the dimensionless frequencies $\chi^2(\underline{k} j)$ defined by

$$\omega^2(\underline{k} j) = \frac{2 \phi''(r_0)}{M} \chi^2(\underline{k} j) \quad (5.4)$$

$$\langle \chi^2(\underline{k} j) \rangle = 2 \quad (5.5)$$

Substituting eq. (5.4) in eq. (5.3) we get:

$$\sum_{\underline{k} j} \frac{[n \cdot e(\underline{k} j)]^2 (1 - c_0 \pi a_0 \underline{k} \cdot \underline{n})}{\chi^2(\underline{k} j)} = N \quad (5.6)$$

There are three diagrams which contain only closed loops.

These are F(1.1), F(2.1) and F(3.1). All of them can be evaluated using eq. (5.6), and we illustrate the calculation for diagram F(3.1) whose expression can be written in the following form if we consider the leading term of temperature in eq. (4.18) and substitute from eqs. (2.29) and (5.4)

$$\begin{aligned}
F(3.1) &= \frac{(K_B T)^4}{384 \times 2^7 N^3} \frac{\phi^{VIII}}{[\phi'']^4} \sum_{\underline{n}} \left\{ \sum_{\underline{k}, \underline{k}'} \frac{[\underline{n} \cdot e(\underline{k}, \underline{k}')]^2 (1 - \cos \pi a_0 \underline{k} \cdot \underline{n})}{\chi^2(\underline{k}, \underline{k}')} \right\}^4 \\
&= \frac{(K_B T)^4}{384 \times 2^7 N^3} \frac{\phi^{VIII}}{[\phi'']^4} N^4 \times 12 \\
&= \frac{N (K_B T)^4}{2^{10}} \frac{\phi^{VIII}}{[\phi'']^4} \tag{5.7}
\end{aligned}$$

where in obtaining (5.7), we have made use of (5.6) and the factor 12 comes from the summation over nearest neighbours.

Shukla and Cowley [9] have presented another sum rule which allows us to carry out certain sums analytically. This sum rule is given by

$$\sum_{\underline{n}} \frac{[\underline{n} \cdot e(\underline{k}, \underline{k}')] [\underline{n} \cdot e(\underline{k}, \underline{k}'')] (1 - \cos \pi a_0 \underline{k} \cdot \underline{n})}{\chi(\underline{k}, \underline{k}') \chi(\underline{k}, \underline{k}'')} = 4 \delta_{j,j'} \tag{5.8}$$

where the sum over \underline{n} is over nearest neighbours.

As an example of applying this formula, let us consider the expression for diagram F(2.2) which can be obtained from eq. (4.12) by retaining only the first term in the expansion. Substituting eqs. (2.29) and (5.3) and arranging the terms, F(2.2) becomes

$$\begin{aligned}
F(2.2) = & - \frac{(K_B T)^3 [\phi^{IV}]^2}{2^{10} N^2 [\phi''']^4} \sum_{\vec{n}_1 \vec{n}_2} \sum_{\vec{k}_{22} \vec{j}_3} \left\{ \frac{\sum_{\vec{k}_{11} \vec{j}_1} [\vec{n}_1 \cdot e(\vec{k}_{11} \vec{j}_1)]^2 (1 - \cos \pi a_0 \vec{k}_{11} \cdot \vec{n}_1)}{\lambda^2(\vec{k}_{11} \vec{j}_1)} \right\} \\
& \left\{ \frac{\sum_{\vec{k}_{44} \vec{j}_4} [\vec{n}_2 \cdot e(\vec{k}_{44} \vec{j}_4)]^2 (1 - \cos \pi a_0 \vec{k}_{44} \cdot \vec{n}_2)}{\lambda^2(\vec{k}_{44} \vec{j}_4)} \right\} \left\{ \frac{[\vec{n}_1 \cdot e(\vec{k}_{22} \vec{j}_2)] [\vec{n}_1 \cdot e(\vec{k}_{23} \vec{j}_3)] (1 - \cos \pi a_0 \vec{k}_{22} \cdot \vec{n}_1)}{\lambda(\vec{k}_{22} \vec{j}_2) \lambda(\vec{k}_{23} \vec{j}_3)} \right\} \\
& \left\{ \frac{[\vec{n}_2 \cdot e(\vec{k}_{22} \vec{j}_2)] [\vec{n}_2 \cdot e(\vec{k}_{23} \vec{j}_3)] (1 - \cos \pi a_0 \vec{k}_{22} \cdot \vec{n}_2)}{\lambda(\vec{k}_{22} \vec{j}_2) \lambda(\vec{k}_{23} \vec{j}_3)} \right\} \quad (5.9)
\end{aligned}$$

Making use of eqs. (5.6) and (5.8), exact result is given by

$$F(2.2) = - \frac{3}{2^6} \sim (K_B T)^3 \frac{[\phi^{IV}]^2}{[\phi''']^4} \quad (5.10)$$

Applying Ludwig's approximation to the same diagram, we get

$$\begin{aligned}
F(2.2) = & - \frac{(K_B T)^3}{2^{14} N^2} \frac{[\phi^{IV}]^2}{[\phi''']^4} \sum_{\vec{n}_1 \vec{n}_2} \left\{ \sum_{\vec{k}_{11} \vec{j}_1} [\vec{n}_1 \cdot e(\vec{k}_{11} \vec{j}_1)]^2 (1 - \cos \pi a_0 \vec{k}_{11} \cdot \vec{n}_1) \right\} \\
& \left\{ \sum_{\vec{k}_{44} \vec{j}_4} [\vec{n}_4 \cdot e(\vec{k}_{44} \vec{j}_4)]^2 (1 - \cos \pi a_0 \vec{k}_{44} \cdot \vec{n}_4) \right\} \\
& \sum_{\vec{k}_2} \sum_{\vec{j}_2} [\vec{n}_1 \cdot e(\vec{k}_2 \vec{j}_2)] [\vec{n}_2 \cdot e(\vec{k}_2 \vec{j}_2)] \\
& \sum_{\vec{j}_3} [\vec{n}_1 \cdot e(\vec{k}_2 \vec{j}_3)] [\vec{n}_2 \cdot e(\vec{k}_2 \vec{j}_3)] \\
& (1 - \cos \pi a_0 \vec{k}_2 \cdot \vec{n}_1) (1 - \cos \pi a_0 \vec{k}_2 \cdot \vec{n}_2) \quad (5.11)
\end{aligned}$$

We can evaluate the sum over j_2 in equation (5.11) as follows:

$$\begin{aligned}
 \sum_{j_2} [n_1 \cdot e(\kappa_2 j_2)] [n_2 \cdot e(\kappa_2 j_2)] &= \sum_{j_2} \sum_{\alpha\beta} n_{1\alpha} n_{2\beta} e_{\alpha}(\kappa_2 j_2) e_{\beta}(\kappa_2 j_2) \\
 &= \sum_{\alpha\beta} n_{1\alpha} n_{2\beta} \delta_{\alpha\beta} \\
 &= (n_1 \cdot n_2)
 \end{aligned} \tag{5.12}$$

where in obtaining eq. (5.12) we have made use of the relation (2.10).

Making use of eqs. (5.5), (5.6), (5.11), (5.12) and the following delta function relation

$$\Delta(n) = \frac{1}{N} \sum_n \exp(i\pi a_0 \kappa \cdot n) \tag{5.13}$$

we get

$$\begin{aligned}
 F(2.2) &= - \frac{2^4 (k_B T)^3}{2^{18} N^2} \frac{[\phi^{IV}]^2}{[\phi'']^4} \sum_{n_1, n_2} (2N)^2 (n_1 \cdot n_2)^2 N [1 - \Delta(n_1) - \Delta(n_2) \\
 &\quad + \frac{1}{2} \{ \Delta(n_1 + n_2) + \Delta(n_1 - n_2) \}] \\
 &= - \frac{15 \times 2^{10}}{2^{18}} N (k_B T)^3 \frac{[\phi^{IV}]^2}{[\phi'']^4}
 \end{aligned}$$

We have also evaluated this diagram using Ludwig's approximation and the sum rule (5.8) which can be written on this basis as:

$$\sum_n [n \cdot e(\kappa j)] [n \cdot e(\kappa j')] (1 - \cos \pi a_0 \kappa \cdot n) = 8 \delta_{jj'} \tag{5.14}$$

from eqs. (5.4), (5.6), (5.9) and (5.14) the free energy expression for diagram F(2.2) becomes:

$$F(2.2) = - \frac{3}{2^6} N (k_B T)^3 \frac{[\phi^{IV}]^2}{[\phi'']^4}$$

This result is the same as that of the exact result (eq. (5.10)).

For those diagrams which cannot be evaluated analytically, we use the plane-wave expansion to eliminate the delta functions which expresses the wave-vector conservation at each vertex. The expression is

$$\Delta(\underline{k}_1 + \dots + \underline{k}_s) = \frac{1}{N} \sum_{\underline{m}} \exp[\pi i a_0 (\underline{k}_1 + \dots + \underline{k}_s) \cdot \underline{m}] \quad (5.15)$$

Now, let us consider the diagram F(1.2). Its expression can be obtained from eq. (4.9) by retaining only the first term. Making use of Eqs. (2.29), (5.4), (5.15) and the symmetry between \underline{k} 's and \underline{j} 's, we get [6]

$$F(1.2) = - \frac{(k_B T)^2 [\phi'']^2}{3 \times 2^{10} N^2 [\phi'']^3} \sum_{\underline{m}, \underline{n}_1, \underline{n}_2} \left\{ \frac{\sum_{\underline{k}_1, \underline{j}_1} e^{\pi i a_0 \underline{k}_1 \cdot \underline{m}} [\underline{n}_1 \cdot e(\underline{k}_1)] [\underline{n}_2 \cdot e(\underline{j}_1)] (1 - e^{-\pi i a_0 \underline{k}_1 \cdot \underline{n}_1}) (1 - e^{-\pi i a_0 \underline{j}_1 \cdot \underline{n}_2})}{\chi^2(\underline{k}_1, \underline{j}_1)} \right\}^3 \quad (5.16)$$

Using eq. (5.5) and (5.12), we get

$$F(1.2) = - \frac{1}{3 \times 2^{13}} N (k_B T)^2 \frac{[\phi'']^2}{[\phi'']^3} \sum_{\underline{m}, \underline{n}_1, \underline{n}_2} F^3(\underline{m}, \underline{n}_1, \underline{n}_2) \quad (5.17)$$

where

$$F(\underline{m}, \underline{n}_1, \underline{n}_2) = (\underline{n}_1 \cdot \underline{n}_2) \left[\Delta(\underline{m}) - \Delta(\underline{m} - \underline{n}_1) - \Delta(\underline{m} + \underline{n}_2) + \Delta(\underline{m} - \underline{n}_1 + \underline{n}_2) \right] \quad (5.18)$$

The structure of this function appears in most diagrams of different order.

From the properties of delta function, \underline{m} takes only four values zero, \underline{n}_1 , $-\underline{n}_2$ and $(\underline{n}_1 - \underline{n}_2)$. \underline{n}_1 runs over the twelve nearest neighbour positions.

We have followed the same procedure for computing the rest of the diagrams of order χ^4 and χ^6 . The corresponding formulas for diagrams F(2.3) and F(2.4) are given by

$$F(2.3) = - \frac{N (k_B T)^3}{3 \times 2^{14}} \frac{\phi''' \phi^v}{[\phi'']^4} \sum_{\underline{m}, \underline{n}_1, \underline{n}_2} (\underline{n}_1 \cdot \underline{n}_2) F^3(\underline{m}, \underline{n}_1, \underline{n}_2) \quad (5.19)$$

$$F(2.4) = \frac{N(K_B T)^3 [\phi^{IV}] [\phi''']^2}{2^{17} [\phi'']^5} \sum_{n_1 n_2 n_3} \frac{(n_1 \cdot n_2) (n_1 \cdot n_3)}{(n_2 \cdot n_3)} \\ \left[2F(n_1, n_2, n_3) - F(n_1 + n_2, n_3) - F(n_1 - n_2, n_3) \right] \\ F^2(n_1, n_2, n_3) \quad (5.20)$$

If we use the sum rule (5.14), the last expression becomes:

$$F(2.4) = \frac{N(K_B T)^3 \phi^{IV} [\phi''']^2}{2^{15} [\phi'']^5} \sum_{n_1 n_2 n_3} F^3(n_1, n_2, n_3) \quad (5.21)$$

For diagram (2.5), the expression turns out to be:

$$F(2.5) = - \frac{(K_B T)^3 N [\phi^{IV}]^2}{3 \times 2^{18} [\phi'']^4} \sum_{n_1 n_2} F^4(n_1, n_2) \quad (5.22)$$

The free energy expression for diagram (2.6) in high temperature limit and using Ludwig approximation can be derived with the aid of eqs. (2.29), (4.15), (5.4), (5.5) and (5.18). It finally becomes:

$$F(2.6) = - \frac{N(K_B T)^3 [\phi''']^4}{2^{26} [\phi'']^6} \sum_{n_1 n_2 n_3} \sum_{n_1 n_2 n_3 n_4} F(n_1 + n_2 + n_3, n_1, n_2) \\ F(n_3, n_2, n_1) F^2(n_1, n_2, n_3) F^2(n_2, n_3, n_4) \quad (5.23)$$

This diagram and a similar diagram in $O(\lambda^6)$ can be easily evaluated using the following matrix

$$M(\underline{k}, \underline{j}, \underline{j}') = C_1 \sum_{n_1 n_2} \frac{V(\underline{k}, \underline{j}, \underline{k}_1 \underline{j}_1, \underline{k}_2 \underline{j}_2) V(-\underline{k}, \underline{j}', -\underline{k}_1 \underline{j}_1, -\underline{k}_2 \underline{j}_2)}{\omega(\underline{k}) \omega^2(\underline{k}_1) \omega^2(\underline{k}_2) \omega(\underline{k}')} \quad (5.24)$$

Substituting from eqs. (2.29), (5.4), (5.5) and (5.18) we get

$$M(\underline{k}, j, j') = C_2 \sum_{\substack{m, n_1, n_2 \\ \underline{k} = \underline{k}_1 + \underline{k}_2}} e^{\pi i a_0 \underline{k} \cdot \underline{m}} \{n_1 \cdot e(\underline{k}_1)\} \{n_2 \cdot e(\underline{k}_2)\} (1 - e^{\pi i a_0 \underline{k} \cdot \underline{n}_1}) \\ (1 - e^{\pi i a_0 \underline{k} \cdot \underline{n}_2}) F^2(m, n_1, n_2) \quad (5.25)$$

C_1 and C_2 are constants to be found for different diagrams. The contribution from diagram (2.6) can be written as follows:

$$F(2.6) = - \frac{N(k_B T)^3 [\phi''']^4}{2^{26} [\phi'']^6} \left\{ \sum_{\underline{k}, j, j'} M(\underline{k}, j, j') M(\underline{k}, j', j) \right. \\ \left. \sum_{\underline{k}} M^2 \right\} \quad (5.26)$$

The summations over \underline{k} have been carried out for 32, 108, 256, and 500 wave vectors in the whole zone. We have also evaluated diagram $F(1.2)$ using the same method. Its expression is given by:

$$F(1.2) = - \frac{N(k_B T)^2}{3 \times 2^{13}} \frac{[\phi''']^2}{[\phi'']^3} \sum_{\underline{k}, j, j'} M(\underline{k}, j, j') \delta_{j, j'} \quad (5.27)$$

In Ludwig's approximation, the remaining diagrams of $\mathcal{O}(2^4)$ can be evaluated.

The expressions are:

$$F(2.7) = \frac{N(k_B T)^3}{2^{21}} \frac{[\phi^{(v)}][\phi''']^2}{[\phi'']^5} \sum_{\substack{m_1, m_2 \\ \underline{m}_1 + \underline{m}_2 = \underline{m}}} \sum_{\substack{n_1, n_2, n_3 \\ \underline{n}_1 + \underline{n}_2 + \underline{n}_3 = \underline{n}}} F^2(m_1, n_2, n_1) F(m_1 + m_2, n_2, n_3) \\ F^2(m_2, n_1, n_3) \quad (5.28)$$

$$F(2.8) = - \frac{N(k_B T)^3}{3 \times 2^{25}} \frac{[\phi''']^4}{[\phi'']^6} \sum_{\substack{m_1, m_2, m_3 \\ \underline{m}_1 + \underline{m}_2 + \underline{m}_3 = \underline{m}}} \sum_{\substack{n_1, n_2, n_3, n_4 \\ \underline{n}_1 + \underline{n}_2 + \underline{n}_3 + \underline{n}_4 = \underline{n}}} F(m_1 - m_2, n_1, n_2) \\ F(m_1 - m_3, n_1, n_3) F(m_1, n_1, n_4) F(m_2, n_2, n_4) \\ F(m_2 - m_3, n_2, n_3) F(m_3, n_3, n_4) \quad (5.29)$$

Diagrams of order λ^6 :

We have only considered the leading term of temperatures given in section 4. Similar procedures have been followed in deriving the corresponding expansion to all diagrams.

We can use the exact result of diagram F(1.2) in evaluating exactly diagram F(3.2) after making use of the sum rule in eq. (5.6).

The expression of this diagram is given by:

$$F(3.2) = -\frac{(k_B T)^4}{3 \times 2^{14}} \frac{\phi''' \phi^{vii}}{[\phi'']^5} \sum_{\tilde{n}_1 \tilde{n}_2} \left[\frac{\sum_{\tilde{k}_1} [\tilde{n}_1 e(\tilde{k}_1)] (1 - \cos \pi a_0 \tilde{k}_1 \cdot \tilde{n}_1)}{\lambda^2(\tilde{k}_1)} \right]^2$$

$$\left[\frac{\sum_{\tilde{k}_3} e^{\pi i a_0 \tilde{k}_3 \cdot \tilde{n}} [\tilde{n}_1 e(\tilde{k}_3)] [\tilde{n}_2 e(\tilde{k}_3)] (1 - e^{-\pi i a_0 \tilde{k}_3 \cdot \tilde{n}_1}) (1 - e^{\pi i a_0 \tilde{k}_3 \cdot \tilde{n}_2})}{\lambda^2(\tilde{k}_3)} \right]^3 \quad (5.30)$$

In Ludwig's approximation the expression becomes:

$$F(3.2) = \frac{N(k_B T)^4}{3 \times 2^{19}} \frac{\phi''' \phi^{vii}}{[\phi'']^5} \sum_{\tilde{n}_1 \tilde{n}_2} (\tilde{n}_1 \cdot \tilde{n}_1)^2 F^3(\tilde{n}, \tilde{n}_1, \tilde{n}_2) \quad (5.31)$$

Making use of the exact value of diagram F(2.5) given by Shukla and Cowley [19] we can evaluate diagram F(3.3).

In Ludwig approximation, its expression is:

$$F(3.3) = \frac{N(k_B T)^4}{3 \times 2^{20}} \frac{\phi^{iv} \phi^{vi}}{[\phi'']^5} \sum_{\tilde{n}_1 \tilde{n}_2} (\tilde{n}_2 \cdot \tilde{n}_2) F^4(\tilde{n}, \tilde{n}_1, \tilde{n}_2) \quad (5.32)$$

Diagram F(3.4) can be evaluated in the same manner as diagram F(2.2). The remaining two of the two vertex diagrams can be worked out to give:

$$F(3.5) = -\frac{N(K_B T)^4}{5 \times 3 \times 2^{21}} \frac{[\phi^V]^2}{[\phi'']^5} \sum_{\underline{n}, \underline{n}_1, \underline{n}_2} F^5(\underline{n}, \underline{n}_1, \underline{n}_2) \quad (5.33)$$

$$F(3.6) = -\frac{N(K_B T)^4}{3 \times 2^{17}} \frac{[\phi^V]^2}{[\phi'']^5} \sum_{\underline{n}, \underline{n}_1, \underline{n}_2} F^3(\underline{n}, \underline{n}_1, \underline{n}_2) \quad (5.34)$$

The first of the three vertex diagram gives the following expression

$$F(3.7) = \frac{(K_B T)^4}{3 \times 2^{19}} \frac{[\phi^{IV}]^3}{[\phi'']^6} \sum_{\underline{n}_1, \underline{n}_2, \underline{n}_3} \left[\frac{[\underline{n}_1 \cdot e(\underline{\kappa}_1 \underline{j}_1)]^2 (1 - \cos \pi \alpha_0 \underline{\kappa}_1 \cdot \underline{n}_1)}{\lambda^2(\underline{\kappa}_1 \underline{j}_1)} \right]^3$$

$$\sum_{\underline{\kappa}_2 \underline{j}_2 \underline{j}_6} \left[\frac{[\underline{n}_1 \cdot e(\underline{\kappa}_2 \underline{j}_2)][\underline{n}_1 \cdot e(\underline{\kappa}_2 \underline{j}_6)] (1 - \cos \pi \alpha_0 \underline{\kappa}_2 \cdot \underline{n}_1)}{\lambda(\underline{\kappa}_2 \underline{j}_2) \lambda(\underline{\kappa}_2 \underline{j}_6)} \right]$$

$$\left[\frac{[\underline{n}_2 \cdot e(\underline{\kappa}_2 \underline{j}_2)][\underline{n}_2 \cdot e(\underline{\kappa}_2 \underline{j}_4)] (1 - \cos \pi \alpha_0 \underline{\kappa}_2 \cdot \underline{n}_2)}{\lambda(\underline{\kappa}_2 \underline{j}_2) \lambda(\underline{\kappa}_2 \underline{j}_4)} \right]$$

$$\left[\frac{[\underline{n}_3 \cdot e(\underline{\kappa}_2 \underline{j}_4)][\underline{n}_3 \cdot e(\underline{\kappa}_2 \underline{j}_6)] (1 - \cos \pi \alpha_0 \underline{\kappa}_2 \cdot \underline{n}_3)}{\lambda(\underline{\kappa}_2 \underline{j}_4) \lambda(\underline{\kappa}_2 \underline{j}_6)} \right] \quad (5.35)$$

Using the sum rules given by eqs. (5.6) and (5.8), it is straightforward calculation for this diagram. In Ludwig's approximation the expression becomes:

$$F(3.7) = \frac{N(K_B T)^4}{3 \times 2^{25}} \frac{[\phi^{IV}]^3}{[\phi'']^6} \sum_{\underline{n}_1, \underline{n}_2, \underline{n}_3} (\underline{n}_1 \cdot \underline{n}_2)(\underline{n}_1 \cdot \underline{n}_3)(\underline{n}_2 \cdot \underline{n}_3) \left[1 + \frac{1}{2} \Delta(\underline{n}_1 + \underline{n}_2) \right.$$

$$+ \frac{1}{2} \Delta(\underline{n}_1 - \underline{n}_2) + \frac{1}{2} \Delta(\underline{n}_1 + \underline{n}_3) + \frac{1}{2} \Delta(\underline{n}_1 - \underline{n}_3) + \frac{1}{2} \Delta(\underline{n}_2 + \underline{n}_3)$$

$$+ \frac{1}{2} \Delta(\underline{n}_2 - \underline{n}_3) - \frac{1}{4} \Delta(\underline{n}_1 + \underline{n}_2 + \underline{n}_3) - \frac{1}{4} \Delta(\underline{n}_1 - \underline{n}_2 - \underline{n}_3) - \frac{1}{4} \Delta(\underline{n}_1 + \underline{n}_2 - \underline{n}_3)$$

$$\left. - \frac{1}{4} \Delta(\underline{n}_1 - \underline{n}_2 + \underline{n}_3) \right] \quad (5.36)$$

which can be done analytically.

We have also evaluated this diagram in Ludwig's approximation using the sum rules. The numerical answer comes out different from the one given by eq. (5.36). Diagram F(3.8) can be evaluated exactly. The expression can be derived from eq. (4.25). In Ludwig's approximation the expression is:

$$F(3.8) = \frac{N(K_B T)^4}{3 \times 2^{26}} \frac{[\phi^{IV}]^3}{[\phi'']^6} \left[\sum_{n_1, n_2, n_3} (n_1 \cdot n_2)^2 (n_2 \cdot n_3)^2 + \sum_{n_1, n_2} (n_1 \cdot n_2)^2 (n_1 \cdot n_2)^2 \right. \\ \left. + \sum_{n_1, n_3} (n_1 \cdot n_1)^2 (n_1 \cdot n_3)^2 + \sum_{n_1} (n_1 \cdot n_1)^4 \right] \quad (5.37)$$

Diagram F(3.9) has been calculated in Ludwig approximation using the sum rule as well as without using it. The expressions respectively are:

$$F(3.9) = \frac{N(K_B T)^4}{2^{24} \times 3} \frac{[\phi^{IV}]^3}{[\phi'']^6} \sum_{n_1, n_2, n_3} F^4(n_1, n_2, n_3) \\ F(3.9) = \frac{N(K_B T)^4}{2^{24} \times 3} \frac{[\phi^{IV}]^3}{[\phi'']^6} \sum_{n_1, n_2, n_3} F^3(n_1, n_2, n_3) \frac{(n_1 \cdot n_2)(n_1 \cdot n_3)}{(n_2 \cdot n_3)} \\ \left[2 F(n_1, n_2, n_3) - F(n_1 + n_2, n_2, n_3) - F(n_1 - n_2, n_2, n_3) \right] \quad (5.38)$$

In Ludwig approximation, the corresponding expression from diagram F(3.10) is:

$$F(3.10) = \frac{N(K_B T)^4}{3 \times 2^{25}} \frac{[\phi^{IV}]^3}{[\phi'']^6} \sum_{m_1, m_2} \sum_{n_1, n_2, n_3} F^2(m_1 + m_2, n_1, n_2) \\ F^2(n_1, n_1, n_3) F^2(n_2, n_3, n_2) \quad (5.39)$$

The expression arising from diagram F(3.11) and F(3.12) can be evaluated exactly using the sum rules. In the case of Ludwig approximation we have carried out the calculations using the sum rules and without using them, the expressions respectively are:

$$F(3.11) = \frac{N(K_B T)^4}{3 \times 2^{16}} \frac{[\phi^{IV}]^3}{[\phi'']^6} \sum_{n_1 n_2 n_3} F^3(n_1, n_2, n_3) \quad (5.40)$$

$$F(3.11) = \frac{N(K_B T)^4}{3 \times 2^{24}} \frac{[\phi^{IV}]^3}{[\phi'']^6} \sum_{n_1 n_2 n_3} (n_1 n_2)^2 F^3(n_1, n_2, n_3) \left[1 + \frac{1}{2} \Delta(n_1 + n_2) + \frac{1}{2} \Delta(n_1 - n_2) \right] \quad (5.41)$$

$$F(3.12) = \frac{N(K_B T)^4}{2^{16}} \frac{\phi''' \phi^{IV} \phi^V}{[\phi'']^6} \sum_{n_1 n_2 n_3} F(n_1, n_2, n_3) \quad (5.42)$$

$$F(3.12) = \frac{N(K_B T)^4}{2^{24}} \frac{\phi''' \phi^{IV} \phi^V}{[\phi'']^6} \sum_{n_1 n_2 n_3} F^2(n_1, n_2, n_3) \frac{(n_1 \cdot n_2)(n_1 \cdot n_3)}{(n_2 \cdot n_3)} \left[2F(n_1, n_2, n_3) - F(n_1 + n_2, n_2, n_3) - F(n_1 - n_2, n_2, n_3) \right] \quad (5.43)$$

For diagrams F(3.13) and F(3.14) the expressions are:

$$F(3.13) = \frac{N(K_B T)^4}{2^{22}} \frac{\phi''' \phi^{IV} \phi^V}{[\phi'']^6} \sum_{n_1 n_2} \sum_{n_1' n_2' n_3} F^2(n_1, n_1', n_2) F(n_1 + n_2, n_1', n_3) F^2(n_2, n_2', n_3) \quad (5.44)$$

$$F(3.14) = \frac{N(K_B T)^4}{3 \times 2^{23}} \frac{\phi''' \phi^{IV} \phi^V}{[\phi'']^6} \sum_{n_1 n_2} \sum_{n_1' n_2' n_3} F(n_1 + n_2, n_1', n_3) F^3(n_1, n_1', n_2) F^2(n_2, n_2', n_3) \quad (5.45)$$

The same expression arises in both cases with the use of the sum rules or without it.

In the same manner we can write the corresponding expression for diagram F(3.15) as

$$F(3.15) = \frac{N(K_B T)^4}{3^2 \times 2^4} \frac{[\phi''']^2 [\phi^{IV}]}{[\phi'']^6} \sum_{n_2} \left[\sum_{m_1, n_1} F^3(m_1, n_1, n_2) \right]^2 \quad (5.46)$$

The contribution from diagram F(3.16) can be evaluated exactly with the same method used in evaluating diagrams F(1.2) using the sum rules. In Ludwig's approximation we have obtained the following two expressions:

i) using the sum rule:

$$F(3.16) = \frac{N(K_B T)^4}{2^{18}} \frac{\phi''' \phi^{IV} \phi^V}{[\phi'']^6} \sum_{m, n_1, n_2} F^3(m, n_1, n_2) \quad (5.47)$$

ii) without using the sum rule:

$$F(3.16) = \frac{N(K_B T)^4}{2^{22}} \frac{\phi''' \phi^{IV} \phi^V}{[\phi'']^6} \sum_{m, n_1, n_2, n_3} F^2(m, n_2, n_3) \frac{(n_1, n_2)(n_1, n_3)}{(n_2, n_3)} \quad (5.48)$$

$$\left[2F(m, n_2, n_3) - F(m+n_1, n_2, n_3) - F(m-n_1, n_2, n_3) \right]$$

Exact calculations can be worked out for diagram F(3.17) using the exact result of diagram F(2.7). Making use of Ludwig's approximation and the first sum rule we can evaluate diagram F(3.17) whose expression can be worked out to give:

$$F(3.17) = \frac{N(K_B T)^4}{2^{23}} \frac{\phi''' \phi^{IV} \phi^V}{[\phi'']^6} \sum_{m_1, n_2} \sum_{n_1, n_2, n_3} F^2(m_1, n_1, n_2) F^2(m_2, n_3, n_1) \quad (5.49)$$

$$F(m_1 + m_2, n_3, n_2)$$

With the aid of the result of diagram F(2.6) we can evaluate the contribution from the first of the four vertex diagrams. It is also possible to calculate this diagram in Ludwig's approximation with the expression:

$$F(3.18) = - \frac{N(K_B T)^4}{2^{26}} \frac{[\phi''']^3 \phi^v}{[\phi'']^7} \sum_{m_1, m_2, m_3} \sum_{n_1, n_2, n_3} F(m_1 + m_2 + m_3, n_1, n_4) \\ F(m_3, n_2, n_3) F^2(m_1, n_1, n_2) F^2(m_2, n_3, n_4) \quad (5.50)$$

Ludwig's approximation expression in the case of diagram F(3.19) and F(3.20) are given in the following:

$$F(3.19) = - \frac{N(K_B T)^4}{3 \times 2^{28}} \frac{[\phi''']^3 \phi^v}{[\phi'']^7} \sum_{m_1, m_2, m_3} \sum_{n_1, n_2, n_3, n_4} F^3(m_1, n_1, n_2) F(m_2 + m_3, n_2, n_3) \\ F(m_3, n_2, n_4) F^2(m_2, n_3, n_4) \quad (5.51)$$

$$F(3.20) = - \frac{N(K_B T)^4}{2^{28}} \frac{[\phi''']^3 [\phi^v]}{[\phi'']^7} \sum_{m_1, m_2, m_3} \sum_{n_1, n_2, n_3, n_4} F^2(m_1, n_1, n_4) F(m_1 - m_2, n_1, n_2) \\ F(m_2, n_2, n_4) F(m_2 - m_3, n_2, n_3) F^2(m_3, n_3, n_4) \quad (5.52)$$

Diagram F(3.21) is similar to diagram F(2.8) since we can evaluate exactly the contribution from the loop. In Ludwig's approximation the expression becomes:

$$F(3.21) = - \frac{N(K_B T)^4}{3 \times 2^{25}} \frac{[\phi''']^3 \phi^v}{[\phi''']^7} \sum_{m_1, m_2, m_3} \sum_{n_1, n_2, n_3, n_4} F(m_1 - m_2, n_2, n_1) \\ F(m_1, n_4, n_1) F(m_1 - m_2, n_3, n_1) F(m_3, n_4, n_3) \\ F(m_3 - m_2, n_2, n_3) F(m_2, n_4, n_2) \quad (5.53)$$

The corresponding expressions to the next five diagrams can be evaluated with or without using the sum rules in Ludwig's approximation. Their expressions respectively are:

$$(i) F(3.22) = - \frac{N(K_B T)^4}{2^{19}} \frac{[\phi''']^2 [\phi^{IV}]^2}{[\phi'']^7} \sum_{\tilde{m} \tilde{n}_3 \tilde{n}_4} F^3(\tilde{m}, \tilde{n}_3, \tilde{n}_4) \quad (5.54)$$

$$(ii) F(3.22) = - \frac{N(K_B T)^4}{2^{27}} \frac{[\phi''']^2 [\phi^{IV}]^2}{[\phi'']^7} \sum_{\tilde{m} \tilde{n}_1 \tilde{n}_2 \tilde{n}_3 \tilde{n}_4} \left\{ (\tilde{n}_1 \cdot \tilde{n}_2)^2 + \frac{1}{3} \right\} \frac{(\tilde{n}_2 \cdot \tilde{n}_3)(\tilde{n}_2 \cdot \tilde{n}_4)}{(\tilde{n}_3 \cdot \tilde{n}_4)} \\ [2F(\tilde{m}, \tilde{n}_3, \tilde{n}_4) - F(\tilde{m} + \tilde{n}_2, \tilde{n}_3, \tilde{n}_4) - F(\tilde{m} - \tilde{n}_2, \tilde{n}_3, \tilde{n}_4)] F^2(\tilde{m}, \tilde{n}_3, \tilde{n}_4) \quad (5.55)$$

$$(i) F(3.23) = - \frac{N(K_B T)^4}{2^{23}} \frac{[\phi''']^2 [\phi^{IV}]^2}{[\phi'']^7} \sum_{\tilde{m}_1 \tilde{m}_2 \tilde{n}_3} \sum_{\tilde{n}_1 \tilde{n}_2 \tilde{n}_3 \tilde{n}_4} F^2(\tilde{m}_1, \tilde{n}_1, \tilde{n}_2) F^2(\tilde{m}_2, \tilde{n}_2, \tilde{n}_4) \\ F(\tilde{m}_1 + \tilde{m}_2, \tilde{n}_1, \tilde{n}_4) \quad (5.56)$$

$$(ii) F(3.23) = - \frac{N(K_B T)^4}{2^{27}} \frac{[\phi''']^2 [\phi^{IV}]^2}{[\phi'']^7} \sum_{\tilde{m}_1 \tilde{m}_2} \sum_{\tilde{n}_1 \tilde{n}_2 \tilde{n}_3 \tilde{n}_4} F^2(\tilde{m}_1, \tilde{n}_1, \tilde{n}_2) F^2(\tilde{m}_2, \tilde{n}_2, \tilde{n}_4) \\ \frac{(\tilde{n}_1 \cdot \tilde{n}_3)(\tilde{n}_3 \cdot \tilde{n}_4)}{(\tilde{n}_1 \cdot \tilde{n}_4)} \left[2F(\tilde{m}_1 + \tilde{m}_2, \tilde{n}_1, \tilde{n}_4) - F(\tilde{m}_1 + \tilde{m}_2 + \tilde{n}_3, \tilde{n}_1, \tilde{n}_4) \right. \\ \left. - F(\tilde{m}_1 + \tilde{m}_2 - \tilde{n}_3, \tilde{n}_1, \tilde{n}_4) \right] \quad (5.57)$$

$$(i) F(3.24) = - \frac{N(K_B T)^4}{2^{17}} \frac{[\phi''']^2 [\phi^{IV}]^2}{[\phi'']^7} \sum_{\tilde{m} \tilde{n}_1 \tilde{n}_2} F^3(\tilde{m}, \tilde{n}_1, \tilde{n}_2) \quad (5.58)$$

$$\begin{aligned}
 (i) F(3.24) = & - \frac{(k_B T)^4}{2^{25}} \frac{[\phi''']^2 [\phi^{IV}]^2}{[\phi'']^7} \sum_m \sum_{n_1 n_2 n_3 n_4} \frac{(n_1 \cdot n_2)(n_1 \cdot n_3)}{(n_2 \cdot n_3)} \left[2F(m, n_2, n_3) \right. \\
 & \left. - F(m + n_1, n_2, n_3) - F(m - n_1, n_2, n_3) \right] \frac{(n_2 \cdot n_4)(n_3 \cdot n_4)}{(n_2 \cdot n_3)} \\
 & F(m, n_2, n_3) \left[2F(m, n_2, n_3) - F(m + n_4, n_2, n_3) - F(m - n_4, n_2, n_3) \right] \quad (5.59)
 \end{aligned}$$

$$(i) F(3.25) = - \frac{N(k_B T)^4}{2^{17}} \frac{[\phi^{IV}]^2 [\phi''']^2}{[\phi'']^7} \sum_{m, n_1, n_2} F^3(m, n_1, n_2) \quad (5.60)$$

$$\begin{aligned}
 (ii) F(3.25) = & - \frac{N(k_B T)^4}{2^{25}} \frac{[\phi''']^2 [\phi^{IV}]^2}{[\phi'']^7} \sum_m \sum_{n_1 n_2 n_3 n_4} F^2(m, n_3, n_4) \frac{(n_1 \cdot n_2)(n_1 \cdot n_4)(n_2 \cdot n_3)}{(n_3 \cdot n_4)} \\
 & \left[4F(m, n_3, n_4) - 2F(m + n_2, n_3, n_4) - 2F(m - n_2, n_3, n_4) \right. \\
 & - 2F(m + n_1, n_3, n_4) + F(m + n_1 + n_2, n_3, n_4) + F(m + n_1 - n_2, n_3, n_4) \\
 & - 2F(m - n_1, n_3, n_4) + F(m - n_1 + n_2, n_3, n_4) \\
 & \left. + F(m - n_1 - n_2, n_3, n_4) \right] \quad (5.61)
 \end{aligned}$$

$$(i) F(3.26) = - \frac{N(k_B T)^4}{2^{21}} \frac{[\phi''']^2 [\phi^{IV}]^2}{[\phi'']^7} \sum_{n_1 n_2} \sum_{n_1 n_2 n_3 n_4} F^2(m_1, n_3, n_2) F^2(m_2, n_2, n_4) F(m_1 + m_2, n_3, n_4) \quad (5.62)$$

$$\begin{aligned}
 (ii) F(3.26) = & - \frac{N(k_B T)^4}{2^{25}} \frac{[\phi''']^2 [\phi^{IV}]^2}{[\phi'']^7} \sum_{n_1 n_2} \sum_{n_1 n_2 n_3 n_4} \frac{(n_1 \cdot n_3)(n_1 \cdot n_2)}{(n_2 \cdot n_3)} \left[2F(m, n_3, n_2) \right. \\
 & \left. - F(m + n_1, n_3, n_2) - F(m - n_1, n_3, n_2) \right] F(m_1, n_3, n_2) \\
 & F^2(m_2, n_2, n_4) F(m_1 + m_2, n_3, n_4) \quad (5.63)
 \end{aligned}$$

The remaining four of the four-vertex diagram can be evaluated in Ludwig's approximation. Their expressions are:

$$F(3.27) = -\frac{N(K_B T)^4}{3 \times 2^{28}} \frac{[\phi''']^2 [\phi^{IV}]^2}{[\phi'']^7} \sum_{\tilde{m}_1 \tilde{m}_2 \tilde{m}_3} \sum_{\tilde{n}_1 \tilde{n}_2 \tilde{n}_3 \tilde{n}_4} F^2(\tilde{m}_1, \tilde{n}_1, \tilde{n}_2) F(\tilde{m}_1 + \tilde{m}_2 + \tilde{n}_3, \tilde{n}_1, \tilde{n}_4) \\ F(\tilde{m}_3, \tilde{n}_3, \tilde{n}_2) F^3(\tilde{m}_2, \tilde{n}_3, \tilde{n}_4) \quad (5.64)$$

$$F(3.28) = -\frac{N(K_B T)^4}{2^{29}} \frac{[\phi''']^2 [\phi^{IV}]^2}{[\phi'']^7} \sum_{\tilde{m}_1 \tilde{m}_2 \tilde{m}_3} \sum_{\tilde{n}_1 \tilde{n}_2 \tilde{n}_3 \tilde{n}_4} F^2(\tilde{m}_1 - \tilde{m}_2, \tilde{n}_1, \tilde{n}_2) \\ F^2(\tilde{m}_1, \tilde{n}_1, \tilde{n}_3) F(\tilde{m}_2, \tilde{n}_2, \tilde{n}_4) F^2(\tilde{m}_3, \tilde{n}_3, \tilde{n}_4) \quad (5.65)$$

$$F(3.29) = -\frac{N(K_B T)^4}{2^{28}} \frac{[\phi''']^2 [\phi^{IV}]^2}{[\phi'']^7} \sum_{\tilde{m}_1 \tilde{m}_2 \tilde{m}_3} \sum_{\tilde{n}_1 \tilde{n}_2 \tilde{n}_3 \tilde{n}_4} F(\tilde{m}_1, \tilde{n}_1, \tilde{n}_4) \\ F(\tilde{m}_1 + \tilde{m}_3, \tilde{n}_1, \tilde{n}_3) F(\tilde{m}_1 - \tilde{m}_2, \tilde{n}_1, \tilde{n}_2) F(\tilde{m}_2 + \tilde{m}_3, \tilde{n}_2, \tilde{n}_3) \\ F(\tilde{m}_2, \tilde{n}_2, \tilde{n}_4) F^2(\tilde{m}_3, \tilde{n}_3, \tilde{n}_4) \quad (5.66)$$

$$F(3.30) = -\frac{N(K_B T)^4}{2^{28}} \frac{[\phi''']^2 [\phi^{IV}]^2}{[\phi'']^7} \sum_{\tilde{m}_1 \tilde{m}_2 \tilde{m}_3} \sum_{\tilde{n}_1 \tilde{n}_2 \tilde{n}_3 \tilde{n}_4} F(\tilde{m}_1 - \tilde{m}_2, \tilde{n}_1, \tilde{n}_2) \\ F(\tilde{m}_1, \tilde{n}_1, \tilde{n}_4) F^2(\tilde{m}_1 - \tilde{m}_3, \tilde{n}_1, \tilde{n}_3) F(\tilde{m}_2, \tilde{n}_2, \tilde{n}_4) \\ F(\tilde{m}_3, \tilde{n}_3, \tilde{n}_4) \quad (5.67)$$

So far, it was possible to execute all contributions to the free energy in reasonable computational time. In the fifth order contributions, the computational time is almost exceeding fifty times the previous calculations. We have tried to use the symmetry in the arguments whenever possible. However, the computational time for diagrams F(3.36) and F(3.37) exceeds an hour.

The contribution from diagram F(3.31) can be written in the form

$$F(3.31) = \frac{N(K_B T)^4}{2^{34}} \frac{[\phi''']^4 \phi^{1v}}{[\phi'']^8} \sum_{n_3} \left[\sum_{n_1} \sum_{n_2} F^2(n_1, n_1, n_2) \{ 2F(n_1, n_1, n_2) - F(n_1 - n_3, n_1, n_2) - F(n_1 + n_3, n_1, n_2) \} \frac{(n_1 \cdot n_3)(n_2 \cdot n_3)}{(n_1 \cdot n_2)} \right]^2 \quad (5.68)$$

The next three of the five-vertex diagram can be evaluated exactly using the result of the contributions from diagrams F(2.6) and F(2.8) and also the sum rules. Their expressions can easily be derived from eqs. (4.49), (4.50), and (4.51). In Ludwig approximation we have executed these diagrams with and without the sum rules. Their expressions respectively are:

$$(i) F(3.32) = \frac{N(K_B T)^4}{2^{26}} \frac{[\phi''']^4 \phi^{1v}}{[\phi'']^8} \sum_{n_1 n_2 n_3} \sum_{n_1 n_2 n_3 n_4} F(n_1 + n_2 + n_3, n_1, n_4) F(n_3, n_2, n_3) F^2(n_1, n_1, n_2) F^2(n_2, n_3, n_4) \quad (5.69)$$

$$(ii) F(3.32) = \frac{N(K_B T)^4}{2^{30}} \frac{[\phi''']^4 \phi^{1v}}{[\phi'']^8} \sum_{n_1 n_2 n_3} \sum_{n_1 n_2 n_3 n_4 n_5} \frac{(n_1 \cdot n_2)(n_1 \cdot n_3)}{(n_2 \cdot n_3)} \left[2F(n_1, n_2, n_3) - F(n_1 + n_1, n_2, n_3) - F(n_1 - n_1, n_2, n_3) \right] F(n_1, n_2, n_3) F(n_1 + n_2 + n_3, n_2, n_5) F(n_3, n_3, n_4) F^2(n_2, n_4, n_5) \quad (5.70)$$

$$(i) F(3.33) = \frac{N(K_B T)^4}{2^{26}} \frac{[\phi''']^4 \phi^{IV}}{[\phi'']^8} \sum_{m_1, m_2, m_3} \sum_{n_1, n_2, n_3, n_4} F(m_1, n_1, n_2) F(m_1 + m_3, n_1, n_4)$$

$$F(m_1 - m_2, n_1, n_3) F(m_2, n_3, n_2) F(m_2 + m_3, n_3, n_4)$$

$$F(m_3, n_2, n_4)$$

(5.71)

$$(ii) F(3.33) = \frac{N(K_B T)^4}{2^{30}} \frac{[\phi''']^4 \phi^{IV}}{[\phi'']^8} \sum_{m_1, m_2, m_3} \sum_{n_1, n_2, n_3, n_4, n_5} F(m_1, n_1, n_2) F(m_1 + m_2, n_1, n_5)$$

$$F(m_1 - m_2, n_1, n_3) F(m_2, n_3, n_2) F(m_2 + m_3, n_3, n_5)$$

$$\frac{(n_2 \cdot n_4)(n_5 \cdot n_4)}{(n_2 \cdot n_5)} \left[2 F(m_3, n_2, n_5) - F(m_3 + n_4, n_2, n_5) \right.$$

$$\left. - F(m_3 - m_4, n_2, n_5) \right]$$

(5.72)

$$(i) F(3.34) = \frac{N(K_B T)^4}{2^{27}} \frac{[\phi''']^4 \phi^{IV}}{[\phi'']^8} \sum_{m_1, m_2, m_3} \sum_{n_1, n_2, n_3, n_4} F(m_1 + m_2 + m_3, n_1, n_4)$$

$$F(m_3, n_2, n_3) F^2(m_1, n_1, n_2) F^2(m_2, n_3, n_4) \quad (5.73)$$

$$(ii) F(3.34) = \frac{N(K_B T)^4}{2^{31}} \frac{[\phi''']^4 \phi^{1v}}{[\phi'']^8} \sum_{m_1, m_2, m_3} \sum_{n_1, n_2, n_3, n_4, n_5} F^2(m_1, n_1, n_4)$$

$$F(m_3, n_4, n_5) F^2(m_2, n_5, n_3) \frac{(n_1 \cdot n_2)(n_2 \cdot n_3)}{(n_1 \cdot n_3)}$$

$$\left[2F(m_1 + m_2 + m_3, n_1, n_3) - F(m_1 + m_2 + m_3 + n_2, n_1, n_3) - F(m_1 + m_2 + m_3 - n_2, n_1, n_3) \right] \quad (5.74)$$

The time of computation for the contribution from diagram F(3.35) in Ludwig approximation was 29 minutes on Burroughs 5500.

The expression is given by:

$$F(3.35) = \frac{N(K_B T)^4}{2^{31}} \frac{[\phi''']^4 \phi^{1v}}{[\phi'']^8} \sum_{m_1, m_2, m_3, m_4} \sum_{n_1, n_2, n_3, n_4, n_5} F^2(m_1, n_1, n_2)$$

$$F(m_1 + m_4, n_1, n_4) F(m_2, n_3, n_4) F^2(m_3, n_4, n_5)$$

$$F(m_4, n_2, n_3) F(m_2 + m_3, n_3, n_5) \quad (5.75)$$

Time of executions for diagrams F(3.36) and F(3.37) are 72 and 100 minutes, respectively. Their expressions are:

$$F(3.36) = \frac{N(K_B T)^4}{2^{33}} \frac{[\phi''']^4 [\phi^{1v}]}{[\phi'']^8} \sum_{m_1, m_2, m_3} \sum_{n_1, n_2, n_3, n_4, n_5} F^2(m_1, n_1, n_3) F^2(m_2, n_2, n_1)$$

$$F^2(m_3, n_4, n_5) \frac{(n_2 \cdot n_4)(n_3 \cdot n_5)}{(n_4 \cdot n_5)} \left[F(m_1 + m_2 + m_3, n_4, n_5) \right.$$

$$- F(m_1 + m_2 + m_3 - n_2, n_4, n_5) - F(m_1 + m_2 + m_3 + n_3, n_4, n_5)$$

$$\left. + F(m_1 + m_2 + m_3 - n_2 + n_3, n_4, n_5) \right] \quad (5.76)$$

$$\begin{aligned}
F(3.37) &= \frac{N(K_B T)^4}{2^{31}} \frac{[\phi''']^4 [\phi^{IV}]}{[\phi'']^8} \sum_{m_1 m_2 m_3 m_4} \sum_{n_1 n_2 n_3 n_4 n_5} F(m_1 - m_2, n_1, n_2) \\
&\quad F(m_1, n_1, n_5) F(m_3, n_1, n_3) F(m_3 + m_4 - m_1, n_4, n_3) \\
&\quad F(m_2, n_2, n_5) F(m_2 + m_3 - m_1, n_2, n_3) F^2(m_4, n_4, n_5)
\end{aligned} \quad (5.77)$$

Making use of the symmetry of the sums over n_i , the expression which corresponds to diagram F(3.38) reduced to:

$$\begin{aligned}
F(3.38) &= \frac{N(K_B T)^4}{2^{32}} \frac{[\phi''']^4 [\phi^{IV}]}{[\phi'']^8} \sum_{m_1 m_4} \sum_{n_1 n_3 n_5} F(m_1, n_1, n_3) F(m_4, n_3, n_5) \\
&\quad \left[\sum_{n_2 n_2} F(m_1 - m_2, n_1, n_2) F(m_2, n_2, n_3) F(m_2 + m_4, n_2, n_5) \right]^2
\end{aligned} \quad (5.78)$$

Time of execution for the last expression was 188 seconds. There are five diagrams in the sixth order each of them involves summations over five m 's and six n 's. In other words the computational time is exceeding once more by a factor of fifty. However, we have succeeded in using the symmetry for two diagrams F(3.44) and F(3.45). In the case of diagram F(3.39) we have used the method discussed in evaluating diagram F(2.6). Its expression is given by:

$$F(3.39) = - \frac{N(K_B T)^4}{3 \times 2^{37}} \frac{[\phi''']^6}{[\phi'']^9} \sum_{K, j, j''} M(K, j, j') M(K, j', j'') M(K, j'', j) \quad (5.79)$$

where $M(\kappa, j, j')$ is given by eq. (5.24).

Time of execution was 168 seconds. We have found that the value converges after the fifth mesh size. Diagram F(3.40) is one of the most difficult diagrams. It has taken nine hours on Burroughs 5500.

Its expression is:

$$\begin{aligned}
 F(3.40) = & - \frac{N(K_B T)^4}{2^{38}} \frac{[\phi''']^6}{[\phi'']^9} \sum_{m_1 m_2 m_3 m_4} \sum_{n_1 n_2 n_3 n_4 n_5 n_6} (n_1, n_2) F(m_3 - m_2 - m_4, n_3, n_2) \\
 & F(n_2, n_2, n_4) F(m_3 - m_4, n_3, n_4) F(m_4, n_4, n_6) \\
 & F(m_3, n_3, n_6) F^2(m_1, n_1, n_5) \\
 & [F(m_1 - m_2 - m_4, n_6, n_5) - F(m_1 - m_2 - m_4 - n_1, n_6, n_5) \\
 & - F(m_1 - m_2 - m_4 + n_2, n_6, n_5) + F(m_1 - m_2 - m_4 - n_1 + n_2, n_6, n_5)] \quad (5.80)
 \end{aligned}$$

Diagram F(3.41) has been executed on CDC6600 in Chalk River in ten minutes.

Its expression is:

$$\begin{aligned}
 F(3.41) = & - \frac{N(K_B T)^4}{2^{38}} \frac{[\phi''']^6}{[\phi'']^9} \sum_{m_1 m_2 m_3 m_4 m_5} \sum_{n_1 n_2 n_3 n_4 n_5 n_6} F(m_1, n_1, n_2) \\
 & F(m_1 + m_2, n_1, n_3) F(m_1 + m_2 + m_3 + m_4, n_1, n_4) F(m_2, n_2, n_3)
 \end{aligned}$$

$$F(m_3, n_3, n_5) F(m_2 + m_3 + m_4 + m_5, n_2, n_6) F(m_4, n_5, n_4)$$

$$F(m_4 + m_5, n_5, n_6) F(m_5, n_4, n_6)$$

(5.81)

The contributions from diagrams F(3.42) and F(3.43) is reduced to:

$$F(3.42) = - \frac{N(K_B T)^4}{2^{39}} \frac{[\phi^{(1)}]^6}{[\phi^{(1)}]^9} \sum_{m_3, n_5, n_6} F(m_3, n_6, n_5) \left[\sum_{\substack{n_1, n_2 \\ m_1, m_4}} F^2(m_1, n_1, n_2) \right.$$

$$\left. F(m_1 + m_3 + m_4, n_1, n_5) F(m_4, n_2, n_6) \right]^2 \quad (5.82)$$

$$F(3.43) = - \frac{N(K_B T)^4}{9 \times 2^{36}} \frac{[\phi^{(1)}]^6}{[\phi^{(1)}]^9} \sum_{m_2, m_4, m_5} \sum_{n_2, n_4, n_5, n_6} F(m_2, n_2, n_6)$$

$$F(m_4, n_4, n_6) F(m_5, n_5, n_6) \left[\sum_{\substack{m_1, n_1}} F(m_1, n_1, n_2) \right.$$

$$\left. F(m_1 + m_2 - n_5, n_1, n_5) F(m_1 + m_2 - m_4, n_1, n_4) \right]^2 \quad (5.83)$$

VI. Discussion

The knowledge of a two-body potential function is essential to obtain the different order derivatives and to make a direct comparison of the magnitude of the various contributions to Helmholtz free energy. We have first assumed the Lennard-Jones form for the two-body potential which is defined by:

$$\phi(r) = \epsilon \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right] \quad (6.1)$$

where in eq. (6.1) ϵ is the well depth and r_0 is the nearest neighbour distance corresponding to the minimum in the potential for the nearest neighbour face-centered cubic crystal model. These parameters can be obtained from the review by Horton [26]. The λ^2 , λ^4 and λ^6 contributions to the free energy in the high temperature limit are expressed in the units of $N (k_B T)^2 / \epsilon$; $N (k_B T)^3 / \epsilon^2$ and $N (k_B T)^4 / \epsilon^3$, respectively.

Maradudin et al. [6] have worked out the contributions of order λ^2 to the Helmholtz free energy in Ludwig's approximation (LA) as well as the exact calculation. The contributions from the diagrams of order λ^2 have been presented, along with the corresponding totals, in table (1), where the first column gives the tables of the diagrams presented in Fig. (1), the second gives the exact values, the third gives the results using LA and the fourth gives the percentage deviation of the results using LA from the exact ones. It is found that LA gives an exact result for diagram F(1.1) whereas it is about 16% low in the case of diagram F(1.2).

We have presented the individual as well as final total contribution from all diagrams of order λ^4 in table (2). The first four columns have the same structure as table (1); the fifth column gives the

contribution from each diagram in Ludwig's approximation using the sum rule (LAUS) mentioned in eq. (5.8) and the sixth column gives the percentage deviation of the results applying LAUS from the exact calculations which has been carried out by Shukla and Cowley [9]. Wilk [10] and Aggarwal and Pathak [11] have worked out the contributions of order λ^4 to the free energy using LA. Our calculations are in agreement with theirs. LA is found to give exact result for diagram F(2.1); it underestimates most of the diagrams by about 18% and overestimates diagrams F(2.3) and F(2.4) by about 20%. We have obtained exact results using LAUS for diagrams F(2.1) and F(2.3); one diagram is overestimated by about 14% and the rest of the diagrams are underestimated by about 18%. The total free energy in all cases is of negative signs. There are significant differences between the exact results and those obtained in LA which indicates that this approximation is not very good. The ratio of the total contribution of order λ^4 to that of order λ^2 in the exact calculation (F_E), LA (F_{LA}) and LAUS (F_{LAUS}) are respectively given by

$$F_E(\lambda^4) / F_E(\lambda^2) = -0.554 \quad K_B T / \epsilon \quad (6.2)$$

$$F_{LA}(\lambda^4) / F_{LA}(\lambda^2) = -0.915 \quad K_B T / \epsilon \quad (6.3)$$

$$F_{LAUS}(\lambda^4) / F_{LAUS}(\lambda^2) = -0.748 \quad K_B T / \epsilon \quad (6.4)$$

For the inert-gas crystals, the potential well depth corresponds to a temperature of approximately twice the melting temperature. In view of the exact ratio discussed by Shukla and Cowley [9] the convergence of the

perturbation expansion, in LA and LAUS cannot be relied upon. Shukla and Cowley [9] have also grouped the diagrams according to the set of diagrams summed in the SC1 theory, the ISC and SC2. We have followed the same set of grouping the diagrams, in LA and LAUS as presented in table (5). In all calculations, only ISC gives a subtotal which is close to the complete value. This suggests that ISC is a reliable theory. In the case of SC1 and SC2, the numbers have the same sign but differ in magnitude from the final total.

Explicit expressions for the forty three diagrams contributing to the free energy in $O(\lambda^6)$ have been derived. The calculation for some diagrams in this order are quite complicated. The difficulty is a computational one since they involve summations over the Brillouin zone and these take considerable time even on a fast modern computer. For twenty four diagrams we have been able to carry out exact calculations. In table (3) we have presented the contributions from all diagrams of order λ^6 . LA gives exact result for diagram F(3.1). In comparison with the exact results where we have been able to perform the calculations, we have found that LA overestimates some diagrams by about 34% and underestimates some diagrams by about 20%. LAUS gives exact results for diagrams F(3.1), F(3.4), F(3.7) and F(3.8). It underestimates most of the diagrams by about 15% and overestimates diagrams F(3.3), F(3.5) and F(3.9) by about 11% i.e. using the sum rule has given more reasonable estimates for most diagrams.

The ratio of the total contribution of order λ^6 to that of order λ^4 in LA and LAUS are respectively given by

$$F_{LA}(\lambda^6) / F_{LA}(\lambda^4) = -3.312 \quad k_B T / \epsilon \quad (6.5)$$

$$F_{LAUS}(\lambda^6) / F_{LAUS}(\lambda^4) = -2.328 \quad K_B T / \epsilon \quad (6.6)$$

The ratio in each case is negative and that is the same as the ratio in eqs. (6.2), (6.3) and (6.4). The totals also turn out to be opposite in sign than that of order λ^4 whereas we did expect the sign to be the same since the lowest order perturbation theory (PT) is inadequate and we are adding corrections to it. This indicates that probably LA is not a very good approximation.

As it has been mentioned by Maradudin et al. [6] that the main usefulness of LA lies in the evaluation of the more complex diagrams.

We have presented in table (5) the numbers for SC1 and ISC in all calculations of order λ^6 . We have also given the SC2 in LA and LAUS. All numbers in SC1 and ISC have the same negative sign. LAUS has given the same value as that of exact calculation. The number in LA is close. ISC gives for all calculations a close negative value which we may rely upon more than the total value. The ratios of the total of ISC of order λ^6 to that of order λ^4 in the exact calculation and LA and LAUS in units of (KT/ϵ) are: 2.782, 1.472 and 1.828. Although the signs in all ratios are the same and as we expect, LA and LAUS are 47% and 34% low respectively. SC2 is positive in LA. Three diagrams remaining in the exact calculation, all of them negative in sign when added to the number, may change the final number and its sign which will indicate that LA is unreliable.

All diagrams containing a loop (or loops) give rise to T^2 coefficient to the free energy and hence T in the specific heat at high-temperatures. We have worked out the contributions from all diagrams and the results have

been presented in table (4). The ratio of the total contribution of order λ^6 , T^4 coefficient, to that of the same order, T^2 coefficient is 73.64 in the unit of $\hbar^2 \epsilon / M (\kappa_B T)^2$ which is very small, i.e. the leading term of temperature is sufficient to deal with. As shown experimentally (Brooks [1] and Leadbetter [2]), the terms up to λ^4 include linear and quadratic terms in the specific heat at high temperatures. Order λ^6 gives rise to a cubic term of temperature in specific heat at high temperatures. Also all powers of temperatures descending and ascending will be included as we proceed to higher order PT.

We have repeated the previous calculations using Morse potential which is given by:

$$\phi(r) = \epsilon \left\{ e^{-2\alpha(r-r_0)} - 2 e^{-\alpha(r-r_0)} \right\}$$

where ϵ and r_0 are parameters carrying the same meaning as those in Lennard-Jones potential. α is an additional parameter. These parameters are given in the review paper of Horton [26] and more recently they have been determined by Glyde [27] for rare gas crystals. The individual diagrams gave the same percentage deviation as previously discussed. The total contribution in the case of λ^6 using LA and LAUS are respectively 0.162 and 0.647 which is again positive indicating that LA is doubtful.

Exponential six (Buckingham) potential has also been used fairly widely in rare gas crystals, Horton [26]. It takes the form:

$$\phi(r) = \epsilon \left[e^{-12\left(\frac{r}{r_0} - 1\right)} - 2\left(\frac{r_0}{r}\right)^6 \right]$$

The total results in λ^6 using Ludwig's approximations with and without the use of the sum rule are respectively 0.577 and 1.032. In both

potentials Morse and Exp. 6 the convergence of the perturbation theory is better than that of Lennard-Jones.

Table 1

The Free Energy for an Anharmonic Crystal of $O(\lambda^2)$ Applying Lennard-Jones
 Potential in units of $\sim (k_B T)^2 / \epsilon$

Diagram	Exact Sum E	Ludwig's Approximation (LA)	% Deviation
(1.1)	0.966	0.966	0%
(1.2)	-0.344	-0.287	-16%
Total	0.622	0.679	

Table 2

The Free Energy for an Anharmonic Crystal of $O(\lambda^4)$ Applying Lennard-Jones
 Potential in units of $N(K_B T)^3/\epsilon^2$

Diagram	E	LA	% Deviation	LA using the sum rule (LAUS)	% Deviation between LAUS and E
(2.1)	0.345	0.345	0%	0.345	0%
(2.2)	-1.245	-1.556	25%	-1.245	0%
(2.3)	-0.732	-0.611	-16%	-0.611	-16%
(2.4)	1.328	1.3176	-0.78%	1.110	-16%
(2.5)	-0.216	-0.246	14%	-0.246	14%
(2.6)	-0.359	-0.293	-18%	-0.293	-18%
(2.7)	0.619	0.491	-20%	0.491	-20%
(2.8)	-0.086	-0.0687	-20%	-0.0687	-20%
Total	-0.346	-0.621		-0.518	

Table 3

The Free Energy for an Anharmonic Crystal of $\alpha(\text{Al})$ using the Lennard-Jones Potential in units of $\sim (k_B T)^{1/3} / \text{\AA}^3$

Diagram	E	LA	% Deviation	LAUS	% Deviation between LAUS and E
(3.1)	0.107	0.107	0%	0.107	0%
(3.2)	-0.417	-0.349	-16.3%	-0.349	-16.3%
(3.3)	-0.463	-0.528	14%	-0.528	14%
(3.4)	-1.334	-1.667	20%	-1.334	0%
(3.5)	-0.086	-0.081	5%	-0.081	5%
(3.6)	-0.389	-0.326	-19%	-0.3255	-19%
(3.7)	1.0688	1.336	25%	1.0688	0%
(3.8)	1.603	2.505	56%	1.603	0%
(3.9)	1.112	1.641	47%	1.269	14%
(3.10)		0.435		0.435	
(3.11)	0.942	0.788	-16%	0.788	-16%
(3.12)	2.827	2.806	-0.74%	2.363	-16%
(3.13)	1.317	1.046	-20%	1.046	-20%
(3.14)		0.905		0.905	
(3.15)		0.0991		0.0991	
(3.16)	0.711	0.706	-0.70%	0.595	-16%
(3.17)	0.663	0.526	-20%	0.526	-20%
(3.18)	-1.528	-1.249	-18%	-1.249	-18%
(3.19)		-0.417		-0.417	
(3.20)		-0.525		-0.525	
(3.21)	-0.368	-0.293	-20%	-0.293	-20%
(3.22)	-1.71	-2.121	24%	-1.429	-16%
(3.23)	-0.797	-0.71	-11%	-0.633	-20%
(3.24)	-1.71	-1.029	-40%	-1.429	-16%
(3.25)	-1.71	-2.326	36%	-1.43	-16%
(3.26)	-3.187	-3.138	1.5%	-2.53	-20%
(3.27)		-0.258		-0.258	
(3.28)		-0.252		-0.252	
(3.29)		-0.477		-0.477	
(3.30)		-0.535		-0.5346	
(3.31)		0.0112		0.0112	
(3.32)	1.848	1.215	-34%	1.511	-18%
(3.33)	0.667	1.585	137%	0.531	-20%
(3.34)	0.924	0.987	6.8%	0.756	-18%
(3.35)		1.366		1.366	
(3.36)		0.336		0.336	
(3.37)		0.419		0.419	
(3.38)		0.380		0.3803	
(3.39)		-0.147		-0.147	
(3.40)		-0.290		-0.290	
(3.41)		-0.113		-0.0113	
(3.42)		-0.4027		-0.4027	
(3.43)		-0.0086		-0.0086	
Total		2.058		1.1797	

Table 4

T^2 Coefficient for An Anharmonic Crystal of $O(\lambda^6)$ Applying Lennard-Jones Potential

Diagram	LAUS	LA
(3.1)	0.071	0.071
(3.2)	-0.116	-0.116
(3.3)	-0.088	-0.088
(3.4)	-0.667	-0.834
(3.5)	0.000	0
(3.6)	-0.1085	-0.1085
(3.7)	0.534	0.668
(3.8)	0.534	0.835
(3.9)	0.212	0.273
(3.10)	0.000	0
(3.11)	0.131	0.131
(3.12)	0.788	0.935
(3.13)	0.174	0.174
(3.14)	0.000	0
(3.15)	0.000	0
(3.16)	0.198	0.235
(3.17)	0.088	0.088
(3.18)	-0.208	-0.208
(3.19)	0	0
(3.20)	0	0
(3.21)	-0.049	-0.049
(3.22)	-0.238	-0.354
(3.23)	-0.105	-0.118
(3.24)	-0.476	-0.343
(3.25)	-0.476	-0.775
(3.26)	-0.422	-0.523
(3.27)	0	0
(3.28)	0	0
(3.29)	0	0
(3.30)	0	0
(3.31)	0	0
(3.32)	0.252	0.202
(3.33)	0.885	0.264
(3.34)	0.126	0.165
(3.35)	0	0
(3.36)	0	0
(3.37)	0	0
(3.38)	0	0
(3.39)	0	0
(3.40)	0	0
(3.41)	0	0
(3.42)	0	0
(3.43)	0	0
Total	0.242	0.526

Table 5

Grouping the diagrams of $O(\lambda^6)$
according to SC1, ISC and SC2 theories

Diagram	E	LA	LAUS
(3.1)	0.107	0.107	0.107
(3.4)	-1.334	-1.667	-1.334
(3.7)	<u>1.069</u>	<u>1.336</u>	<u>1.069</u>
SC1	-0.158	-0.224	-0.158
(3.2)	-0.417	-0.349	-0.349
(3.6)	-0.389	-0.326	-0.326
(3.12)	2.827	2.806	2.363
(3.16)	0.711	0.706	0.595
(3.24)	-1.710	-1.029	-1.429
(3.25)	<u>-1.710</u>	<u>-2.326</u>	<u>-1.429</u>
ISC	-0.846	-0.742	-0.733
(3.3)	-0.463	-0.528	-0.528
(3.5)	-0.086	-0.081	-0.081
(3.9)	1.112	1.641	1.269
(3.11)	0.942	0.788	0.788
(3.18)	-1.528	-1.249	-1.249
(3.19)		-0.417	-0.417
(3.27)		-0.258	-0.258
(3.32)	1.848	1.215	1.511
(3.34)	0.924	0.987	0.755
(3.39)		<u>-0.147</u>	<u>-0.147</u>
SC2		1.209	0.916

VII Conclusion

In this thesis we have evaluated the anharmonic contribution of order λ^6 to the free energy of a face-centered-cubic lattice with nearest neighbour central-force interactions in the high-temperature limit using the leading term and the Ludwig approximations. As has been shown, Ludwig's approximation has given a considerable simplification in the computation of various summations which arise in the free energy expressions. One diagram has given exact value, some diagrams are overestimated by about 34% and some are underestimated by about 20%. Using the sum rule in eq. (5.8) have offered more reliable results. This procedure has given exact results for four diagrams; it overestimates three diagrams by about 11%, and underestimates some by about 15%. The most highly connected diagrams, such as F(3.5), F(3.31), F(3.41) and F(3.43) give the smallest contributions of all diagrams confirming Choquard's prediction [12]. We have also derived the next higher terms in the high temperature limit. T^2 coefficients have been evaluated for all diagrams of order λ^6 . The ratio of the T^2 coefficients of order λ^6 to that of order λ^2 is negligible indicating that the linear term contribution to anharmonic C_v comes mainly from the λ^2 term in free energy.

Figure (1)

DIAGRAMS OF ORDER λ^2

DIAGRAM FROM V_4 TERM

(1.1)



P.S.

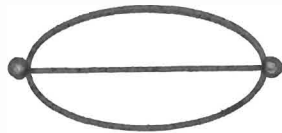
T.E.D.

3

1

DIAGRAM FROM $V_3 - V_3$ TERM

(1.2)



P.S.

T.E.D.

6

1



9

1

TOTAL OF P.S.

15

Figure (2)

DIAGRAMS OF ORDER λ^4

DIAGRAM FROM V_6 TERM



P.S.

T.E.D.

15

1

DIAGRAMS FROM V_3-V_5 TERM



60

2



45

2

TOTAL OF P.S. 105

DIAGRAMS FROM V_4-V_4 TERM



9

1



72

1



24

1

TOTAL OF P.S. 105

DIAGRAMS FROM $V_3-V_3-V_4$ TERM



P.S.

T.E.D.

18

3



27

3



108

6



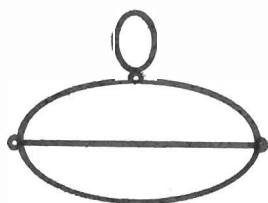
72

6



108

3



216

3



216







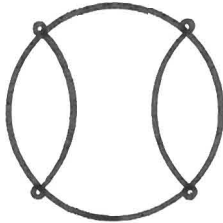
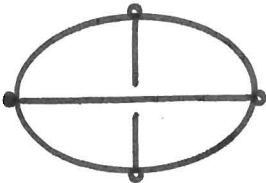
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TOTAL OF P.S.

945

3

DIAGRAMS FROM $V_3 - V_3 - V_3 - V_3$ TERMS

	P.S.	T.E.D.
	36	3
	54	6
	81	3
	162	6
	162	4
	324	12
	324	6
	2196	1
TOTAL OF P.S.	10,395	1

THE DIAGRAMS WHICH GIVE CONTRIBUTION TO THE FREE ENERGY OF ORDER λ^4



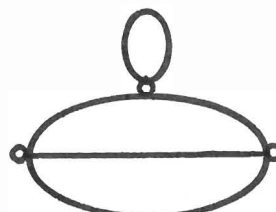
F(2.1)



F(2.2)



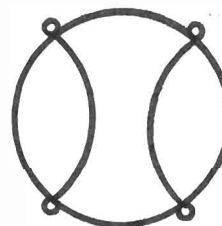
F(2.3)



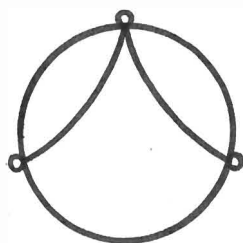
F(2.4)



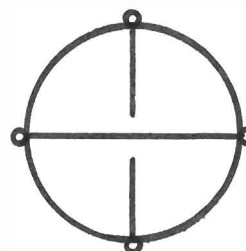
F(2.5)



F(2.6)



F(2.7)



F(2.8)

Figure (3)

DIAGRAMS OF ORDER λ^6

DIAGRAM FROM V_8 TERM

P.S.

T.E.D.

(3.1)

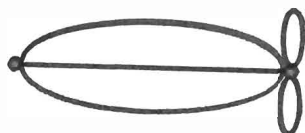


105

1

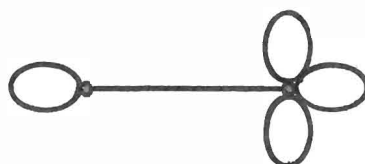
DIAGRAMS FROM V_3-V_7 TERM

(3.2)



315

2



630

2

TOTAL OF P.S. 945

DIAGRAM FROM V_4-V_6 TERM



45

2

(3.3)



360

2

(3.4)



540

2

TOTAL OF P.S. 945

DIAGRAMS FROM $V_5 - V_5$ TERMS



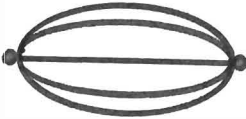


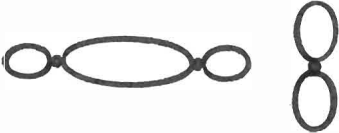
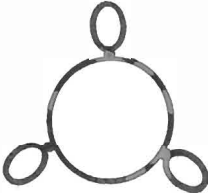

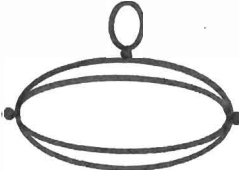
		P.S.	T.E.D.
		225	1
(3.5)		600	1
(3.6)		120	1
	TOTAL	945	

DIAGRAM FROM $V_4 - V_4 - V_4$ TERM

		27	1
		72	3
		216	3
(3.7)		1728	1
(3.8)		864	3
(3.9)		1152	3

(3.10)



TOTAL

P.S.

1728

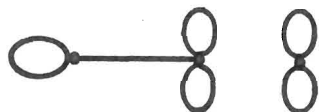
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T.E.D.

1

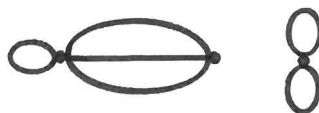
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DIAGRAMS FROM $V_3 - V_4 - V_5$ TERM



135

6



180

6



360

6



360

6



540

6



720

6



1080

6



540

6

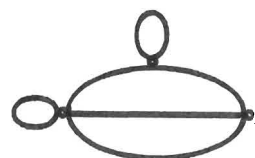
(3.11)



720



6

(3.12)









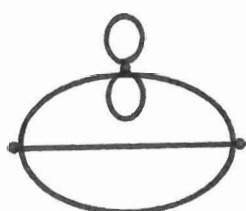



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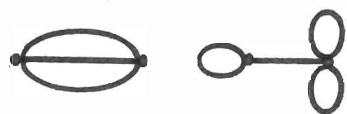
6

		P.S.	T.E.D.
(3.13)		2160	6
(3.14)		<u>1440</u>	<u>6</u>
	TOTAL	10,395	6

Diagrams from $V_3 - V_3 - V_6$ term.

			90	3
			135	3
		810	3	
		810	6	
		1080	6	
(3.15)		720	3	
(3.16)		1620	3	
(3.17)		<u>3240</u>	<u>3</u>	
	TOTAL	10,395	3	

DIAGRAMS FROM $V_3-V_3-V_3-V_5$ TERM



P.S.

T.E.D.

270

12



405

12



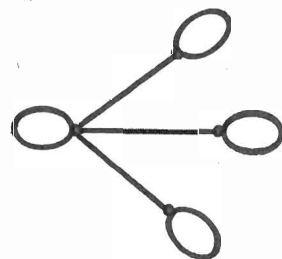
360

12



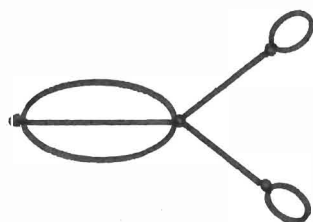
540

12



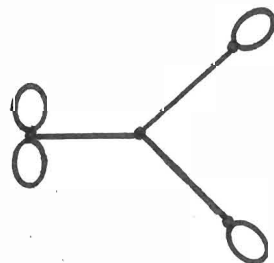
1620

4



1080

12



810

12





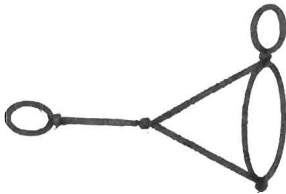


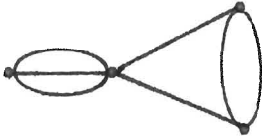

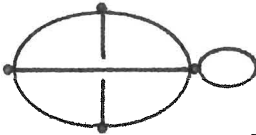


1620


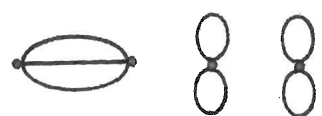





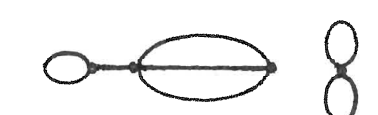



24

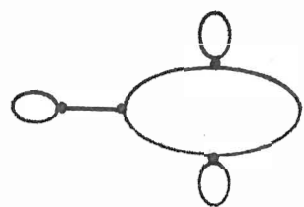
P.S.

T.E.D.

		1080	24
		810	24
		3240	12
		3240	12
		3240	24
		1620	12
(3.18)		3240	24
(3.19)		2160	12
(3.20)		6480	12
(3.21)		<u>12,960</u>	<u>4</u>
	TOTAL	135,135	4

DIAGRAMS FROM $V_3 - V_3 - V_4 - V_4$ TERM

	P.S.	T.E.D.
	81	6
	54	6
	216	6
	144	6
	648	6
	432	6
	324	24
	216	24
	324	12
	648	12
	648	12

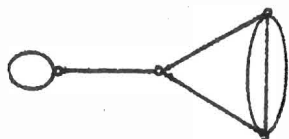


P.S.

T.E.D.

2592

12



1728

12



1296

24



864

24



1296

12



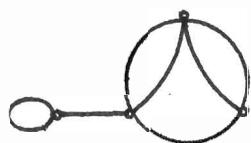
864

12



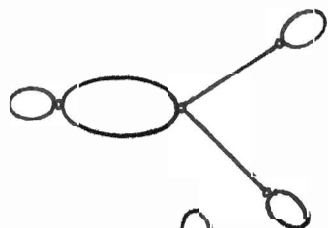
1296

24



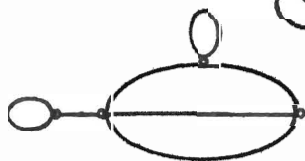
2592

24



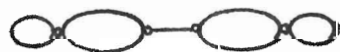
1296

12



2592

24



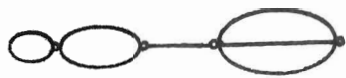
1296

12



576

12



864

24

(3.22)



2592

12

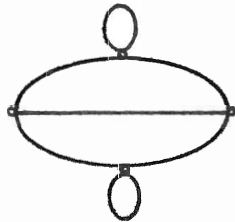
(3.23)



2592

12

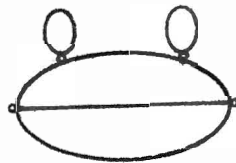
(3.24)



5184

6

(3.25)



2592

12

(3.26)



5184

24

(3.27)



1728

12

(3.28)



2592

12

(3.29)



10368

6

(3.30)



5184




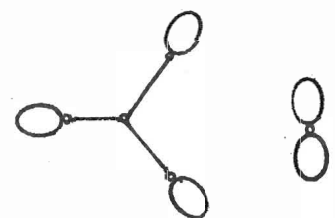
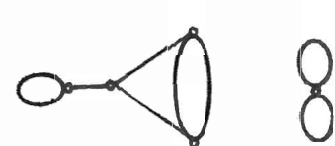
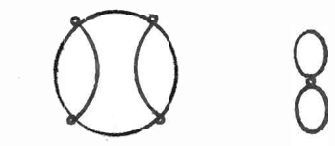
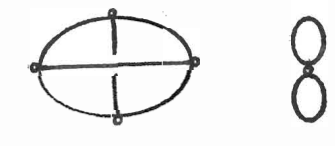





12

TOTAL

135,135

6

DIAGRAMS FROM $V_3-V_3-V_3-V_3-V_4$ TERM

	P.S.	T.E.D.
	108	15
	162	30
	243	15
	486	20
	972	60
	972	30
	3888	5
	486	60
	648	60
	972	60
	432	60
	648	60



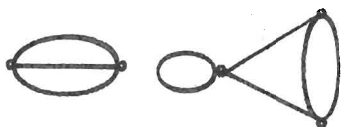
648

30



972

30



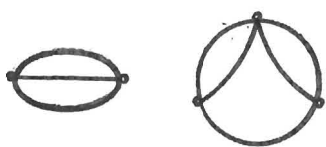
1296

30



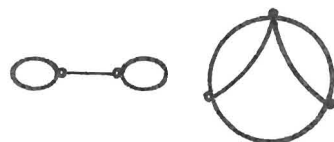
1944

30



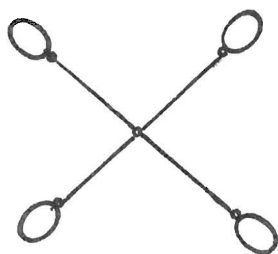
1296

30



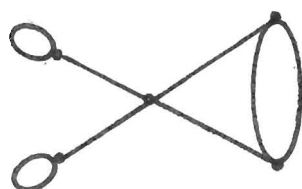
1944

30



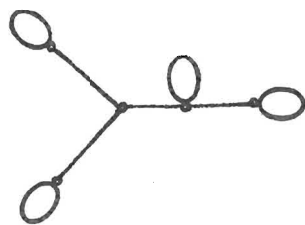
1944

5



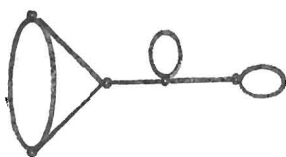
3888

30



1944

60

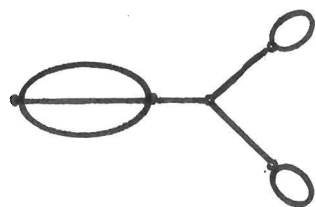


3888

60

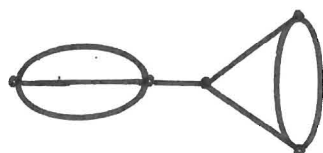
P.S.

T.E.D.



1296

60



2592

60



1296

120



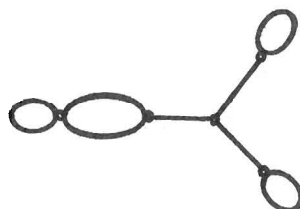
1944

120



1944

120



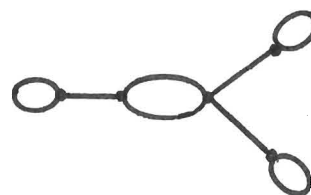
1944

60



3888

60



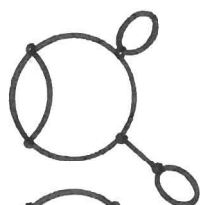
1944

60



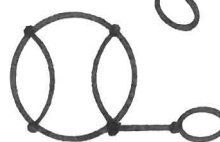
3888

60



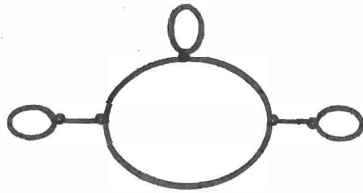
3888

120



3888

120



3888

60



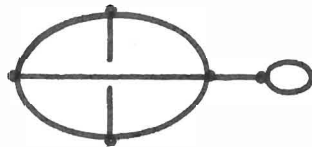
3888

60



1944

60



15552

20



7776

120



3888

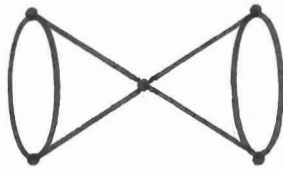
120



7776

60

(3.31)



7776

15

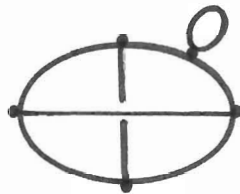
(3.32)



7776

60

(3.33)



15552

30

(3.34)



3888

60

(3.35)



7776

60

(3.36)



3888

120

(3.37)



15552

60

(3.38)







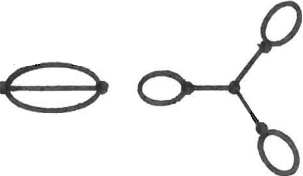

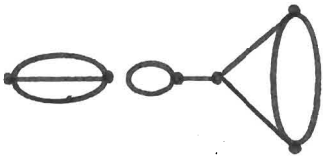
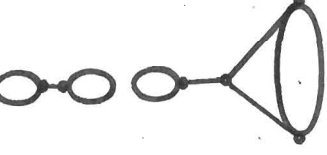
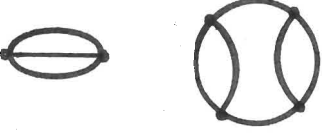

3110415

TOTAL

2,027,025

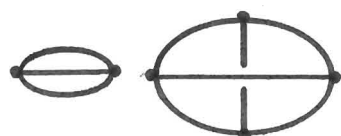
5

DIAGRAMS FROM $V_3-V_3-V_3-V_3-V_3-V_3$ TERM

	P.S.	T.E.D.
	216	15
	324	45
	486	45
	729	15
	972	180
	1458	180
	972	60
	1458	60
	1944	180
	2916	180
	1944	90
	2916	60

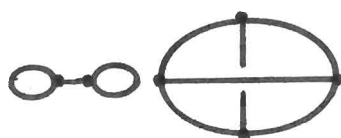
P.S.

T.E.D.



7776

15



11664

15



2916

360



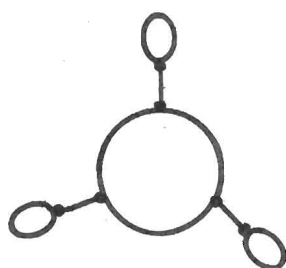
5832

360



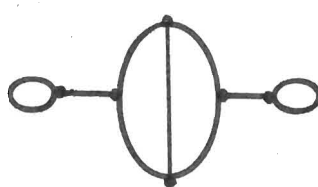
2916

360



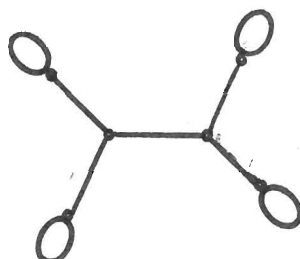
5832

120



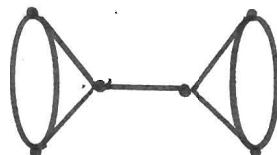
11664

180



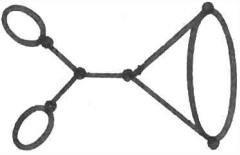
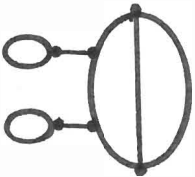
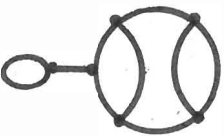

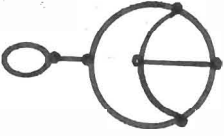





2916

90



11664

90

		P.S.	T.E.D.
		5832	180
		5832	360
		11664	360
		5832	360
		23328	180
(3.39)		5832	120
(3.40)		23328	180
(3.41)		46656	60
(3.42)		11664	60
(3.43)		<u>46656</u>	<u>10</u>
	TOTAL	34,459,425	1

Appendix A

Regarding equations (2.20) and (2.21) we can write the cubic term in the following form:

$$V(\tilde{\kappa}_1 j_1, \tilde{\kappa}_2 j_2, \tilde{\kappa}_3 j_3) = C \Delta(\tilde{\kappa}_1 + \tilde{\kappa}_2 + \tilde{\kappa}_3) \sum_{\alpha_1, \alpha_2, \alpha_3} Q_{\alpha_1}(\tilde{\kappa}_1 j_1) Q_{\alpha_2}(\tilde{\kappa}_2 j_2) Q_{\alpha_3}(\tilde{\kappa}_3 j_3) \quad (1A)$$

$$\sum_{\ell_2, \ell_3} \phi_{\alpha_1, \alpha_2, \alpha_3} (0 \ell_2 \ell_3) \exp[2\pi i \tilde{\kappa}_2 \cdot \tilde{x}(\ell_2)] \exp[2\pi i \tilde{\kappa}_3 \cdot \tilde{x}(\ell_3)]$$

where,

$$C = \frac{1}{3! \sqrt{N} M^{3/2}} \left(\frac{\hbar}{2}\right)^{3/2} \quad (2A)$$

$$Q_{\alpha}(\tilde{\kappa} j) = \frac{e_{\alpha}(\tilde{\kappa} j)}{\sqrt{\omega(\tilde{\kappa} j)}} \quad (3A)$$

Applying the two body forces (i.e. ℓ_2 and ℓ_3 take the values zero or ℓ) we can write eq. (1A) as:

$$V(\tilde{\kappa}_1 j_1, \tilde{\kappa}_2 j_2, \tilde{\kappa}_3 j_3) = C \Delta(\tilde{\kappa}_1 + \tilde{\kappa}_2 + \tilde{\kappa}_3) \sum_{\alpha_1, \alpha_2, \alpha_3} Q_{\alpha_1}(\tilde{\kappa}_1 j_1) Q_{\alpha_2}(\tilde{\kappa}_2 j_2) Q_{\alpha_3}(\tilde{\kappa}_3 j_3)$$

$$\left[\phi_{\alpha_1, \alpha_2, \alpha_3} (0 0 0) + \sum_{\ell} \phi_{\alpha_1, \alpha_2, \alpha_3} (0 \ell 0) e^{2\pi i \tilde{\kappa}_2 \cdot \tilde{x}(\ell)} \right.$$

$$\left. + \sum_{\ell} \phi_{\alpha_1, \alpha_2, \alpha_3} (0 0 \ell) e^{2\pi i \tilde{\kappa}_3 \cdot \tilde{x}(\ell)} + \sum_{\ell} \phi_{\alpha_1, \alpha_2, \alpha_3} (0 \ell \ell) e^{2\pi i (\tilde{\kappa}_2 + \tilde{\kappa}_3) \cdot \tilde{x}(\ell)} \right] \quad (4A)$$

The prime on the summation excludes $\ell = 0$

from equation (2.22) we get the following relations:

$$\phi_{\alpha_1, \alpha_2, \alpha_3} (0 0 0) = \sum_{\ell} \phi_{\alpha_1, \alpha_2, \alpha_3} (\ell 0 0) \quad (5A)$$

$$\phi_{\alpha_1, \alpha_2, \alpha_3} (0 \ell \ell) = - \phi_{\alpha_1, \alpha_2, \alpha_3} (0 0 \ell) \quad (6A)$$

In the second and third terms of equation (4A) we shall change the sign of ℓ . In order to satisfy the delta function we have:

$$\underline{k}_1 + \underline{k}_2 + \underline{k}_3 = \underline{\tau}$$

therefore:

$$\begin{aligned} \exp[2\pi i(\underline{k}_2 + \underline{k}_3) \cdot \underline{x}(\ell)] &= \exp(-2\pi i \underline{\tau} \cdot \underline{x}(\ell)) \exp(-2\pi i \underline{k}_1 \cdot \underline{x}(\ell)) \\ &= \exp(-2\pi i \underline{k}_1 \cdot \underline{x}(\ell)) \end{aligned}$$

We also have that:

$$\phi_{\alpha_1 \alpha_2 \alpha_3}(\ell 0 0) = \phi_{\alpha_1 \alpha_2 \alpha_3}(0 \ell 0) = \phi_{\alpha_1 \alpha_2 \alpha_3}(0 0 \ell)$$

Equation (4A) can then be written as:

$$\begin{aligned} V(\underline{k}_1 j_1, \underline{k}_2 j_2, \underline{k}_3 j_3) &= \frac{1}{2} \Delta(\underline{k}_1 + \underline{k}_2 + \underline{k}_3) \sum_{\alpha_1 \alpha_2 \alpha_3} Q_{\alpha_1}(\underline{k}_1 j_1) Q_{\alpha_2}(\underline{k}_2 j_2) Q_{\alpha_3}(\underline{k}_3 j_3) \\ &\quad \sum_{\ell} \phi_{\alpha_1 \alpha_2 \alpha_3}(\ell 0 0) \left[1 - e^{-2\pi i \underline{k}_1 \cdot \underline{x}(\ell)} \right. \\ &\quad - e^{-2\pi i \underline{k}_2 \cdot \underline{x}(\ell)} - e^{-2\pi i \underline{k}_3 \cdot \underline{x}(\ell)} - e^{-2\pi i (\underline{k}_1 + \underline{k}_2 + \underline{k}_3) \cdot \underline{x}(\ell)} \\ &\quad + e^{-2\pi i (\underline{k}_2 + \underline{k}_3) \cdot \underline{x}(\ell)} + e^{-2\pi i (\underline{k}_1 + \underline{k}_3) \cdot \underline{x}(\ell)} \\ &\quad \left. + e^{-2\pi i (\underline{k}_1 + \underline{k}_2) \cdot \underline{x}(\ell)} \right] \end{aligned} \quad (7A)$$

In eq. (7A) the factor half appeared because the first four terms are the same as the last four.

Eq. (7A) can be written as:

$$\begin{aligned} V(\underline{k}_1 j_1, \underline{k}_2 j_2, \underline{k}_3 j_3) &= \frac{1}{3!} N^{1-\frac{3}{2}} \Delta(\underline{k}_1 + \underline{k}_2 + \underline{k}_3) \left[\frac{\hbar^3}{2^3 \omega(\underline{k}_1 j_1) \omega(\underline{k}_2 j_2) \omega(\underline{k}_3 j_3)} \right]^{\frac{1}{2}} \\ &\quad \phi(\underline{k}_1 j_1, \underline{k}_2 j_2, \underline{k}_3 j_3) \end{aligned}$$

where,

$$\phi(\underline{k}_1^j, \underline{k}_2^j, \underline{k}_3^j) = \frac{1}{2 M^{3/2}} \sum_{\ell} \phi_{\alpha_1 \alpha_2 \alpha_3}(\ell) (1 - e^{-2\pi i \underline{k}_1 \cdot \underline{x}(\ell)})$$

$$(1 - e^{-2\pi i \underline{k}_2 \cdot \underline{x}(\ell)}) (1 - e^{-2\pi i \underline{k}_3 \cdot \underline{x}(\ell)})$$

Appendix B

From the definition of Green's function we have:

$$G(\underline{k}, \underline{k}', s) = \langle T \tilde{A}_{\underline{k}, j}(s) \tilde{A}_{\underline{k}', j'}^+(0) \rangle \quad (1B)$$

which can be written in the form:

$$G(\underline{k}, \underline{k}', s) = \frac{\sum_{n_{\underline{k}, j}, n_{\underline{k}', j'}} \langle n_{\underline{k}, j} | e^{-\beta H_0} \tilde{A}_{\underline{k}, j}(s) \tilde{A}_{\underline{k}', j'}^+(0) | n_{\underline{k}', j'} \rangle}{\sum_{n_{\underline{k}, j}, n_{\underline{k}', j'}} \langle n_{\underline{k}, j} | e^{-\beta H_0} | n_{\underline{k}', j'} \rangle} \quad (2B)$$

Equations (2.16) and (3.6) give:

$$\tilde{A}_{\underline{k}, j}(s) = e^{sH_0} \tilde{A}_{\underline{k}, j}(0) e^{-sH_0} \quad (3B)$$

The creation $a_{\underline{k}, j}^+$ and annihilation $a_{\underline{k}, j}$ operators satisfy the following commutation relations:

$$\begin{aligned} [a_{\underline{k}, j}, a_{\underline{k}', j'}^+] &= \Delta(\underline{k} - \underline{k}') \delta_{jj'} \\ [a_{\underline{k}, j}, a_{\underline{k}', j'}] &= [a_{\underline{k}, j}^+, a_{\underline{k}', j'}^+] = 0 \end{aligned} \quad (4B)$$

where, $\Delta(\underline{k}) = 1$ if $\underline{k} = 0$ or a reciprocal lattice vector
 $= 0$ otherwise

and $\delta_{jj'} = 1$ if $j = j'$
 $= 0$ otherwise

The creation and annihilation operators also have the property that applied to the $3nN$ particles eigenstate $|n_{\underline{k}, j}\rangle$ specified by the $3nN$ quantum numbers $\{n_{\underline{k}, j}\}$, they yield:

$$\begin{aligned} a_{\underline{k}, j}^+ | \dots n_{\underline{k}, j} \dots \rangle &= \sqrt{n_{\underline{k}, j} + 1} | \dots n_{\underline{k}, j} + 1 \dots \rangle \\ a_{\underline{k}, j} | \dots n_{\underline{k}, j} \dots \rangle &= \sqrt{n_{\underline{k}, j}} | \dots n_{\underline{k}, j} - 1 \dots \rangle \end{aligned} \quad (5B)$$

We also have:

$$\tilde{A}_{\underline{k}j} = a_{\underline{k}j} + a_{-\underline{k}j}^+ \quad (6B)$$

$$e^{-\beta H_0} |n_{\underline{k}j}\rangle = e^{-\beta E_{n_{\underline{k}j}}} |n_{\underline{k}j}\rangle \quad (7B)$$

Making use of the above relations, we can write the Green's function as:

$$G(\underline{k}j, \underline{k}'j', \beta) = \left[\sum_{n_{\underline{k}j}, n_{\underline{k}'j'}} e^{-\beta E_{n_{\underline{k}'j'}}} (n_{\underline{k}'j'} + 1) e^{\beta(E_{n_{\underline{k}'j'}} - E_{n_{\underline{k}'j'}+1})} \delta_{\underline{k}\underline{k}'} \delta_{jj'} \right. \\ \left. + \sum_{n_{\underline{k}j}, n_{\underline{k}'j'}} e^{-\beta E_{n_{\underline{k}'j'}}} n_{\underline{k}'j'} e^{\beta(E_{n_{\underline{k}'j'}} - E_{n_{\underline{k}'j'}-1})} \delta_{\underline{k}\underline{k}'} \delta_{jj'} \right] \\ / \sum_{n_{\underline{k}j}, n_{\underline{k}'j'}} e^{-\beta E_{n_{\underline{k}'j'}}} \quad (8B)$$

Substituting,

$$E_{n_{\underline{k}j}} = (n_{\underline{k}j} + \frac{1}{2}) \hbar \omega(\underline{k}j) \quad (9B)$$

in equation (8B) we get:

$$G(\underline{k}j, \underline{k}'j', \beta) = e^{-|\beta| \hbar \omega(\underline{k}'j')} \delta_{\underline{k}\underline{k}'} \delta_{jj'} \frac{\sum_{n_{\underline{k}j}, n_{\underline{k}'j'}} e^{-\beta E_{n_{\underline{k}'j'}}} (n_{\underline{k}'j'} + 1)}{\sum_{n_{\underline{k}j}, n_{\underline{k}'j'}} e^{-\beta E_{n_{\underline{k}'j'}}}} \\ + e^{|\beta| \hbar \omega(\underline{k}'j')} \delta_{\underline{k}\underline{k}'} \delta_{jj'} \frac{\sum_{n_{\underline{k}j}, n_{\underline{k}'j'}} e^{-\beta E_{n_{\underline{k}'j'}}} n_{\underline{k}'j'}}{\sum_{n_{\underline{k}j}, n_{\underline{k}'j'}} e^{-\beta E_{n_{\underline{k}'j'}}}} \quad (10B)$$

Consider,

$$\begin{aligned}
\frac{\sum_{n_{kj}} e^{-\beta(n_{kj} + \frac{1}{2})\hbar\omega(kj)} (n_{kj} + 1)}{\sum_{n_{kj}} e^{-\beta(n_{kj} + \frac{1}{2})\hbar\omega(kj)}} &= \frac{\partial}{\partial(-\beta\hbar\omega(kj))} \left\{ \ln \sum_{n_{kj}} e^{-\beta(n_{kj} + \frac{1}{2})\hbar\omega(kj)} \right\} + \frac{1}{2} \\
&= \frac{\partial}{\partial(-\beta\hbar\omega(kj))} \left\{ \ln \frac{e^{-\frac{1}{2}\hbar\beta\omega(kj)}}{1 - e^{-\beta\hbar\omega(kj)}} \right\} + \frac{1}{2} \\
&= \bar{n}_{kj} + \frac{1}{2}
\end{aligned} \tag{11B}$$

where,

$$\bar{n}_{kj} = 1 / \{ e^{\beta\hbar\omega(kj)} - 1 \} \tag{12B}$$

is the phonon's occupation number.

Therefore,

$$G(kj, kj', s) = \left[\bar{n}_{kj'} e^{s\hbar\omega(kj')} + (n_{kj'} + 1) e^{-s\hbar\omega(kj')} \right] \delta_{kj, kj'} \tag{13B}$$

In order to prove the periodicity of Green's function, consider the following:

$$G(kj, kj', s + \beta) = \langle T \tilde{A}_{kj}^+(s + \beta) \tilde{A}(0) \rangle \quad -\beta < s < 0$$

$$= \langle e^{-\beta H_0} \tilde{A}_{kj}^+(s) e^{\beta H_0} \tilde{A}_{kj'}(0) \rangle$$

$$= \frac{\text{Tr } e^{-2\beta H_0} \tilde{A}_{kj}^+(s) e^{\beta H_0} \tilde{A}_{kj'}(0)}{\text{Tr } e^{-\beta H_0}}$$

Using the cyclic property of the trace

$$\text{Tr } ABC = \text{Tr } BCA = \text{Tr } CAB$$

therefore:

$$\begin{aligned} G(\underline{k}j\underline{k}'j', s+\beta) &= \frac{\text{Tr } e^{-\beta H_0} \tilde{A}_{\underline{k}j}^{\dagger}(s) \tilde{A}_{\underline{k}'j'}(0)}{\text{Tr } e^{-\beta H_0}} \\ &= \langle \tilde{A}_{\underline{k}j}^{\dagger}(s) \tilde{A}_{\underline{k}'j'}(0) \rangle \\ &= G(\underline{k}j\underline{k}'j', s) \end{aligned} \quad (14B)$$

Applying Fourier expansion, we can write:

$$G(\underline{k}j\underline{k}'j', s) = \sum_{n=-\infty}^{\infty} G(\underline{k}j\underline{k}'j', i\omega_n) e^{i\omega_n s} \quad (15B)$$

where,

$$\omega_n = 2\pi n / \beta \hbar$$

The Fourier coefficients in equation (15B) are given by:

$$\begin{aligned} G(\underline{k}j\underline{k}'j', i\omega_n) &= \frac{1}{2\beta} \int_{-\beta}^{\beta} ds G(\underline{k}j\underline{k}'j', s) e^{-i\omega_n s} \\ &= \frac{1}{2\beta} \int_{-\beta}^0 ds G(\underline{k}j\underline{k}'j', s) e^{-i\omega_n |s|} \\ &\quad + \frac{1}{2\beta} \int_0^{\beta} ds G(\underline{k}j\underline{k}'j', s) e^{-i\omega_n |s|} \end{aligned} \quad (16B)$$

From equations (13B) and (16B) and integrate, we get

$$G(\underline{k}j\underline{k}'j', i\omega_n) = \frac{2\omega(\underline{k}'j')}{\hbar\beta [\omega^2(\underline{k}'j') + \omega_n^2]} \delta_{\underline{k}\underline{k}'} \delta_{jj'} \quad (17B)$$

Appendix C

The Hamiltonian of interacting Einstein oscillators is given by (Shukla and Muller [20]):

$$H = H_0 + V \quad (1C)$$

where,

$$V = - \frac{\hbar \omega_0}{4} \sum_k \cos kd A_k A_k^\dagger \quad (2C)$$

$$= \sum_k V_k A_k A_k^\dagger \quad (3C)$$

We can follow the same procedure presented in section [3] to reach to a similar equation as (3.4).

The first order contribution to the partition function can be then obtained by putting $n = 1$ to give:

$$\begin{aligned} P_1 &= \frac{(-1)'}{1!} \sum_k V_k \int_0^\beta d\sigma_1 \langle T \tilde{V}(\sigma_1) \rangle_0 \\ &= \frac{(-1)'}{1!} \sum_k V_k \int_0^\beta d\sigma_1 \langle T \tilde{A}_k(\sigma_1) \tilde{A}_k^\dagger(\sigma_1) \rangle_0 \end{aligned}$$

Substituting from eqs. (3.8) and (15B), we get

$$P_1 = \frac{(-1)'}{1!} \beta \sum_{n,k} V_k G(k, i\omega_n) \quad (4C)$$

which can be rewritten as:

$$P_1 = \frac{(-1)'}{1!} \beta x \quad (5C)$$

where $x = \sum_{n,k} V_k G(k, i\omega_n)$ which can be represented by diagram x (Fig. 4).

The second order contribution to the partition function can be derived by putting $n = 2$

$$\begin{aligned} \therefore P_2 &= \frac{(-1)^2}{2!} \int_0^\beta ds_1 \int_0^\beta ds_2 [\langle T \{ \tilde{V}(s_1) \tilde{V}(s_2) \} \rangle_0] \\ &= \frac{(-1)^2}{2!} \sum_{kk'} V_k V_{k'} \int_0^\beta ds_1 \int_0^\beta ds_2 \langle T \tilde{A}_k(s_1) \tilde{A}_k^\dagger(s_1) \tilde{A}_{k'}(s_2) \tilde{A}_{k'}^\dagger(s_2) \rangle_0 \end{aligned}$$

Applying Wick's Theorem, we get:

$$\begin{aligned} P_2 &= \frac{(-1)^2}{2!} \sum_{kk'} V_k V_{k'} \int_0^\beta ds_1 \int_0^\beta ds_2 [\langle T \tilde{A}_k(s_1) \tilde{A}_{k'}^\dagger(s_2) \rangle_0 \langle \tilde{A}_k^\dagger(s_1) \tilde{A}_{k'}(s_2) \rangle_0 \\ &\quad + \langle T \tilde{A}_k(s_1) \tilde{A}_k^\dagger(s_1) \rangle_0 \langle T \tilde{A}_{k'}(s_2) \tilde{A}_{k'}^\dagger(s_2) \rangle_0 \\ &\quad + \langle T \tilde{A}_k(s_1) \tilde{A}_{k'}(s_2) \rangle_0 \langle T \tilde{A}_k^\dagger(s_1) \tilde{A}_{k'}^\dagger(s_2) \rangle_0] \quad (6C) \end{aligned}$$

The third term vanishes because the two operators are of the same type.

Put $u = s_1 - s_2$ in equation (6C) we get:

$$P_2 = \frac{(-1)^2}{2!} \sum_{kk'} V_k V_{k'} \left[2 \int_0^\beta du G^2(k, u) \int_0^\beta ds_1 + \sum_{nn'} G(k, i\omega_n) G(k', i\omega_{n'}) \beta^2 \right] \quad (7C)$$

Substituting from eq. (15B) and making use of

$$\int_0^\beta du \exp [2\pi i (n - n') / \beta] = \beta \delta_{nn'} \quad (8C)$$

we find:

$$P_2 = \frac{(-1)^2}{2!} \left[2\beta^2 \sum_{n,k} V_k^2 G^2(k, i\omega_n) + \beta^2 \sum_{k,n} V_k G(k, i\omega_n) \sum_{k',n'} V_{k'} G(k', i\omega_{n'}) \right]$$

which gives:

$$\begin{aligned} P_2 &= \frac{(-1)^2}{2!} \beta^2 [2y + x^2] \\ \text{where} \quad y &= \sum_{n,k} V_k^2 G^2(k, i\omega_n) \end{aligned} \quad (9C)$$

The factor 2 appears because of the existence of the two equal terms arising in the integration. It corresponds to the pairing schemes factors for this diagram. Similarly, the third, fourth, fifth and sixth contribution to the partition function can be derived to give:

$$P_3 = \frac{(-1)^3}{3!} \beta^3 [8Z + 6xY + x^3] \quad (10C)$$

$$P_4 = \frac{(-1)^4}{4!} \beta^4 [16u + 32xZ + 12Y^2 + 12x^2Y + x^4] \quad (11C)$$

$$P_5 = \frac{(-1)^5}{5!} \beta^5 [32v + 80xu + 160yZ + 160x^2Z + 60xy^2 + 20x^3Y + x^5] \quad (12C)$$

$$P_6 = \frac{(-1)^6}{6!} [64w + 192xv + 480yu + 480x^2u + 640Z^2 + 960xyZ + 960x^3Z + 120Y^3 + 360x^2Y^2 + 360x^4Y + x^6] \quad (13C)$$

Therefore,

$$\begin{aligned} \frac{Z}{Z_0} &= 1 + P_1 + P_2 + P_3 + \dots \\ &= \left[1 + \frac{(-\beta x)}{1!} + \frac{(-\beta x)^2}{2!} + \dots \right] \left[1 + (\beta^2 y) + \frac{1}{2!} (\beta^2 y)^2 + \dots \right] \\ &\quad \left[1 + \frac{(-\frac{16}{9} \beta^3 z)}{1!} + \frac{1}{2!} \left(-\frac{16}{9} \beta^3 z \right)^2 + \dots \right] \dots \\ &= \exp \left[-\beta x + \beta^2 Y - \frac{16}{9} \beta^3 Z + \dots \right] \\ &= \exp [Z^c] \end{aligned} \quad (14C)$$

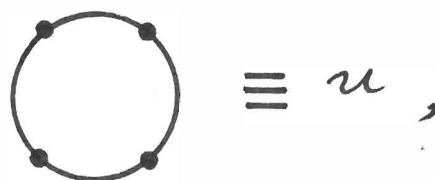
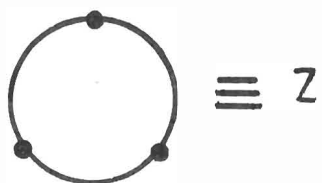
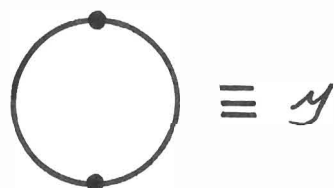
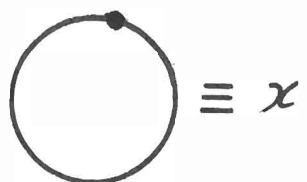
where, \sum^c means the sum over all connected diagrams. Taking the logarithm of eq. (14C) and dividing by $-\beta$ we get

$$-\frac{1}{\beta} \log Z = -\frac{1}{\beta} \log Z_0 - \frac{1}{\beta} \sum^c$$

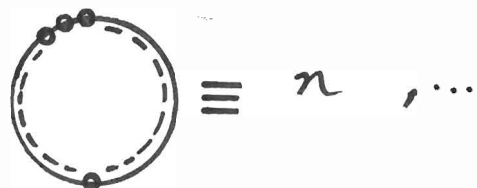
or

$$F = F_0 - \frac{1}{\beta} \sum^c$$

(15C)



...



Connected Diagrams, (x) first order, (y) second order,
etc. , (n) nth order.

Fig. (4)

Appendix D

Evaluation of the sum:

$$\sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{1}{n_1^2 n_2^2 (n_1 - n_2)^2} \quad (1D)$$

This can be evaluated by the contour integration in the complex plane.

The sum of residues at all integral values gives the value of this sum.

The function $\cot \pi z$ has simple poles at all integral values. Thus,

we can write the sum in the form:

$$I = \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{1}{n_1^2 n_2^2 (n_1 - n_2)^2} = \frac{1}{2\pi i} \int_{C_1} \frac{\pi \cot \pi z_1 dz_1}{z_1^2} \times \frac{1}{2\pi i} \int_{C_2} \frac{\pi \cot \pi z_2 dz_2}{z_2^2 (z_1 - z_2)^2}$$

Since the resulting enclosed area contains no singularities except at

$z_2 = 0$, we have then shrunk this contour down to the infinitesimal circle C' surrounding the origin.

Expanding the integrand in powers of z_2 about $z_2 = 0$, only the terms involving $1/z_2$ contribute to the integral while the other powers of

z_2 do not. Thus:

$$\begin{aligned} I &= \frac{1}{2i \times 2i} \int_{C_1} \frac{\pi \cot \pi z_1}{z_1^2} dz_1 \int_{C_2} dz_2 \frac{1}{\pi z_2^2 (z_1 - z_2)^2} \left[1 - \frac{1}{3} \pi^2 z_2^2 - \frac{1}{45} \pi^4 z_2^4 - \dots \right] \\ &= \frac{1}{2i \times 2i} \int_{C_1} dz_1 \frac{\cot \pi z_1}{z_1^2} \int_{C_2} dz_2 \left[-\frac{\pi}{3} \frac{1}{z_2 (z_1 - z_2)^2} + \text{other powers of } z_2 \right] \\ &= \frac{1}{2i \times 2i} \int_{C_1} dz_1 \frac{\cot \pi z_1}{z_1^2} \left[(-2\pi i) \left(-\frac{\pi}{3z_1^2} \right) \right] \\ &= \frac{1}{2i} \frac{\pi^2}{3} \int_{C_1} dz_1 \frac{\cot \pi z_1}{z_1^4} \end{aligned}$$

The contour C_1 , is shown in the Fig. (5b)

Expanding $\cot \pi z_1$, we get

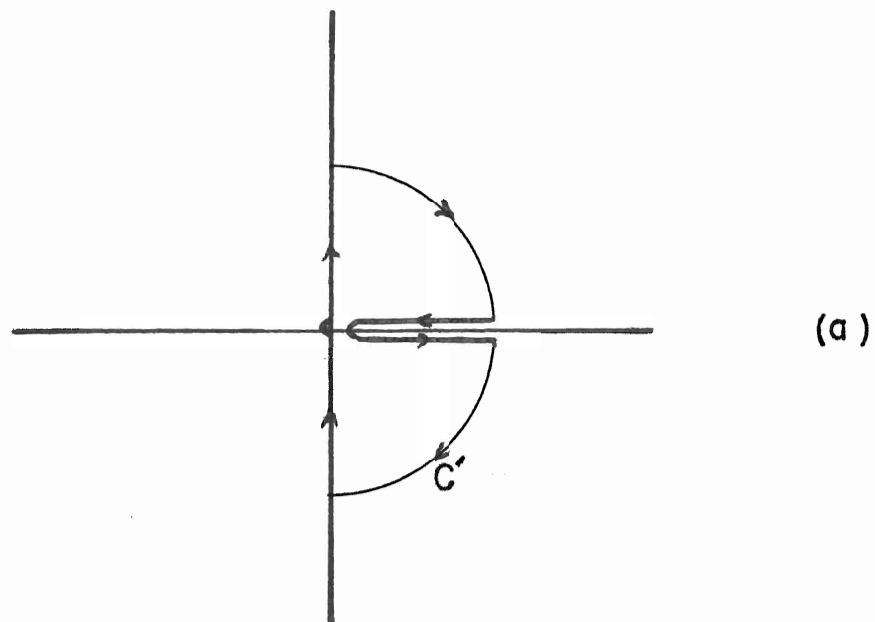
$$\begin{aligned}
I &= \frac{1}{2i} \frac{\pi^2}{3} \int_{C_1} dz_1 \frac{1}{\pi z_1^5} \left[1 - \frac{1}{3} \pi^2 z_1^2 + \frac{1}{45} \pi^4 z_1^4 - \dots \right] \\
&= -\frac{1}{2i} \frac{\pi^2}{3} \int_{C_1} dz_1 \left[\left(-\frac{\pi^3}{45} \right) \frac{1}{z_1} + \text{other powers of } z_1 \right] \\
&= \frac{1}{2i} \frac{\pi^2}{3} \times (-2\pi i) \left(-\frac{\pi^3}{45} \right) = \frac{\pi^6}{135}
\end{aligned}$$

(2D)

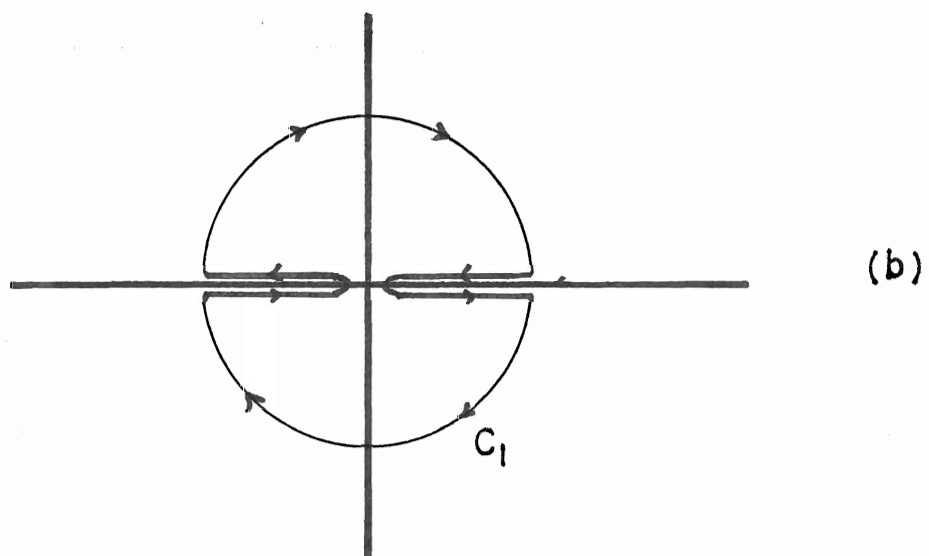
Thus, from eq. (1D) we get:

$$\sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{1}{n_1^2 n_2^2 (n_1 - n_2)^2} = \frac{\pi^6}{135}$$

(3D)



The contour C' closed by the semicircle at infinity



The contour C_1

Fig. (5)

APPENDIX E

The analytical expressions for the x's which are tabulated in section 4 are given by

$$X(2.1) = \frac{\hbar^4}{120 (k_B T)^4} \left[-\omega^4(\kappa_1 \dot{\theta}_1) + 5 \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_2 \dot{\theta}_2) \right] + \frac{\hbar^6}{60480 (k_B T)^6} \left[2 \omega^6(\kappa_1 \dot{\theta}_1) - 42 \omega^4(\kappa_1 \dot{\theta}_1) \right. \\ \left. \omega^2(\kappa_2 \dot{\theta}_2) + 35 \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_2 \dot{\theta}_2) \omega^2(\kappa_3 \dot{\theta}_3) \right]$$

$$X(2.2) = \frac{\hbar^4}{720 (k_B T)^4} \left[5 \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_4 \dot{\theta}_4) + \omega^2(\kappa_2 \dot{\theta}_2) \omega^2(\kappa_3 \dot{\theta}_3) - 2 \omega^4(\kappa_1 \dot{\theta}_1) \right] \\ + \frac{\hbar^6}{60480 (k_B T)^6} \left[4 \omega^6(\kappa_1 \dot{\theta}_1) - 2 \omega^2(\kappa_2 \dot{\theta}_2) \omega^2(\kappa_3 \dot{\theta}_3) \{ \omega^2(\kappa_2 \dot{\theta}_2) + \omega^2(\kappa_3 \dot{\theta}_3) \} + 9 \omega^2(\kappa_1 \dot{\theta}_1) \right. \\ \left. \{ \omega^2(\kappa_2 \dot{\theta}_2) \omega^2(\kappa_3 \dot{\theta}_3) - \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_4 \dot{\theta}_4) \} \right] \\ + \frac{\hbar^8}{7257600 (k_B T)^8} \left[-12 \omega^8(\kappa_1 \dot{\theta}_1) + 6 \omega^2(\kappa_2 \dot{\theta}_2) \omega^2(\kappa_3 \dot{\theta}_3) \{ \omega^4(\kappa_2 \dot{\theta}_2) + \omega^2(\kappa_2 \dot{\theta}_2) \right. \\ \left. \omega^2(\kappa_3 \dot{\theta}_3) + \omega^4(\kappa_3 \dot{\theta}_3) \} + \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_4 \dot{\theta}_4) \{ 172 \omega^4(\kappa_1 \dot{\theta}_1) - 62 \omega^2(\kappa_1 \dot{\theta}_1) \right. \\ \left. \omega^2(\kappa_4 \dot{\theta}_4) \} - 2 \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_2 \dot{\theta}_2) \omega^2(\kappa_3 \dot{\theta}_3) \{ 146 (\omega^2(\kappa_2 \dot{\theta}_2) + \omega^2(\kappa_3 \dot{\theta}_3)) + 104 \omega^2(\kappa_1 \dot{\theta}_1) \} \right. \\ \left. + 11 \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_2 \dot{\theta}_2) \omega^2(\kappa_3 \dot{\theta}_3) \omega^2(\kappa_4 \dot{\theta}_4) \right]$$

$$X(2.3) = \frac{\hbar^4}{720 (k_B T)^4} \left[-\omega^4(\kappa_4 \dot{\theta}_4) + 2 \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_3 \dot{\theta}_3) \right] \\ + \frac{\hbar^6}{60480 (k_B T)^6} \left[\omega^6(\kappa_1 \dot{\theta}_1) - 2 \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_3 \dot{\theta}_3) \{ \omega^2(\kappa_1 \dot{\theta}_1) + \omega^2(\kappa_3 \dot{\theta}_3) \} + 9 \{ 2 \omega^2(\kappa_1 \dot{\theta}_1) \right. \\ \left. \omega^2(\kappa_3 \dot{\theta}_3) \omega^2(\kappa_4 \dot{\theta}_4) + \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_2 \dot{\theta}_2) \omega^2(\kappa_4 \dot{\theta}_4) \} + 23 \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_2 \dot{\theta}_2) \omega^2(\kappa_3 \dot{\theta}_3) \right] \\ + \frac{\hbar^8}{14515200 (k_B T)^8} \left[12 \omega^8(\kappa_4 \dot{\theta}_4) + 24 \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_3 \dot{\theta}_3) \{ \omega^4(\kappa_1 \dot{\theta}_1) + \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_3 \dot{\theta}_3) \} \right]$$

$$\begin{aligned}
& + \omega^4(\kappa_3 j_3) \{ -24 \omega^2(\kappa_1 j_1) \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) \{ \omega^2(\kappa_1 j_1) + \omega^2(\kappa_3 j_3) + \omega^2(\kappa_4 j_4) \} \\
& - 92 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \{ \omega^2(\kappa_1 j_1) + \omega^2(\kappa_2 j_2) + \omega^2(\kappa_3 j_3) \} - 56 \omega^2(\kappa_1 j_1) \\
& \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) \{ \omega^2(\kappa_1 j_1) + \omega^2(\kappa_3 j_3) \} - 56 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^4(\kappa_4 j_4) \\
& + 99 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) \}
\end{aligned}$$

$$\begin{aligned}
X(2.4) &= \frac{\hbar^4}{720 (K_B T)^4} \left[\omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) - \omega^4(\kappa_5 j_5) \right] \\
&+ \frac{\hbar^6}{60480 (K_B T)^6} \left[2 \omega^6(\kappa_5 j_5) - 4 \omega^4(\kappa_3 j_3) \omega^2(\kappa_4 j_4) + 9 \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \right. \\
&+ 2 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_4 j_4) \left. \right] \\
&+ \frac{\hbar^8}{3628800 (K_B T)^8} \left[3 \omega^8(\kappa_5 j_5) + 3 \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) \{ 2 \omega^4(\kappa_3 j_3) + \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) \} \right. \\
&- \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \{ 26 \omega^2(\kappa_3 j_3) + 10 \omega^2(\kappa_5 j_5) \} - 3 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_4 j_4) \\
&\{ \omega^2(\kappa_1 j_1) + \omega^2(\kappa_2 j_2) + \omega^2(\kappa_4 j_4) \} + 26 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) + 22 \omega^2(\kappa_1 j_1) \\
&\omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) \left. \right]
\end{aligned}$$

$$\begin{aligned}
X(2.5) &= \frac{\hbar^4}{120 (K_B T)^4} \left[\omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) + \frac{\hbar^6}{40320 (K_B T)^6} \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \{ -24 \omega^2(\kappa_1 j_1) \right. \\
&+ \omega^2(\kappa_4 j_4) \} \left. \right] + \frac{\hbar^8}{14515200 (K_B T)^8} \left[720 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \{ \omega^4(\kappa_1 j_1) + \omega^2(\kappa_1 j_1) \right. \\
&\omega^2(\kappa_2 j_2) + \omega^4(\kappa_2 j_2) \} - 9 \{ \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_4 j_4) \{ 4 \omega^2(\kappa_1 j_1) + 4 \omega^2(\kappa_2 j_2) + \omega^2(\kappa_4 j_4) \} \\
&+ 19 \omega^4(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \} + 203 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) \left. \right]
\end{aligned}$$

$$X(2.6) = \frac{\hbar^4}{360(K_B T)^4} \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) + \frac{\hbar^6}{7560(K_B T)^6} \left[\omega^4(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) + \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_5 \underline{j}_5) \omega^2(\underline{\kappa}_6 \underline{j}_6) \right]$$

$$X(2.7) = \frac{\hbar^4}{360(K_B T)^4} \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) + \frac{\hbar^6}{7560(K_B T)^6} \left[\omega^4(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) + \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) \right]$$

$$X(2.8) = \frac{\hbar^6}{30240(K_B T)^6} \left[\omega^2(\underline{\kappa}_4 \underline{j}_4) \omega^2(\underline{\kappa}_5 \underline{j}_5) \omega^2(\underline{\kappa}_6 \underline{j}_6) + \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_6 \underline{j}_6) + \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_5 \underline{j}_5) + \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_3 \underline{j}_3) \right]$$

$$X(3.1) = \frac{\hbar^4}{360(K_B T)^4} \left[-\omega^4(\underline{\kappa}_1 \underline{j}_1) + 15 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \right] + \frac{\hbar^6}{15120(K_B T)^6} \left[2 \omega^6(\underline{\kappa}_1 \underline{j}_1) - 7 \omega^4(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) + 35 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_3 \underline{j}_3) \right]$$

$$X(3.2) = \frac{\hbar^4}{720(K_B T)^4} \left[3 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) - 2 \omega^4(\underline{\kappa}_4 \underline{j}_4) + 6 \omega^2(\underline{\kappa}_4 \underline{j}_4) \omega^2(\underline{\kappa}_5 \underline{j}_5) \right] \\ + \frac{\hbar^6}{30240(K_B T)^6} \left[4 \omega^6(\underline{\kappa}_4 \underline{j}_4) - 6 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \{ \omega^2(\underline{\kappa}_1 \underline{j}_1) + \omega^2(\underline{\kappa}_2 \underline{j}_2) \} \right. \\ - 18 \omega^4(\underline{\kappa}_4 \underline{j}_4) \omega^2(\underline{\kappa}_5 \underline{j}_5) + 32 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) + 15 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \\ \left. \omega^2(\underline{\kappa}_3 \underline{j}_3) + 2 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_4 \underline{j}_4) \right] \\ + \frac{\hbar^8}{3628800(K_B T)^8} \left[-6 \omega^8(\underline{\kappa}_4 \underline{j}_4) - 6 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_3 \underline{j}_3) \{ \omega^4(\underline{\kappa}_1 \underline{j}_1) + \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_3 \underline{j}_3) \} \right. \\ + \omega^4(\underline{\kappa}_3 \underline{j}_3) \{ \omega^2(\underline{\kappa}_4 \underline{j}_4) \omega^2(\underline{\kappa}_5 \underline{j}_5) \{ 2 \omega^2(\underline{\kappa}_4 \underline{j}_4) + 10 \omega^2(\underline{\kappa}_4 \underline{j}_4) \omega^2(\underline{\kappa}_5 \underline{j}_5) \} - 4 \omega^2(\underline{\kappa}_1 \underline{j}_1) \\ \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) \{ 13 \omega^2(\underline{\kappa}_1 \underline{j}_1) + 10 \omega^2(\underline{\kappa}_4 \underline{j}_4) \} - 5 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_3 \underline{j}_3) \\ \{ \omega^2(\underline{\kappa}_1 \underline{j}_1) + \omega^2(\underline{\kappa}_2 \underline{j}_2) + \omega^2(\underline{\kappa}_3 \underline{j}_3) \} - 2 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_4 \underline{j}_4) \{ 10 \omega^2(\underline{\kappa}_1 \underline{j}_1) + \\ \left. 10 \omega^2(\underline{\kappa}_2 \underline{j}_2) + 7 \omega^2(\underline{\kappa}_4 \underline{j}_4) \} + 130 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) \omega^2(\underline{\kappa}_5 \underline{j}_5) + \frac{313}{2} \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) \right]$$

$$\begin{aligned}
X(3.3) = & \frac{\hbar^4}{720 (K_B T)^4} \left[-\omega^4(\underline{\kappa}_1 \underline{j}_1) + 6\omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_3 \underline{j}_3) \right] + \frac{\hbar^6}{120960 (K_B T)^6} \left[4\omega^6(\underline{\kappa}_1 \underline{j}_1) \right. \\
& - 24\omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_3 \underline{j}_3) \{ \omega^2(\underline{\kappa}_2 \underline{j}_2) + \omega^2(\underline{\kappa}_3 \underline{j}_3) \} + 54\omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_3 \underline{j}_3) \\
& + 54\omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_5 \underline{j}_5) + 87\omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_5 \underline{j}_5) \left. \right] \\
& + \frac{\hbar^8}{14515200 (K_B T)^8} \left[-12\omega^8(\underline{\kappa}_1 \underline{j}_1) + 48\omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_3 \underline{j}_3) \{ \omega^4(\underline{\kappa}_2 \underline{j}_2) + \omega^2(\underline{\kappa}_2 \underline{j}_2) \right. \\
& \omega^2(\underline{\kappa}_3 \underline{j}_3) + \omega^4(\underline{\kappa}_3 \underline{j}_3) \} - 24\omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_3 \underline{j}_3) \{ \omega^2(\underline{\kappa}_1 \underline{j}_1) + \omega^2(\underline{\kappa}_2 \underline{j}_2) \\
& + \omega^2(\underline{\kappa}_3 \underline{j}_3) \} - 48\omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_5 \underline{j}_5) \{ \omega^2(\underline{\kappa}_1 \underline{j}_1) + \omega^2(\underline{\kappa}_2 \underline{j}_2) + \omega^2(\underline{\kappa}_5 \underline{j}_5) \} \\
& - 249\omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_5 \underline{j}_5) \{ \omega^2(\underline{\kappa}_2 \underline{j}_2) + \omega^2(\underline{\kappa}_3 \underline{j}_3) + \omega^2(\underline{\kappa}_5 \underline{j}_5) \} + 547\omega^2(\underline{\kappa}_2 \underline{j}_2) \\
& \left. \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) \omega^2(\underline{\kappa}_5 \underline{j}_5) + 2199\omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_5 \underline{j}_5) \right] \\
X(3.4) = & \frac{\hbar^4}{720 (K_B T)^4} \left[-3\omega^4(\underline{\kappa}_1 \underline{j}_1) + 18\omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_4 \underline{j}_4) + \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_2 \underline{j}_3) \right] \\
& + \frac{\hbar^6}{120960 (K_B T)^6} \left[12\omega^6(\underline{\kappa}_1 \underline{j}_1) - 2\omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_2 \underline{j}_3) \{ \omega^2(\underline{\kappa}_2 \underline{j}_2) + \omega^2(\underline{\kappa}_2 \underline{j}_3) \} \right. \\
& - 54\omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_4 \underline{j}_4) \{ \omega^2(\underline{\kappa}_1 \underline{j}_1) + \omega^2(\underline{\kappa}_4 \underline{j}_4) \} + 24\omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_2 \underline{j}_3) \\
& + 92\omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_4 \underline{j}_4) \omega^2(\underline{\kappa}_5 \underline{j}_5) \left. \right] + \frac{\hbar^8}{10886400 (K_B T)^8} \left[-27\omega^8(\underline{\kappa}_1 \underline{j}_1) + 9\omega^2(\underline{\kappa}_2 \underline{j}_2) \right. \\
& \omega^2(\underline{\kappa}_2 \underline{j}_3) \{ \omega^4(\underline{\kappa}_2 \underline{j}_2) + \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_2 \underline{j}_3) + \omega^4(\underline{\kappa}_2 \underline{j}_3) \} + 9\omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_4 \underline{j}_4) \{ 13\omega^4(\underline{\kappa}_1 \underline{j}_1) \\
& + 10\omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_4 \underline{j}_4) + 13\omega^4(\underline{\kappa}_4 \underline{j}_4) \} - 9\omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_2 \underline{j}_3) \{ 10\omega^2(\underline{\kappa}_1 \underline{j}_1) \\
& + 13\omega^2(\underline{\kappa}_2 \underline{j}_2) + 13\omega^2(\underline{\kappa}_2 \underline{j}_3) \} - 375\omega^4(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_4 \underline{j}_4) \omega^2(\underline{\kappa}_5 \underline{j}_5) + 510\omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_2 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) \\
& \left. + 13\omega^2(\underline{\kappa}_2 \underline{j}_2) + 13\omega^2(\underline{\kappa}_2 \underline{j}_3) \} - 375\omega^4(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_4 \underline{j}_4) \omega^2(\underline{\kappa}_5 \underline{j}_5) + 510\omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_2 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.5) = & \frac{\hbar^4}{720 (K_B T)^4} \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) + \frac{\hbar^6}{120960 (K_B T)^6} \left[40 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \right. \\
& \left. \{ \omega^2(\underline{\kappa}_1 \underline{j}_1) + \omega^2(\underline{\kappa}_2 \underline{j}_2) \} - 174 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_5 \underline{j}_5) - 4 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \right. \\
& \left. \omega^2(\underline{\kappa}_3 \underline{j}_3) \right] + \frac{\hbar^8}{174182400 (K_B T)^8} \left[1440 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \{ \omega^2(\underline{\kappa}_1 \underline{j}_1) \right. \\
& + \omega^2(\underline{\kappa}_2 \underline{j}_2) \} - 6 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_5 \underline{j}_5) \{ 996 \omega^2(\underline{\kappa}_1 \underline{j}_1) + 996 \omega^2(\underline{\kappa}_2 \underline{j}_2) \\
& + 969 \omega^2(\underline{\kappa}_5 \underline{j}_5) \} + 36 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_3 \underline{j}_3) \{ 4 \omega^2(\underline{\kappa}_1 \underline{j}_1) + 4 \omega^2(\underline{\kappa}_2 \underline{j}_2) \\
& + \omega^2(\underline{\kappa}_3 \underline{j}_3) \} + 2800 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_5 \underline{j}_5) + 1072 \omega^2(\underline{\kappa}_1 \underline{j}_1) \\
& \left. \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.6) = & \frac{\hbar^4}{720 (K_B T)^4} \left[-2 \omega^4(\underline{\kappa}_1 \underline{j}_1) + 6 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) + 3 \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) \right] \\
& + \frac{\hbar^6}{60480 (K_B T)^6} \left[4 \omega^6(\underline{\kappa}_1 \underline{j}_1) - 9 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \{ \omega^2(\underline{\kappa}_1 \underline{j}_1) + \omega^2(\underline{\kappa}_2 \underline{j}_2) \} - 6 \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) \right. \\
& \left. \{ \omega^2(\underline{\kappa}_3 \underline{j}_3) + \omega^2(\underline{\kappa}_4 \underline{j}_4) \} + 18 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_5 \underline{j}_5) + 9 \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_5 \underline{j}_5) \right. \\
& + 9 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_4 \underline{j}_4) \omega^2(\underline{\kappa}_5 \underline{j}_5) + 16 \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) \omega^2(\underline{\kappa}_5 \underline{j}_5) + 2 \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) \\
& \left. + 2 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) \right] + \frac{\hbar^8}{14515200 (K_B T)^8} \left[-24 \omega^8(\underline{\kappa}_1 \underline{j}_1) + 36 \omega^2(\underline{\kappa}_3 \underline{j}_3) \right. \\
& \left. \omega^2(\underline{\kappa}_4 \underline{j}_4) \{ \omega^4(\underline{\kappa}_3 \underline{j}_3) + \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) + \omega^4(\underline{\kappa}_4 \underline{j}_4) \} + \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \{ 2572 \omega^4(\underline{\kappa}_1 \underline{j}_1) \right. \\
& + 2572 \omega^4(\underline{\kappa}_2 \underline{j}_2) + 1804 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \} - 4 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_5 \underline{j}_5) \{ 652 \omega^2(\underline{\kappa}_1 \underline{j}_1) \\
& + 652 \omega^2(\underline{\kappa}_5 \underline{j}_5) + 460 \omega^2(\underline{\kappa}_3 \underline{j}_3) \} - \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) \omega^2(\underline{\kappa}_5 \underline{j}_5) \{ 68 \omega^2(\underline{\kappa}_3 \underline{j}_3) + 68 \omega^2(\underline{\kappa}_4 \underline{j}_4) \\
& + 83 \omega^2(\underline{\kappa}_5 \underline{j}_5) - 2 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) \{ 640 \omega^2(\underline{\kappa}_1 \underline{j}_1) + 640 \omega^2(\underline{\kappa}_4 \underline{j}_4) + 448 \omega^2(\underline{\kappa}_3 \underline{j}_3) \} \\
& + 1108 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) \omega^2(\underline{\kappa}_5 \underline{j}_5) + 344 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_5 \underline{j}_5) \\
& \left. + 152 \omega^2(\underline{\kappa}_1 \underline{j}_1) \omega^2(\underline{\kappa}_2 \underline{j}_2) \omega^2(\underline{\kappa}_3 \underline{j}_3) \omega^2(\underline{\kappa}_4 \underline{j}_4) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.7) = & \frac{\hbar^4}{720 (K_B T)^4} \left[-3 \omega^4(\kappa_1 j_1) + 18 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) + 3 \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \right] \\
& + \frac{\hbar^6}{120960 (K_B T)^6} \left[12 \omega^6(\kappa_1 j_1) - 54 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \{ \omega^2(\kappa_1 j_1) + \omega^2(\kappa_2 j_2) \} - 12 \omega^2(\kappa_4 j_4) \right. \\
& \quad \left. \omega^2(\kappa_5 j_5) \{ \omega^2(\kappa_4 j_4) + \omega^2(\kappa_5 j_5) \} + 45 \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) + 53 \right. \\
& \quad \left. \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) + 162 \omega^2(\kappa_1 j_1) \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \right] \\
& + \frac{\hbar^8}{3628800 (K_B T)^8} \left[-9 \omega^8(\kappa_1 j_1) + 3 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \{ 13 \omega^4(\kappa_1 j_1) + 10 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) + 13 \omega^4(\kappa_2 j_2) \} \right. \\
& \quad + 9 \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \{ \omega^4(\kappa_4 j_4) + \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) + \omega^4(\kappa_5 j_5) \} - 540 \omega^4(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) \\
& \quad - 195 \omega^4(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) - 9 \omega^2(\kappa_1 j_1) \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \{ 10 \omega^2(\kappa_1 j_1) + 13 \omega^2(\kappa_4 j_4) \\
& \quad \left. + 13 \omega^2(\kappa_5 j_5) \} + 405 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.8) = & \frac{\hbar^4}{720 (K_B T)^4} \left[-2 \omega^4(\kappa_1 j_1) + 2 \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) + 6 \omega^2(\kappa_1 j_1) \omega^2(\kappa_6 j_6) \right] \\
& + \frac{\hbar^6}{60480 (K_B T)^6} \left[4 \omega^6(\kappa_1 j_1) - 4 \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \{ \omega^2(\kappa_2 j_2) + \omega^2(\kappa_3 j_3) \} - 9 \omega^2(\kappa_1 j_1) \right. \\
& \quad \left. \omega^2(\kappa_6 j_6) \{ \omega^2(\kappa_1 j_1) + \omega^2(\kappa_6 j_6) \} + 18 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) + 18 \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \omega^2(\kappa_6 j_6) \right] \\
& + \frac{\hbar^8}{7257600 (K_B T)^8} \left[-12 \omega^8(\kappa_1 j_1) + 12 \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \{ \omega^4(\kappa_2 j_2) + \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) + \omega^4(\kappa_3 j_3) \} \right. \\
& \quad + 4 \omega^2(\kappa_1 j_1) \omega^2(\kappa_6 j_6) \{ 13 \omega^4(\kappa_1 j_1) + 5 \omega^2(\kappa_1 j_1) \omega^2(\kappa_6 j_6) \} - 4 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \\
& \quad \{ 10 \omega^2(\kappa_1 j_1) + 13 \omega^2(\kappa_2 j_2) + 13 \omega^2(\kappa_3 j_3) \} - 4 \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \omega^2(\kappa_6 j_6) \{ 13 \omega^2(\kappa_2 j_2) \\
& \quad + 13 \omega^2(\kappa_3 j_3) + 10 \omega^2(\kappa_6 j_6) \} + 20 \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \\
& \quad \left. + 134 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \omega^2(\kappa_6 j_6) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.9) = & \frac{\hbar^4}{720(K_B T)^4} \left[-\omega^4(\kappa_1 j_1) + 3\omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \right] \\
& + \frac{\hbar^6}{120960(K_B T)^6} \left[4\omega^6(\kappa_1 j_1) - 12\omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) (\omega^2(\kappa_4 j_4) + \omega^2(\kappa_5 j_5)) \right. \\
& + 12\omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) + 29\omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) + 54\omega^2(\kappa_1 j_1) \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \left. \right] \\
& + \frac{\hbar^8}{58060800(K_B T)^8} \left[48\omega^8(\kappa_1 j_1) + 144\omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \{ \omega^4(\kappa_4 j_4) + \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) + \omega^4(\kappa_5 j_5) \} \right. \\
& - 3\omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \omega^2(\kappa_6 j_6) \{ \omega^2(\kappa_2 j_2) + \omega^2(\kappa_3 j_3) + \omega^2(\kappa_6 j_6) \} - 48\omega^2(\kappa_1 j_1) \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \\
& \{ 13\omega^2(\kappa_4 j_4) + 13\omega^2(\kappa_5 j_5) + 10\omega^2(\kappa_1 j_1) \} + 4\omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) \{ 92\omega^2(\kappa_4 j_4) + 92\omega^2(\kappa_5 j_5) \\
& + 83\omega^2(\kappa_6 j_6) \} + 16\omega^2(\kappa_1 j_1) \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \{ 8\omega^2(\kappa_1 j_1) + 14\omega^2(\kappa_4 j_4) + 14\omega^2(\kappa_5 j_5) \} \\
& + 640\omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) \omega^2(\kappa_6 j_6) + 17800\omega^2(\kappa_1 j_1) \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \\
& \left. \omega^2(\kappa_6 j_6) + 48\omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \omega^2(\kappa_6 j_6) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.10) = & \frac{\hbar^4}{240(K_B T)^4} \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) + \frac{\hbar^6}{30240(K_B T)^6} \left[-3\omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \right. \\
& \left. \{ \omega^2(\kappa_1 j_1) + \omega^2(\kappa_2 j_2) \} \right] + \frac{\hbar^8}{403200(K_B T)^8} \left[\omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \right. \\
& \left. \{ \omega^4(\kappa_1 j_1) + \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) + \omega^4(\kappa_2 j_2) \} + \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \right. \\
& \left. \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.11) = & \frac{\hbar^4}{720(K_B T)^4} \left[\omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) + 3\omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) - \omega^4(\kappa_1 j_1) \right] \\
& + \frac{\hbar^6}{120960(K_B T)^6} \left[4\omega^6(\kappa_1 j_1) - 4\omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \{ \omega^2(\kappa_2 j_2) + \omega^2(\kappa_3 j_3) \} \right.
\end{aligned}$$

$$\begin{aligned}
& -12 \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) \{ \omega^2(\kappa_4 \dot{d}_4) + \omega^2(\kappa_5 \dot{d}_5) \} + 29 \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) \omega^2(\kappa_6 \dot{d}_6) \\
& + 18 \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_2 \dot{d}_2) \omega^2(\kappa_2 \dot{d}_3) + 54 \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5)] \\
& + \frac{\hbar^8}{58060800 (K_B T)^8} \left[-48 \omega^8(\kappa_1 \dot{d}_1) + 48 \omega^2(\kappa_2 \dot{d}_2) \omega^2(\kappa_2 \dot{d}_3) \{ \omega^4(\kappa_2 \dot{d}_2) + \omega^4(\kappa_2 \dot{d}_3) \} \right. \\
& \omega^2(\kappa_2 \dot{d}_3) + \omega^4(\kappa_2 \dot{d}_3) \} + 144 \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) \{ \omega^4(\kappa_4 \dot{d}_4) + \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) + \omega^4(\kappa_5 \dot{d}_5) \} \\
& - 332 \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) \omega^2(\kappa_6 \dot{d}_6) \{ \omega^2(\kappa_4 \dot{d}_4) + \omega^2(\kappa_5 \dot{d}_5) \} + 320 \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) \\
& \omega^4(\kappa_6 \dot{d}_6) - \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_2 \dot{d}_2) \omega^2(\kappa_2 \dot{d}_3) \{ 160 \omega^2(\kappa_1 \dot{d}_1) + 208 \omega^2(\kappa_2 \dot{d}_2) + 208 \omega^2(\kappa_2 \dot{d}_3) \} \\
& - 3 \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) \{ 160 \omega^2(\kappa_1 \dot{d}_1) + 208 \omega^2(\kappa_4 \dot{d}_4) + 208 \omega^2(\kappa_5 \dot{d}_5) \} \\
& \left. + 480 \omega^2(\kappa_2 \dot{d}_2) \omega^2(\kappa_2 \dot{d}_3) \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) + 756 \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) \omega^2(\kappa_6 \dot{d}_6) \right]
\end{aligned}$$

$$\begin{aligned}
\chi(3.12) &= \frac{\hbar^4}{720 (K_B T)^4} \left[-\omega^4(\kappa_1 \dot{d}_1) - \omega^4(\kappa_6 \dot{d}_6) + \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) + 6 \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_6 \dot{d}_6) \right] \\
&+ \frac{\hbar^6}{60480 (K_B T)^6} \left[2 \omega^6(\kappa_1 \dot{d}_1) + 2 \omega^6(\kappa_6 \dot{d}_6) - 2 \omega^4(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) + 16 \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_6 \dot{d}_6) \right. \\
&\{ \omega^2(\kappa_1 \dot{d}_1) + \omega^2(\kappa_6 \dot{d}_6) \} + 4 \omega^2(\kappa_2 \dot{d}_2) \omega^2(\kappa_2 \dot{d}_3) \omega^2(\kappa_4 \dot{d}_4) + 16 \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_4 \dot{d}_4) \\
&\omega^2(\kappa_5 \dot{d}_5) + 16 \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) \omega^2(\kappa_6 \dot{d}_6) \left. \right] \\
&+ \frac{\hbar^8}{14515200 (K_B T)^8} \left[-12 \omega^8(\kappa_1 \dot{d}_1) - 12 \omega^8(\kappa_6 \dot{d}_6) + 12 \omega^4(\kappa_4 \dot{d}_4) \omega^4(\kappa_5 \dot{d}_5) + 24 \omega^6(\kappa_4 \dot{d}_4) \right. \\
&\omega^2(\kappa_5 \dot{d}_5) + 4 \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_6 \dot{d}_6) \{ 13 \omega^4(\kappa_1 \dot{d}_1) + 7 \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_6 \dot{d}_6) + 13 \omega^4(\kappa_6 \dot{d}_6) \} - 24 \\
&\omega^2(\kappa_2 \dot{d}_2) \omega^2(\kappa_2 \dot{d}_3) \omega^2(\kappa_4 \dot{d}_4) \{ \omega^2(\kappa_2 \dot{d}_2) + \omega^2(\kappa_2 \dot{d}_3) + \omega^2(\kappa_4 \dot{d}_4) \} - 4 \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) \\
&\{ 10 \omega^2(\kappa_1 \dot{d}_1) + 13 \omega^2(\kappa_4 \dot{d}_4) + 13 \omega^2(\kappa_5 \dot{d}_5) \} - 4 \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) \omega^2(\kappa_6 \dot{d}_6) \{ 13 \omega^2(\kappa_4 \dot{d}_4) + 13 \omega^2(\kappa_5 \dot{d}_5) \\
&+ 10 \omega^2(\kappa_6 \dot{d}_6) \} + 104 \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_2 \dot{d}_2) \omega^2(\kappa_2 \dot{d}_3) \omega^2(\kappa_4 \dot{d}_4) + 104 \omega^2(\kappa_2 \dot{d}_2) \omega^2(\kappa_2 \dot{d}_3) \omega^2(\kappa_4 \dot{d}_4) \\
&\omega^2(\kappa_5 \dot{d}_5) + 11 \omega^2(\kappa_2 \dot{d}_2) \omega^2(\kappa_2 \dot{d}_3) \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) + 134 \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) \omega^2(\kappa_6 \dot{d}_6) \left. \right]
\end{aligned}$$

$$\begin{aligned}
X(3.13) = & \frac{\hbar^4}{720 (k_B T)^4} \left[-\omega^4(\underline{k}_1 \hat{j}_1) + 2\omega^2(\underline{k}_2 \hat{j}_2) \omega^2(\underline{k}_3 \hat{j}_3) \right] + \frac{\hbar^6}{60480 (k_B T)^6} \left[2\omega^6(\underline{k}_1 \hat{j}_1) - 8\omega^4(\underline{k}_5 \hat{j}_5) \right. \\
& \left. \omega^2(\underline{k}_6 \hat{j}_6) + 8\omega^2(\underline{k}_2 \hat{j}_2) \omega^2(\underline{k}_4 \hat{j}_4) \omega^2(\underline{k}_5 \hat{j}_5) + 18\omega^2(\underline{k}_1 \hat{j}_1) \omega^2(\underline{k}_2 \hat{j}_2) \omega^2(\underline{k}_3 \hat{j}_3) \right] \\
& + \frac{\hbar^8}{58060800 (k_B T)^8} \left[-48\omega^8(\underline{k}_1 \hat{j}_1) + 96\omega^2(\underline{k}_2 \hat{j}_2) \omega^2(\underline{k}_3 \hat{j}_3) \{ 2\omega^4(\underline{k}_2 \hat{j}_2) + \omega^2(\underline{k}_2 \hat{j}_2) \omega^2(\underline{k}_3 \hat{j}_3) \} \right. \\
& - 192\omega^2(\underline{k}_2 \hat{j}_2) \omega^2(\underline{k}_4 \hat{j}_4) \omega^4(\underline{k}_5 \hat{j}_5) \{ \omega^2(\underline{k}_2 \hat{j}_2) + \omega^2(\underline{k}_4 \hat{j}_4) + \omega^2(\underline{k}_5 \hat{j}_5) \} - 32\omega^2(\underline{k}_1 \hat{j}_1) \\
& \omega^2(\underline{k}_2 \hat{j}_2) \omega^2(\underline{k}_3 \hat{j}_3) \{ 10\omega^2(\underline{k}_1 \hat{j}_1) + 13\omega^2(\underline{k}_2 \hat{j}_2) + 13\omega^2(\underline{k}_3 \hat{j}_3) \} + 323\omega^2(\underline{k}_2 \hat{j}_2) \omega^2(\underline{k}_3 \hat{j}_3) \omega^2(\underline{k}_4 \hat{j}_4) \\
& \omega^2(\underline{k}_6 \hat{j}_6) + 664\omega^2(\underline{k}_2 \hat{j}_2) \omega^2(\underline{k}_4 \hat{j}_4) \omega^2(\underline{k}_5 \hat{j}_5) \omega^2(\underline{k}_6 \hat{j}_6) + 128\omega^2(\underline{k}_1 \hat{j}_1) \omega^2(\underline{k}_2 \hat{j}_2) \omega^2(\underline{k}_4 \hat{j}_4) \omega^2(\underline{k}_6 \hat{j}_6) \\
& \left. + 160\omega^2(\underline{k}_2 \hat{j}_2) \omega^2(\underline{k}_3 \hat{j}_3) \omega^2(\underline{k}_5 \hat{j}_5) \omega^2(\underline{k}_6 \hat{j}_6) + 38\omega^2(\underline{k}_1 \hat{j}_1) \omega^2(\underline{k}_2 \hat{j}_2) \omega^2(\underline{k}_4 \hat{j}_4) \omega^2(\underline{k}_5 \hat{j}_5) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.14) = & \frac{\hbar^4}{720 (k_B T)^4} \left[\omega^2(\underline{k}_1 \hat{j}_1) \omega^2(\underline{k}_2 \hat{j}_2) + 3\omega^2(\underline{k}_4 \hat{j}_4) \omega^2(\underline{k}_5 \hat{j}_5) \right] \\
& + \frac{\hbar^6}{30240 (k_B T)^6} \left[-2\omega^2(\underline{k}_1 \hat{j}_1) \omega^4(\underline{k}_2 \hat{j}_2) - 3\omega^2(\underline{k}_4 \hat{j}_4) \omega^2(\underline{k}_5 \hat{j}_5) \{ \omega^2(\underline{k}_4 \hat{j}_4) + \omega^2(\underline{k}_5 \hat{j}_5) \} \right. \\
& \left. + 6\omega^2(\underline{k}_1 \hat{j}_1) \omega^2(\underline{k}_3 \hat{j}_3) \omega^2(\underline{k}_4 \hat{j}_4) + \frac{9}{2} \omega^2(\underline{k}_4 \hat{j}_4) \omega^2(\underline{k}_5 \hat{j}_5) \omega^2(\underline{k}_6 \hat{j}_6) \right] \\
& + \frac{\hbar^8}{1209600 (k_B T)^8} \left[\omega^2(\underline{k}_1 \hat{j}_1) \omega^2(\underline{k}_2 \hat{j}_2) \{ 2\omega^4(\underline{k}_1 \hat{j}_1) + \omega^2(\underline{k}_1 \hat{j}_1) \omega^2(\underline{k}_2 \hat{j}_2) \} + 3\omega^2(\underline{k}_4 \hat{j}_4) \right. \\
& \omega^2(\underline{k}_5 \hat{j}_5) \{ \omega^4(\underline{k}_4 \hat{j}_4) + \omega^2(\underline{k}_4 \hat{j}_4) \omega^2(\underline{k}_5 \hat{j}_5) + \omega^4(\underline{k}_5 \hat{j}_5) \} - 6\omega^2(\underline{k}_1 \hat{j}_1) \omega^2(\underline{k}_3 \hat{j}_3) \omega^2(\underline{k}_4 \hat{j}_4) \\
& \{ \omega^2(\underline{k}_1 \hat{j}_1) + \omega^2(\underline{k}_3 \hat{j}_3) + \omega^2(\underline{k}_4 \hat{j}_4) \} - 32\omega^4(\underline{k}_4 \hat{j}_4) \omega^2(\underline{k}_5 \hat{j}_5) \omega^2(\underline{k}_6 \hat{j}_6) + \frac{320}{48} \omega^2(\underline{k}_1 \hat{j}_1) \\
& \omega^2(\underline{k}_2 \hat{j}_2) \omega^2(\underline{k}_3 \hat{j}_3) \omega^2(\underline{k}_6 \hat{j}_6) + \frac{10}{3} \omega^2(\underline{k}_1 \hat{j}_1) \omega^2(\underline{k}_2 \hat{j}_2) \omega^2(\underline{k}_6 \hat{j}_6) \{ \omega^2(\underline{k}_4 \hat{j}_4) + \omega^2(\underline{k}_5 \hat{j}_5) \} \\
& \left. + \frac{80}{3} \omega^2(\underline{k}_1 \hat{j}_1) \omega^2(\underline{k}_3 \hat{j}_3) \omega^2(\underline{k}_4 \hat{j}_4) \omega^2(\underline{k}_6 \hat{j}_6) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.15) = & \frac{\hbar^4}{120 (k_B T)^4} \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) + \frac{\hbar^6}{60480 (k_B T)^6} \left[-6 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \right. \\
& \left. \{ \omega^2(\kappa_1 j_1) + \omega^2(\kappa_2 j_2) \} + 29 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \right] \\
& + \frac{\hbar^8}{29030400 (k_B T)^8} \left[144 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \{ \omega^4(\kappa_1 j_1) + \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) + \omega^4(\kappa_2 j_2) \} \right. \\
& - \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \{ 332 \omega^2(\kappa_1 j_1) + 332 \omega^2(\kappa_2 j_2) + 323 \omega^2(\kappa_3 j_3) \} + 720 \\
& \left. \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.16) = & \frac{\hbar^4}{720 (k_B T)^4} \left[-2 \omega^4(\kappa_1 j_1) + \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) + 6 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \right] \\
& + \frac{\hbar^6}{60480 (k_B T)^6} \left[4 \omega^6(\kappa_1 j_1) - 2 \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) \{ \omega^2(\kappa_5 j_5) + \omega^2(\kappa_6 j_6) \} - 18 \omega^2(\kappa_1 j_1) \right. \\
& \left. \omega^4(\kappa_2 j_2) + 18 \omega^2(\kappa_1 j_1) \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) + 2 \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) \{ \omega^2(\kappa_6 j_6) + \omega^2(\kappa_5 j_5) \} \right] \\
& + \frac{\hbar^8}{14515200 (k_B T)^8} \left[-24 \omega^8(\kappa_1 j_1) + 3 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \{ 28 \omega^4(\kappa_1 j_1) + 11 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \} \right. \\
& + 12 \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) \{ \omega^4(\kappa_5 j_5) + \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) + \omega^4(\kappa_6 j_6) \} - 24 \omega^2(\kappa_3 j_3) \\
& \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \{ \omega^2(\kappa_3 j_3) + \omega^2(\kappa_4 j_4) + \omega^2(\kappa_5 j_5) \} - 6 \omega^2(\kappa_1 j_1) \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) \\
& \left. \{ \omega^2(\kappa_1 j_1) + 14 \omega^2(\kappa_5 j_5) + 14 \omega^2(\kappa_6 j_6) \} + 104 \omega^2(\kappa_1 j_1) \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) \omega^2(\kappa_6 j_6) + 260 \right. \\
& \left. \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) + 104 \omega^2(\kappa_1 j_1) \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \right. \\
& \left. + 83 \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) + 104 \omega^2(\kappa_1 j_1) \omega^2(\kappa_3 j_3) \omega^2(\kappa_5 j_5) \right. \\
& \left. \omega^2(\kappa_6 j_6) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.17) = & \frac{\hbar^4}{720 (K_B T)^4} \left[-\omega^4(K_1 j_1) + 2 \omega^2(K_2 j_2) \omega^2(K_3 j_3) \right] \\
& + \frac{\hbar^6}{60480 (K_B T)^6} \left[2 \omega^6(K_1 j_1) - 8 \omega^2(K_2 j_2) \omega^4(K_3 j_3) + 8 \omega^2(K_2 j_2) \omega^2(K_4 j_4) \omega^2(K_6 j_6) \right. \\
& + 18 \omega^2(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_3 j_3) \left. \right] + \frac{\hbar^8}{58060800 (K_B T)^8} \left[-48 \omega^8(K_1 j_1) + 96 \omega^2(K_2 j_2) \right. \\
& \omega^2(K_3 j_3) \{ 2 \omega^4(K_2 j_2) + \omega^2(K_2 j_2) \omega^2(K_3 j_3) - 192 \omega^2(K_2 j_2) \omega^2(K_4 j_4) \omega^2(K_6 j_6) \{ \omega^2(K_2 j_2) \\
& + \omega^2(K_4 j_4) + \omega^2(K_6 j_6) \} - 32 \omega^2(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_3 j_3) \{ 10 \omega^2(K_1 j_1) + 13 \omega^2(K_2 j_2) + 13 \omega^2(K_3 j_3) \} \\
& + 1324 \omega^2(K_2 j_2) \omega^2(K_3 j_3) \omega^2(K_4 j_4) \omega^2(K_6 j_6) + 832 \omega^2(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_4 j_4) \omega^2(K_6 j_6) \\
& \left. + 124 \omega^2(K_2 j_2) \omega^2(K_3 j_3) \omega^2(K_4 j_4) \omega^2(K_5 j_5) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.18) = & \frac{\hbar^4}{720 (K_B T)^4} \left[-\omega^4(K_1 j_1) + 2 \omega^2(K_3 j_3) \omega^2(K_4 j_4) \right] + \frac{\hbar^6}{60480 (K_B T)^6} \left[2 \omega^6(K_1 j_1) - 8 \omega^2(K_3 j_3) \right. \\
& \omega^2(K_4 j_4) + 18 \omega^2(K_1 j_1) \omega^2(K_3 j_3) \omega^2(K_4 j_4) \left. \right] + \frac{\hbar^8}{3628800 (K_B T)^8} \left[-3 \omega^8(K_1 j_1) \right. \\
& + 6 \omega^2(K_3 j_3) \omega^2(K_4 j_4) \{ 2 \omega^4(K_3 j_3) + \omega^2(K_3 j_3) \omega^2(K_4 j_4) \} - 2 \omega^2(K_1 j_1) \omega^2(K_3 j_3) \omega^2(K_4 j_4) \\
& \{ 10 \omega^2(K_1 j_1) + 26 \omega^2(K_6 j_6) \} + 10 \omega^2(K_3 j_3) \omega^2(K_4 j_4) \omega^2(K_6 j_6) \omega^2(K_7 j_7) + 12 \omega^2(K_2 j_2) \\
& \left. \omega^2(K_3 j_3) \omega^2(K_5 j_5) \omega^2(K_6 j_6) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.19) = & \frac{\hbar^4}{720 (K_B T)^4} \left[3 \omega^2(K_1 j_1) \omega^2(K_2 j_2) + \omega^2(K_6 j_6) \omega^2(K_7 j_7) \right] + \frac{\hbar^6}{120960 (K_B T)^6} \left[-12 \omega^2(K_1 j_1) \right. \\
& \omega^2(K_2 j_2) \{ \omega^2(K_1 j_1) + \omega^2(K_2 j_2) \} - 4 \omega^4(K_6 j_6) \omega^2(K_7 j_7) + 8 \omega^2(K_4 j_4) \omega^2(K_5 j_5) \omega^2(K_6 j_6) + 29 \omega^2(K_1 j_1) \\
& \omega^2(K_2 j_2) \omega^2(K_3 j_3) \left. \right] + \frac{\hbar^8}{58060800 (K_B T)^8} \left[144 \omega^2(K_1 j_1) \omega^2(K_2 j_2) \{ \omega^4(K_1 j_1) + \omega^2(K_1 j_1) \omega^2(K_2 j_2) \right. \\
& + \omega^4(K_2 j_2) \} + 48 \omega^2(K_6 j_6) \omega^2(K_7 j_7) \{ 2 \omega^4(K_6 j_6) + \omega^2(K_6 j_6) \omega^2(K_7 j_7) \} - 96 \omega^2(K_4 j_4) \omega^2(K_5 j_5) \omega^2(K_6 j_6) \\
& \{ \omega^2(K_4 j_4) + \omega^2(K_5 j_5) + \omega^2(K_6 j_6) \} - \omega^2(K_2 j_2) \omega^2(K_3 j_3) \omega^2(K_1 j_1) \{ 664 \omega^2(K_1 j_1) + 323 \omega^2(K_3 j_3) \} + 480 \\
& \left. \omega^2(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_6 j_6) \omega^2(K_7 j_7) + 332 \omega^2(K_4 j_4) \omega^2(K_5 j_5) \omega^2(K_6 j_6) \omega^2(K_7 j_7) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.20) = & \frac{\hbar^4}{360 (K_B T)^4} \omega^2(K_1 j_1) \omega^2(K_2 j_2) + \frac{\hbar^6}{30240 (K_B T)^6} \left[-4 \omega^2(K_1 j_1) \omega^4(K_2 j_2) + 4 \omega^2(K_1 j_1) \right. \\
& \left. \omega^2(K_5 j_5) \omega^2(K_7 j_7) \right] + \frac{\hbar^8}{58060800 (K_B T)^8} \left[96 \omega^2(K_1 j_1) \omega^2(K_2 j_2) \{ 2 \omega^4(K_1 j_1) + \omega^2(K_1 j_1) \omega^2(K_2 j_2) \} \right. \\
& + 192 \omega^2(K_1 j_1) \omega^2(K_5 j_5) \omega^2(K_7 j_7) \{ \omega^2(K_1 j_1) + \omega^2(K_5 j_5) + \omega^2(K_7 j_7) \} + 646 \omega^2(K_1 j_1) \omega^2(K_2 j_2) \\
& \omega^2(K_5 j_5) \omega^2(K_7 j_7) + 192 \omega^2(K_1 j_1) \omega^2(K_3 j_3) \omega^2(K_5 j_5) \omega^2(K_6 j_6) + 160 \omega^2(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_3 j_3) \\
& \left. \omega^2(K_4 j_4) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.21) = & -\frac{\hbar^4}{720 (K_B T)^4} \omega^4(K_1 j_1) + \frac{\hbar^6}{30240 (K_B T)^6} \left[\omega^4(K_1 j_1) + \omega^2(K_2 j_2) \omega^2(K_4 j_4) \omega^2(K_6 j_6) + \omega^2(K_3 j_3) \right. \\
& \left. \omega^2(K_4 j_4) \omega^2(K_7 j_7) + \omega^2(K_5 j_5) \omega^2(K_6 j_6) \omega^2(K_7 j_7) + \omega^2(K_2 j_2) \omega^2(K_3 j_3) \omega^2(K_5 j_5) \right] \\
& + \frac{\hbar^8}{3628800 (K_B T)^8} \left[-3 \omega^8(K_1 j_1) - 3 \omega^2(K_2 j_2) \omega^2(K_4 j_4) \omega^2(K_6 j_6) \{ \omega^2(K_2 j_2) + \omega^2(K_4 j_4) + \omega^2(K_6 j_6) \} \right. \\
& - 3 \omega^2(K_3 j_3) \omega^2(K_4 j_4) \omega^2(K_7 j_7) \{ \omega^2(K_3 j_3) + \omega^2(K_4 j_4) + \omega^2(K_7 j_7) \} - 3 \omega^2(K_5 j_5) \omega^2(K_6 j_6) \omega^2(K_7 j_7) \\
& \{ \omega^2(K_5 j_5) + \omega^2(K_6 j_6) + \omega^2(K_7 j_7) \} - 3 \omega^2(K_2 j_2) \omega^2(K_3 j_3) \omega^2(K_5 j_5) \{ \omega^2(K_2 j_2) + \\
& \omega^2(K_3 j_3) + \omega^2(K_5 j_5) \} + 13 \omega^2(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_4 j_4) \omega^2(K_6 j_6) + 13 \omega^2(K_1 j_1) \omega^2(K_3 j_3) \\
& \omega^2(K_4 j_4) \omega^2(K_7 j_7) + 13 \omega^2(K_1 j_1) \omega^2(K_5 j_5) \omega^2(K_6 j_6) \omega^2(K_7 j_7) + 13 \omega^2(K_1 j_1) \omega^2(K_2 j_2) \\
& \omega^2(K_3 j_3) \omega^2(K_5 j_5) + 3 \omega^2(K_2 j_2) \omega^2(K_3 j_3) \omega^2(K_6 j_6) \omega^2(K_7 j_7) + 3 \omega^2(K_2 j_2) \omega^2(K_4 j_4) \\
& \left. \omega^2(K_5 j_5) \omega^2(K_7 j_7) + 3 \omega^2(K_3 j_3) \omega^2(K_4 j_4) \omega^2(K_5 j_5) \omega^2(K_6 j_6) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.22) = & \frac{\hbar^4}{720 (K_B T)^4} \left[-\omega^4(K_1 j_1) + \omega^2(K_2 j_2) \omega^2(K_3 j_3) + \omega^2(K_6 j_6) \omega^2(K_7 j_7) \right] \\
& + \frac{\hbar^6}{60480 (K_B T)^6} \left[2 \omega^6(K_1 j_1) - 2 \omega^2(K_2 j_2) \omega^2(K_3 j_3) \{ \omega^2(K_2 j_2) + \omega^2(K_3 j_3) \} - 2 \omega^4(K_6 j_6) \right. \\
& \left. \omega^2(K_7 j_7) + 4 \omega^2(K_4 j_4) \omega^2(K_5 j_5) \omega^2(K_6 j_6) + 9 \omega^2(K_1 j_1) \omega^2(K_2 j_2) \omega^2(K_3 j_3) \right. \\
& \left. + 9 \omega^2(K_1 j_1) \omega^2(K_6 j_6) \omega^2(K_7 j_7) \right]
\end{aligned}$$

$$\begin{aligned}
& + \frac{\hbar^8}{5808000 (k_B T)^8} \left[-48 \omega^8(\kappa_1 j_1) + 48 \omega^2(\kappa_2 j_2) \omega^2(\kappa_2 j_3) \{ \omega^4(\kappa_2 j_2) + \omega^2(\kappa_2 j_2) \right. \\
& \left. \omega^2(\kappa_2 j_3) + \omega^4(\kappa_2 j_3) \} + 48 \omega^2(\kappa_6 j_6) \omega^2(\kappa_7 j_7) \{ 2 \omega^4(\kappa_6 j_6) + \omega^2(\kappa_6 j_6) \omega^2(\kappa_7 j_7) \} \right. \\
& \left. - 48 \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) \{ 2 \omega^2(\kappa_4 j_4) + 2 \omega^2(\kappa_4 j_5) + 2 \omega^2(\kappa_6 j_6) \} - 16 \right. \\
& \left. \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_2 j_3) \{ 11 \omega^2(\kappa_1 j_1) + 14 \omega^2(\kappa_2 j_2) + 14 \omega^2(\kappa_2 j_3) \} - 16 \right. \\
& \left. \omega^2(\kappa_1 j_1) \omega^2(\kappa_6 j_6) \omega^2(\kappa_7 j_7) \{ 11 \omega^2(\kappa_1 j_1) + 14 \omega^2(\kappa_6 j_6) + 14 \omega^2(\kappa_7 j_7) \} + 416 \omega^2(\kappa_1 j_1) \right. \\
& \left. \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) + 160 \omega^2(\kappa_2 j_2) \omega^2(\kappa_2 j_3) \omega^2(\kappa_6 j_6) \omega^2(\kappa_7 j_7) \right. \\
& \left. + 332 \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) \omega^2(\kappa_7 j_7) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.23) &= \frac{\hbar^4}{720 (k_B T)^4} \left[-\omega^4(\kappa_1 j_1) + 2 \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \right] + \frac{\hbar^6}{60480 (k_B T)^6} \left[2 \omega^6(\kappa_1 j_1) \right. \\
& \left. - 8 \omega^4(\kappa_4 j_4) \omega^2(\kappa_5 j_5) + 18 \omega^2(\kappa_1 j_1) \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \right] \\
& + \frac{\hbar^8}{3628800 (k_B T)^8} \left[-3 \omega^8(\kappa_1 j_1) + 6 \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \{ 2 \omega^4(\kappa_4 j_4) + \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \} \right. \\
& \left. - 4 \omega^2(\kappa_1 j_1) \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \{ 5 \omega^2(\kappa_1 j_1) + 13 \omega^2(\kappa_4 j_4) \} + 12 \omega^2(\kappa_2 j_2) \omega^2(\kappa_2 j_3) \right. \\
& \left. \omega^2(\kappa_4 j_4) \omega^2(\kappa_6 j_6) + 10 \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) \omega^2(\kappa_7 j_7) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.24) &= \frac{\hbar^4}{360 (k_B T)^4} \left[-\omega^2(\kappa_1 j_1) + 3 \omega^2(\kappa_1 j_1) \omega^2(\kappa_7 j_7) \right] + \frac{\hbar^6}{60480 (k_B T)^6} \left[4 \omega^6(\kappa_1 j_1) \right. \\
& \left. - 18 \omega^4(\kappa_1 j_1) \omega^2(\kappa_7 j_7) + 4 \omega^2(\kappa_2 j_2) \omega^2(\kappa_2 j_3) \omega^2(\kappa_4 j_4) \right] \\
& + \frac{\hbar^8}{3628800 (k_B T)^8} \left[-6 \omega^8(\kappa_1 j_1) + 2 \omega^2(\kappa_1 j_1) \omega^2(\kappa_7 j_7) \{ 13 \omega^4(\kappa_1 j_1) + 10 \omega^2(\kappa_1 j_1) \right. \\
& \left. \omega^2(\kappa_7 j_7) \} - 6 \omega^2(\kappa_2 j_2) \omega^2(\kappa_2 j_3) \omega^2(\kappa_4 j_4) \{ \omega^2(\kappa_2 j_2) + \omega^2(\kappa_2 j_3) + \omega^2(\kappa_4 j_4) \} + 3 \omega^2(\kappa_2 j_2) \right. \\
& \left. \omega^2(\kappa_2 j_3) \omega^2(\kappa_5 j_5) \omega^2(\kappa_5 j_6) + 52 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_2 j_3) \omega^2(\kappa_4 j_4) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.25) = & \frac{\hbar^4}{720 (K_B T)^4} \left[-2 \omega^4(\kappa_1 \dot{d}_1) + \omega^2(\kappa_6 \dot{d}_6) \omega^2(\kappa_7 \dot{d}_7) + 6 \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_2 \dot{d}_2) \right] \\
& + \frac{\hbar^6}{60480 (K_B T)^6} \left[4 \omega^6(\kappa_1 \dot{d}_1) - 2 \omega^2(\kappa_6 \dot{d}_6) \omega^2(\kappa_7 \dot{d}_7) \{ \omega^2(\kappa_6 \dot{d}_6) + \omega^2(\kappa_7 \dot{d}_7) \} - 18 \omega^4(\kappa_1 \dot{d}_1) \right. \\
& \left. \omega^2(\kappa_2 \dot{d}_2) + 18 \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_6 \dot{d}_6) \omega^2(\kappa_7 \dot{d}_7) \right] \\
& + \frac{\hbar^8}{362880 (K_B T)^8} \left[-6 \omega^8(\kappa_1 \dot{d}_1) + 3 \omega^2(\kappa_6 \dot{d}_6) \omega^2(\kappa_7 \dot{d}_7) \{ \omega^4(\kappa_6 \dot{d}_6) + \omega^2(\kappa_6 \dot{d}_6) \omega^2(\kappa_7 \dot{d}_7) \right. \\
& + \omega^4(\kappa_7 \dot{d}_7) \} + 2 \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_2 \dot{d}_2) \{ 13 \omega^4(\kappa_1 \dot{d}_1) + 5 \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_2 \dot{d}_2) \} - 2 \\
& \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_6 \dot{d}_6) \omega^2(\kappa_7 \dot{d}_7) \{ 10 \omega^2(\kappa_1 \dot{d}_1) + 13 \omega^2(\kappa_6 \dot{d}_6) + 13 \omega^2(\kappa_7 \dot{d}_7) \} + 6 \omega^2(\kappa_3 \dot{d}_3) \\
& \left. \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) \omega^2(\kappa_6 \dot{d}_6) + 65 \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_2 \dot{d}_2) \omega^2(\kappa_6 \dot{d}_6) \omega^2(\kappa_7 \dot{d}_7) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.26) = & \frac{\hbar^4}{720 (K_B T)^4} \left[-\omega^4(\kappa_1 \dot{d}_1) + \omega^2(\kappa_5 \dot{d}_5) \omega^2(\kappa_6 \dot{d}_6) \right] \\
& + \frac{\hbar^6}{60480 (K_B T)^6} \left[2 \omega^6(\kappa_1 \dot{d}_1) - 4 \omega^4(\kappa_5 \dot{d}_5) \omega^2(\kappa_6 \dot{d}_6) + 4 \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) \omega^2(\kappa_7 \dot{d}_7) \right. \\
& \left. + 9 \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_5 \dot{d}_5) \omega^2(\kappa_6 \dot{d}_6) + 2 \omega^2(\kappa_2 \dot{d}_2) \omega^2(\kappa_3 \dot{d}_3) \omega^2(\kappa_4 \dot{d}_4) \right] \\
& + \frac{\hbar^8}{362880 (K_B T)^8} \left[-3 \omega^8(\kappa_1 \dot{d}_1) + 3 \omega^2(\kappa_5 \dot{d}_5) \omega^2(\kappa_6 \dot{d}_6) \{ 2 \omega^4(\kappa_5 \dot{d}_5) + \omega^2(\kappa_5 \dot{d}_5) \omega^2(\kappa_6 \dot{d}_6) \} \right. \\
& - 6 \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) \omega^2(\kappa_7 \dot{d}_7) \{ \omega^2(\kappa_4 \dot{d}_4) + \omega^2(\kappa_5 \dot{d}_5) + \omega^2(\kappa_7 \dot{d}_7) \} - 3 \omega^2(\kappa_2 \dot{d}_2) \omega^2(\kappa_3 \dot{d}_3) \\
& \omega^2(\kappa_4 \dot{d}_4) \{ \omega^2(\kappa_2 \dot{d}_2) + \omega^2(\kappa_3 \dot{d}_3) + \omega^2(\kappa_4 \dot{d}_4) \} - 2 \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_5 \dot{d}_5) \omega^2(\kappa_6 \dot{d}_6) \{ 5 \omega^2(\kappa_1 \dot{d}_1) \\
& + 13 \omega^2(\kappa_5 \dot{d}_5) \} + 6 \omega^2(\kappa_2 \dot{d}_2) \omega^2(\kappa_3 \dot{d}_3) \omega^2(\kappa_5 \dot{d}_5) \omega^2(\kappa_7 \dot{d}_7) + 26 \omega^2(\kappa_1 \dot{d}_1) \\
& \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) \omega^2(\kappa_7 \dot{d}_7) + 83 \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) \omega^2(\kappa_6 \dot{d}_6) \omega^2(\kappa_7 \dot{d}_7) \\
& \left. + 13 \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_2 \dot{d}_2) \omega^2(\kappa_3 \dot{d}_3) \omega^2(\kappa_4 \dot{d}_4) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.27) = & \frac{\hbar^4}{720 (k_B T)^4} \left[\omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) + 3 \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) \right] \\
& + \frac{\hbar^6}{30240 (k_B T)^6} \left[-2 \omega^4(\kappa_1 j_1) \omega^2(\kappa_2 j_2) - 3 \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) \{ \omega^2(\kappa_5 j_5) + \omega^2(\kappa_6 j_6) \} \right] \\
& + \frac{\hbar^8}{58060800 (k_B T)^8} \left[48 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \{ 2 \omega^4(\kappa_1 j_1) + \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \} + 144 \omega^2(\kappa_5 j_5) \right. \\
& \omega^2(\kappa_6 j_6) \{ \omega^4(\kappa_5 j_5) + \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) + \omega^4(\kappa_6 j_6) \} - \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) \omega^2(\kappa_7 j_7) \{ 323 \\
& \omega^2(\kappa_7 j_7) + 664 \omega^2(\kappa_5 j_5) \} + 144 \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) + 480 \omega^2(\kappa_1 j_1) \\
& \left. \omega^2(\kappa_2 j_2) \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) + 144 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \} \right]
\end{aligned}$$

$$\begin{aligned}
X(3.28) = & \frac{\hbar^4}{240 (k_B T)^4} \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) + \frac{\hbar^6}{30240 (k_B T)^6} \left[-6 \omega^4(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \right] \\
& + \frac{\hbar^8}{3628800 (k_B T)^8} \left[6 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \{ 2 \omega^4(\kappa_1 j_1) + \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \} + 21 \omega^2(\kappa_1 j_1) \right. \\
& \left. \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \omega^2(\kappa_7 j_7) + 30 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.29) = & \frac{\hbar^4}{720 (k_B T)^4} \omega^2(\kappa_6 j_6) \omega^2(\kappa_7 j_7) + \frac{\hbar^6}{30240 (k_B T)^6} \left[-2 \omega^4(\kappa_6 j_6) \omega^2(\kappa_7 j_7) + 2 \omega^2(\kappa_1 j_1) \right. \\
& \left. \omega^2(\kappa_3 j_3) \omega^2(\kappa_5 j_5) + 4 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_6 j_6) \right] + \frac{\hbar^8}{3628800 (k_B T)^8} \left[3 \omega^2(\kappa_6 j_6) \right. \\
& \omega^2(\kappa_7 j_7) \{ 2 \omega^4(\kappa_6 j_6) + \omega^2(\kappa_6 j_6) \omega^2(\kappa_7 j_7) \} - 6 \omega^2(\kappa_1 j_1) \omega^2(\kappa_3 j_3) \omega^2(\kappa_5 j_5) \{ \omega^2(\kappa_1 j_1) \\
& + \omega^2(\kappa_3 j_3) + \omega^2(\kappa_5 j_5) \} + 12 \omega^2(\kappa_1 j_1) \omega^2(\kappa_2 j_2) \omega^2(\kappa_6 j_6) \{ \omega^2(\kappa_1 j_1) + \omega^2(\kappa_2 j_2) + \omega^2(\kappa_6 j_6) \} \\
& + 12 \omega^2(\kappa_1 j_1) \omega^2(\kappa_3 j_3) \omega^2(\kappa_4 j_4) \omega^2(\kappa_6 j_6) + \frac{83}{2} \omega^2(\kappa_4 j_4) \omega^2(\kappa_5 j_5) \omega^2(\kappa_6 j_6) \\
& \left. \omega^2(\kappa_7 j_7) \right]
\end{aligned}$$

$$\begin{aligned}
 X(3.30) = & \frac{\hbar^4}{360 (K_B T)^4} \omega^2(K_1 \dot{\theta}_1) \omega^2(K_2 \dot{\theta}_2) + \frac{\hbar^6}{30240 (K_B T)^6} \left[-4 \omega^4(K_1 \dot{\theta}_1) \omega^2(K_2 \dot{\theta}_2) + 4 \omega^2(K_4 \dot{\theta}_4) \right. \\
 & \left. \omega^2(K_5 \dot{\theta}_5) \omega^2(K_7 \dot{\theta}_7) \right] + \frac{\hbar^8}{14515200 (K_B T)^8} \left[24 \omega^2(K_1 \dot{\theta}_1) \omega^2(K_2 \dot{\theta}_2) \{ 2 \omega^4(K_1 \dot{\theta}_1) + \right. \\
 & \left. \omega^2(K_1 \dot{\theta}_1) \omega^2(K_2 \dot{\theta}_2) \} - 48 \omega^2(K_4 \dot{\theta}_4) \omega^2(K_5 \dot{\theta}_5) \omega^2(K_7 \dot{\theta}_7) \{ \omega^2(K_4 \dot{\theta}_4) + \omega^2(K_5 \dot{\theta}_5) + \omega^2(K_7 \dot{\theta}_7) \} \right. \\
 & \left. + 48 \omega^2(K_1 \dot{\theta}_1) \omega^2(K_3 \dot{\theta}_3) \omega^2(K_5 \dot{\theta}_5) \omega^2(K_7 \dot{\theta}_7) + 23 \omega^2(K_4 \dot{\theta}_4) \omega^2(K_5 \dot{\theta}_5) \omega^2(K_6 \dot{\theta}_6) \omega^2(K_7 \dot{\theta}_7) \right. \\
 & \left. + 19 \omega^2(K_1 \dot{\theta}_1) \omega^2(K_2 \dot{\theta}_2) \omega^2(K_6 \dot{\theta}_6) \omega^2(K_7 \dot{\theta}_7) \right]
 \end{aligned}$$

$$\begin{aligned}
 X(3.31) = & \frac{\hbar^4}{360 (K_B T)^4} \omega^2(K_1 \dot{\theta}_1) \omega^2(K_2 \dot{\theta}_2) + \frac{\hbar^6}{30240 (K_B T)^6} \left[-4 \omega^4(K_1 \dot{\theta}_1) \omega^2(K_2 \dot{\theta}_2) + 4 \omega^2(K_1 \dot{\theta}_1) \right. \\
 & \left. \omega^2(K_3 \dot{\theta}_3) \omega^2(K_4 \dot{\theta}_4) \right] + \frac{\hbar^8}{58060800 (K_B T)^8} \left[96 \omega^2(K_1 \dot{\theta}_1) \omega^2(K_2 \dot{\theta}_2) \{ 2 \omega^4(K_1 \dot{\theta}_1) + \omega^2(K_1 \dot{\theta}_1) \omega^2(K_2 \dot{\theta}_2) \} \right. \\
 & \left. - 192 \omega^2(K_1 \dot{\theta}_1) \omega^2(K_3 \dot{\theta}_3) \omega^2(K_4 \dot{\theta}_4) \{ \omega^2(K_1 \dot{\theta}_1) + \omega^2(K_3 \dot{\theta}_3) + \omega^2(K_4 \dot{\theta}_4) \} \right. \\
 & \left. + 646 \omega^2(K_1 \dot{\theta}_1) \omega^2(K_2 \dot{\theta}_2) \omega^2(K_3 \dot{\theta}_3) \omega^2(K_4 \dot{\theta}_4) + 160 \omega^2(K_1 \dot{\theta}_1) \omega^2(K_2 \dot{\theta}_2) \omega^2(K_7 \dot{\theta}_7) \omega^2(K_8 \dot{\theta}_8) \right]
 \end{aligned}$$

$$\begin{aligned}
 X(3.32) = & \frac{\hbar^4}{720 (K_B T)^4} \left[-\omega^4(K_1 \dot{\theta}_1) + \omega^2(K_7 \dot{\theta}_7) \omega^2(K_8 \dot{\theta}_8) \right] \\
 & + \frac{\hbar^6}{60480 (K_B T)^6} \left[2 \omega^6(K_1 \dot{\theta}_1) - 4 \omega^4(K_7 \dot{\theta}_7) \omega^2(K_8 \dot{\theta}_8) + 2 \omega^2(K_2 \dot{\theta}_2) \omega^2(K_3 \dot{\theta}_3) \omega^2(K_4 \dot{\theta}_4) \right. \\
 & \left. + 9 \omega^2(K_1 \dot{\theta}_1) \omega^2(K_7 \dot{\theta}_7) \omega^2(K_8 \dot{\theta}_8) \right] \\
 & + \frac{\hbar^8}{3628800 (K_B T)^8} \left[-3 \omega^8(K_1 \dot{\theta}_1) + 3 \omega^2(K_7 \dot{\theta}_7) \omega^2(K_8 \dot{\theta}_8) \{ 2 \omega^4(K_7 \dot{\theta}_7) + \omega^2(K_7 \dot{\theta}_7) \omega^2(K_8 \dot{\theta}_8) \} \right. \\
 & \left. - 3 \omega^2(K_2 \dot{\theta}_2) \omega^2(K_3 \dot{\theta}_3) \omega^2(K_4 \dot{\theta}_4) \{ \omega^2(K_2 \dot{\theta}_2) + \omega^2(K_3 \dot{\theta}_3) + \omega^2(K_4 \dot{\theta}_4) \} - \omega^2(K_1 \dot{\theta}_1) \right. \\
 & \left. \omega^2(K_7 \dot{\theta}_7) \omega^2(K_8 \dot{\theta}_8) \{ 10 \omega^2(K_1 \dot{\theta}_1) + 26 \omega^2(K_7 \dot{\theta}_7) \} + 6 \omega^2(K_4 \dot{\theta}_4) \omega^2(K_5 \dot{\theta}_5) \right. \\
 & \left. \omega^2(K_6 \dot{\theta}_6) \omega^2(K_7 \dot{\theta}_7) + 13 \omega^2(K_1 \dot{\theta}_1) \omega^2(K_2 \dot{\theta}_2) \omega^2(K_3 \dot{\theta}_3) \omega^2(K_4 \dot{\theta}_4) \right]
 \end{aligned}$$

$$\begin{aligned}
X(3.33) = & -\frac{\hbar^4}{720 (k_B T)^4} \omega^4(\tilde{\kappa}_1 \dot{j}_1) + \frac{\hbar^6}{30240 (k_B T)^6} \left[\omega^6(\tilde{\kappa}_1 \dot{j}_1) + 2 \omega^2(\tilde{\kappa}_4 \dot{j}_4) \omega^3(\tilde{\kappa}_5 \dot{j}_5) \omega^3(\tilde{\kappa}_7 \dot{j}_7) \right] \\
& + \frac{\hbar^8}{3628800 (k_B T)^8} \left[-3 \omega^8(\tilde{\kappa}_1 \dot{j}_1) - 6 \omega^2(\tilde{\kappa}_4 \dot{j}_4) \omega^2(\tilde{\kappa}_5 \dot{j}_5) \omega^2(\tilde{\kappa}_7 \dot{j}_7) \{ \omega^2(\tilde{\kappa}_4 \dot{j}_4) + \omega^2(\tilde{\kappa}_5 \dot{j}_5) \right. \\
& + \omega^2(\tilde{\kappa}_7 \dot{j}_7) \} + 26 \omega^2(\tilde{\kappa}_1 \dot{j}_1) \omega^2(\tilde{\kappa}_4 \dot{j}_4) \omega^2(\tilde{\kappa}_5 \dot{j}_5) \omega^2(\tilde{\kappa}_7 \dot{j}_7) + 3 \omega^2(\tilde{\kappa}_2 \dot{j}_2) \omega^2(\tilde{\kappa}_3 \dot{j}_3) \omega^2(\tilde{\kappa}_4 \dot{j}_4) \\
& \left. \omega^2(\tilde{\kappa}_8 \dot{j}_8) + 3 \omega^2(\tilde{\kappa}_2 \dot{j}_2) \omega^2(\tilde{\kappa}_3 \dot{j}_3) \omega^2(\tilde{\kappa}_5 \dot{j}_5) \omega^2(\tilde{\kappa}_6 \dot{j}_6) + 3 \omega^2(\tilde{\kappa}_4 \dot{j}_4) \omega^2(\tilde{\kappa}_5 \dot{j}_5) \omega^2(\tilde{\kappa}_6 \dot{j}_6) \omega^2(\tilde{\kappa}_8 \dot{j}_8) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.34) = & \frac{\hbar^4}{720 (k_B T)^4} \left[-\omega^4(\tilde{\kappa}_1 \dot{j}_1) + 2 \omega^2(\tilde{\kappa}_4 \dot{j}_4) \omega^2(\tilde{\kappa}_5 \dot{j}_5) \right] + \frac{\hbar^6}{30240 (k_B T)^6} \left[\omega^6(\tilde{\kappa}_1 \dot{j}_1) \right. \\
& \left. - 4 \omega^2(\tilde{\kappa}_4 \dot{j}_4) \omega^4(\tilde{\kappa}_5 \dot{j}_5) + 9 \omega^2(\tilde{\kappa}_1 \dot{j}_1) \omega^2(\tilde{\kappa}_4 \dot{j}_4) \omega^2(\tilde{\kappa}_5 \dot{j}_5) \right] \\
& + \frac{\hbar^8}{3628800 (k_B T)^8} \left[-3 \omega^8(\tilde{\kappa}_1 \dot{j}_1) + 6 \omega^2(\tilde{\kappa}_4 \dot{j}_4) \omega^2(\tilde{\kappa}_5 \dot{j}_5) \{ 2 \omega^4(\tilde{\kappa}_4 \dot{j}_4) + \omega^2(\tilde{\kappa}_4 \dot{j}_4) \omega^2(\tilde{\kappa}_5 \dot{j}_5) \} \right. \\
& \left. - 2 \omega^2(\tilde{\kappa}_1 \dot{j}_1) \omega^2(\tilde{\kappa}_4 \dot{j}_4) \omega^2(\tilde{\kappa}_5 \dot{j}_5) \{ 10 \omega^2(\tilde{\kappa}_1 \dot{j}_1) + 26 \omega^2(\tilde{\kappa}_4 \dot{j}_4) \} + 10 \omega^2(\tilde{\kappa}_4 \dot{j}_4) \omega^2(\tilde{\kappa}_5 \dot{j}_5) \omega^2(\tilde{\kappa}_6 \dot{j}_6) \right. \\
& \left. \omega^2(\tilde{\kappa}_7 \dot{j}_7) \right]
\end{aligned}$$

$$\begin{aligned}
X(3.35) = & \frac{\hbar^4}{720 (k_B T)^4} \left[2 \omega^2(\tilde{\kappa}_1 \dot{j}_1) \omega^2(\tilde{\kappa}_2 \dot{j}_2) \right] + \frac{\hbar^6}{15120 (k_B T)^6} \left[-2 \omega^4(\tilde{\kappa}_1 \dot{j}_1) \omega^2(\tilde{\kappa}_2 \dot{j}_2) \right. \\
& \left. + \omega^2(\tilde{\kappa}_5 \dot{j}_5) \omega^2(\tilde{\kappa}_6 \dot{j}_6) \omega^2(\tilde{\kappa}_8 \dot{j}_8) \right] + \frac{\hbar^8}{14515200 (k_B T)^8} \left[24 \omega^2(\tilde{\kappa}_1 \dot{j}_1) \omega^2(\tilde{\kappa}_2 \dot{j}_2) \{ 2 \omega^4(\tilde{\kappa}_1 \dot{j}_1) \right. \\
& \left. + \omega^2(\tilde{\kappa}_1 \dot{j}_1) \omega^2(\tilde{\kappa}_2 \dot{j}_2) \} - 24 \omega^2(\tilde{\kappa}_5 \dot{j}_5) \omega^2(\tilde{\kappa}_6 \dot{j}_6) \omega^2(\tilde{\kappa}_8 \dot{j}_8) \{ \omega^2(\tilde{\kappa}_5 \dot{j}_5) + \omega^2(\tilde{\kappa}_6 \dot{j}_6) + \omega^2(\tilde{\kappa}_8 \dot{j}_8) \} \right. \\
& \left. + 40 \omega^2(\tilde{\kappa}_1 \dot{j}_1) \omega^2(\tilde{\kappa}_2 \dot{j}_2) \omega^2(\tilde{\kappa}_6 \dot{j}_6) \omega^2(\tilde{\kappa}_7 \dot{j}_7) + 24 \omega^2(\tilde{\kappa}_1 \dot{j}_1) \omega^2(\tilde{\kappa}_3 \dot{j}_3) \omega^2(\tilde{\kappa}_4 \dot{j}_4) \right. \\
& \left. \omega^2(\tilde{\kappa}_5 \dot{j}_5) + 243 \omega^2(\tilde{\kappa}_5 \dot{j}_5) \omega^2(\tilde{\kappa}_6 \dot{j}_6) \omega^2(\tilde{\kappa}_7 \dot{j}_7) \omega^2(\tilde{\kappa}_8 \dot{j}_8) \right]
\end{aligned}$$

$$\begin{aligned}
 X(3.36) = & \frac{\hbar^4}{240 (k_B T)^4} \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_2 \dot{\theta}_2) + \frac{\hbar^6}{5040 (k_B T)^6} \left[-\omega^2(\kappa_1 \dot{\theta}_1) \omega^4(\kappa_2 \dot{\theta}_2) \right] \\
 & + \frac{\hbar^8}{1209600 (k_B T)^8} \left[3 \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_2 \dot{\theta}_2) \{ 2 \omega^4(\kappa_1 \dot{\theta}_1) + \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_2 \dot{\theta}_2) \} + 10 \omega^2(\kappa_1 \dot{\theta}_1) \right. \\
 & \left. \omega^2(\kappa_2 \dot{\theta}_2) \omega^2(\kappa_3 \dot{\theta}_3) \omega^2(\kappa_4 \dot{\theta}_4) \right]
 \end{aligned}$$

$$\begin{aligned}
 X(3.37) = & \frac{\hbar^4}{720 (k_B T)^4} \omega^2(\kappa_7 \dot{\theta}_7) \omega^2(\kappa_8 \dot{\theta}_8) + \frac{\hbar^6}{30240 (k_B T)^6} \left[-2 \omega^4(\kappa_7 \dot{\theta}_7) \omega^2(\kappa_8 \dot{\theta}_8) \right. \\
 & \left. + \omega^2(\kappa_2 \dot{\theta}_2) \omega^2(\kappa_3 \dot{\theta}_3) \omega^2(\kappa_5 \dot{\theta}_5) + \omega^2(\kappa_4 \dot{\theta}_4) \omega^2(\kappa_5 \dot{\theta}_5) \omega^2(\kappa_6 \dot{\theta}_6) \right] \\
 & + \frac{\hbar^8}{1209600 (k_B T)^8} \left[\omega^2(\kappa_7 \dot{\theta}_7) \omega^2(\kappa_8 \dot{\theta}_8) \{ 2 \omega^4(\kappa_7 \dot{\theta}_7) + \omega^2(\kappa_7 \dot{\theta}_7) \omega^2(\kappa_8 \dot{\theta}_8) \} - \right. \\
 & \omega^2(\kappa_2 \dot{\theta}_2) \omega^2(\kappa_3 \dot{\theta}_3) \omega^2(\kappa_5 \dot{\theta}_5) \{ \omega^2(\kappa_3 \dot{\theta}_3) + \omega^2(\kappa_2 \dot{\theta}_2) + \omega^2(\kappa_5 \dot{\theta}_5) \} - \omega^2(\kappa_4 \dot{\theta}_4) \\
 & \omega^2(\kappa_5 \dot{\theta}_5) \omega^2(\kappa_6 \dot{\theta}_6) \{ \omega^2(\kappa_4 \dot{\theta}_4) + \omega^2(\kappa_5 \dot{\theta}_5) + \omega^2(\kappa_6 \dot{\theta}_6) \} + \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_3 \dot{\theta}_3) \\
 & \omega^2(\kappa_6 \dot{\theta}_6) \omega^2(\kappa_8 \dot{\theta}_8) + \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_3 \dot{\theta}_3) \omega^2(\kappa_6 \dot{\theta}_6) \omega^2(\kappa_8 \dot{\theta}_8) + \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_3 \dot{\theta}_3) \\
 & \omega^2(\kappa_6 \dot{\theta}_6) \omega^2(\kappa_7 \dot{\theta}_7) + 2 \omega^2(\kappa_2 \dot{\theta}_2) \omega^2(\kappa_3 \dot{\theta}_3) \omega^2(\kappa_4 \dot{\theta}_4) \omega^2(\kappa_6 \dot{\theta}_6) + 2 \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_2 \dot{\theta}_2) \\
 & \left. \omega^2(\kappa_4 \dot{\theta}_4) \omega^2(\kappa_8 \dot{\theta}_8) \right]
 \end{aligned}$$

$$\begin{aligned}
 X(3.38) = & \frac{\hbar^6}{7560 (k_B T)^6} \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_2 \dot{\theta}_2) \omega^2(\kappa_7 \dot{\theta}_7) \\
 & + \frac{\hbar^8}{1209600 (k_B T)^8} \left[-4 \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_2 \dot{\theta}_2) \omega^2(\kappa_7 \dot{\theta}_7) \{ \omega^2(\kappa_1 \dot{\theta}_1) + \omega^2(\kappa_2 \dot{\theta}_2) + \omega^2(\kappa_7 \dot{\theta}_7) \} \right. \\
 & \left. + 5 \omega^2(\kappa_1 \dot{\theta}_1) \omega^2(\kappa_3 \dot{\theta}_3) \omega^2(\kappa_4 \dot{\theta}_4) \omega^2(\kappa_7 \dot{\theta}_7) \right]
 \end{aligned}$$

$$\begin{aligned}
 X(3.39) = & \frac{\hbar^4}{240 (k_B T)^4} \omega^2(\kappa_{22}) \omega^2(\kappa_{33}) + \frac{\hbar^6}{5060 (k_B T)^6} \left[-\omega^4(\kappa_{22}) \omega^2(\kappa_{33}) \right] \\
 & + \frac{\hbar^8}{1209600 (k_B T)^8} \left[3 \omega^2(\kappa_{22}) \omega^2(\kappa_{33}) \{ 2\omega^4(\kappa_{22}) + \omega^2(\kappa_{22}) \omega^2(\kappa_{33}) \} \right. \\
 & \left. + 10 \omega^2(\kappa_{22}) \omega^2(\kappa_{33}) \omega^2(\kappa_{55}) \omega^2(\kappa_{66}) \right]
 \end{aligned}$$

$$\begin{aligned}
 X(3.40) = & \frac{\hbar^4}{720 (k_B T)^4} \omega^2(\kappa_{11}) \omega^2(\kappa_{22}) + \frac{\hbar^6}{15120 (k_B T)^6} \left[-\omega^4(\kappa_{11}) \omega^2(\kappa_{22}) \right. \\
 & \left. + \omega^2(\kappa_{55}) \omega^2(\kappa_{66}) \omega^2(\kappa_{77}) \right] + \frac{\hbar^8}{1209600 (k_B T)^8} \left[\omega^2(\kappa_{11}) \omega^2(\kappa_{22}) \right. \\
 & \left. \{ 2\omega^4(\kappa_{11}) + \omega^2(\kappa_{11}) \omega^2(\kappa_{22}) \} - 2\omega^2(\kappa_{55}) \omega^2(\kappa_{66}) \omega^2(\kappa_{77}) \{ \omega^2(\kappa_{55}) \right. \\
 & \left. + \omega^2(\kappa_{66}) + \omega^2(\kappa_{77}) \} + \omega^2(\kappa_{55}) \omega^2(\kappa_{66}) \omega^2(\kappa_{88}) \omega^2(\kappa_{99}) \right]
 \end{aligned}$$

$$\begin{aligned}
 X(3.41) = & \frac{\hbar^6}{15120 (k_B T)^6} \omega^2(\kappa_{11}) \omega^2(\kappa_{22}) \omega^2(\kappa_{77}) \\
 & + \frac{\hbar^8}{1209600 (k_B T)^8} \left[-2 \omega^2(\kappa_{11}) \omega^2(\kappa_{22}) \omega^2(\kappa_{77}) \{ \omega^2(\kappa_{11}) + \omega^2(\kappa_{22}) + \omega^2(\kappa_{77}) \} \right. \\
 & \left. + 3 \omega^2(\kappa_{11}) \omega^2(\kappa_{33}) \omega^2(\kappa_{55}) \omega^2(\kappa_{99}) \right]
 \end{aligned}$$

$$\begin{aligned}
 X(3.42) = & \frac{\hbar^4}{360 (k_B T)^4} \omega^2(\kappa_{22}) \omega^2(\kappa_{33}) - \frac{\hbar^6}{7560 (k_B T)^6} \omega^4(\kappa_{22}) \omega^2(\kappa_{33}) \\
 & + \frac{\hbar^8}{1814400 (k_B T)^8} \left[3 \omega^2(\kappa_{22}) \omega^2(\kappa_{33}) \{ 2\omega^4(\kappa_{22}) + \omega^2(\kappa_{22}) \omega^2(\kappa_{33}) \} \right. \\
 & + 2 \omega^2(\kappa_{11}) \omega^2(\kappa_{33}) \omega^2(\kappa_{44}) \omega^2(\kappa_{55}) + 5 \omega^2(\kappa_{22}) \omega^2(\kappa_{33}) \\
 & \left. \omega^2(\kappa_{77}) \omega^2(\kappa_{88}) \right]
 \end{aligned}$$

$$\begin{aligned}
X(3.43) = & \frac{h^8}{1209600(K_B T)^8} \left[\omega^2(\kappa_2 \dot{d}_2) \omega^2(\kappa_3 \dot{d}_3) \omega^2(\kappa_5 \dot{d}_5) \omega^2(\kappa_7 \dot{d}_7) + \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) \right. \\
& \omega^2(\kappa_7 \dot{d}_7) \omega^2(\kappa_8 \dot{d}_8) + \omega^2(\kappa_6 \dot{d}_6) \omega^2(\kappa_7 \dot{d}_7) \omega^2(\kappa_8 \dot{d}_8) \omega^2(\kappa_9 \dot{d}_9) + \omega^2(\kappa_1 \dot{d}_1) \\
& \omega^2(\kappa_3 \dot{d}_3) \omega^2(\kappa_8 \dot{d}_8) \omega^2(\kappa_9 \dot{d}_9) + \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_2 \dot{d}_2) \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_9 \dot{d}_9) \\
& + \omega^2(\kappa_1 \dot{d}_1) \omega^2(\kappa_2 \dot{d}_2) \omega^2(\kappa_5 \dot{d}_5) \omega^2(\kappa_6 \dot{d}_6) + \omega^2(\kappa_2 \dot{d}_2) \omega^2(\kappa_3 \dot{d}_3) \omega^2(\kappa_4 \dot{d}_4) \\
& \omega^2(\kappa_8 \dot{d}_8) + \omega^2(\kappa_4 \dot{d}_4) \omega^2(\kappa_5 \dot{d}_5) \omega^2(\kappa_6 \dot{d}_6) \omega^2(\kappa_9 \dot{d}_9) + \omega^2(\kappa_1 \dot{d}_1) \\
& \left. \omega^2(\kappa_3 \dot{d}_3) \omega^2(\kappa_6 \dot{d}_6) \omega^2(\kappa_7 \dot{d}_7) \right]
\end{aligned}$$

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